Marina Shestakova

**ULTRASOUND-ASSISTED ELECTROCHEMICAL
TREATMENT OF WASTEWATERS CONTAINING
ORGANIC POLLUTANTS BY USING NOVEL
Ti/Ta₂O₅-SnO₂ ELECTRODES**

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium in MUC, Mikkeli University Consortium, Mikkeli, Finland on the 8th of July, 2016, at noon.

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Abstract

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Advanced oxidation processes (AOPs) are modern methods using reactive hydroxyl radicals for the mineralization of organic pollutants into simple inorganic compounds, such as CO₂ and H₂O. Among AOPs electrochemical oxidation (EO) is a method suitable for coloured and turbid wastewaters. The degradation of pollutants occurs on electrocatalytic electrodes. The majority of electrodes contain in their structure either expensive materials (diamond and Pt-group metals) or are toxic for the environment compounds (Sb or Pb). One of the main disadvantages of electrochemical method is the polarization and contamination of electrodes due to the deposition of reaction products on their surface, which results in diminishing of the process efficiency. Ultrasound combined with the electrochemical degradation process eliminates electrode contamination because of the continuous mechanical cleaning effect produced by the formation and collapse of acoustic cavitation bubbles near to the electrode surface. Moreover, high frequency ultrasound generates hydroxyl radicals at water sonolysis. Ultrasound-assisted EO is a non-selective method for oxidation of different organic compounds with high degradation efficiencies.

The aim of this research was to develop novel sustainable and cost-effective electrodes working as electrocatalysts and test their activity in electrocatalytic oxidation of organic compounds such as dyes and organic acids. Moreover, the goal of the research was to enhance the efficiency of electrocatalytic degradation processes by assisting it with ultrasound in order to eliminate the main drawbacks of a single electrochemical oxidation such as electrodes polarization and passivation. Novel Ti/Ta₂O₅-SnO₂ electrodes were developed and found to be electrocatalytically active towards water (with 5% Ta content, 10 oxide film layers) and organic compounds oxidation (with 7.5% Ta content, 8 oxide film layers) and therefore these electrodes can be applicable in both environmental and energy fields. The synergetic effect of combined electrolysis and sonication was shown while conducting sonoelectrochemical (EO/US) degradation of methylene blue (MB) and formic acid (FA). Complete degradation of MB and FA was achieved after 45 and 120 min of EO/US process respectively in neutral media. Mineralization efficiency of FA over 95% was obtained after 2 h of degradation using high frequency ultrasound (381, 863, 1176 kHz) combined with 9.1 mA/cm² current density. EO/US degradation of MB provided over 75% mineralization in 8 h. High degradation kinetic rates and

mineralization efficiencies of model pollutants obtained in EO/US experiments provide the preconditions for further extrapolation of this treatment method to pilot scale studies with industrial wastewaters.

Keywords: sonoelectrochemical degradation, electrolysis, sonication, Ti/Ta₂O₅-SnO₂ electrodes, cyclic voltammetry, methylene blue, formic acid

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Marina Shestakova
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Abstract

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List of publications

- I. Shestakova, M., Bonete, P., Gómez R., Sillanpää, M. and Tang, W. Z. (2014). Novel Ti/Ta₂O₅-SnO₂ electrodes for water electrolysis and electrocatalytic oxidation of organics. *Electrochimica Acta*, 120, pp. 302-307.
- II. Shestakova, M., Vinatoru, M., Mason, T.J. and Sillanpää, M. (2015). Sonoelectrocatalytic decomposition of methylene blue using Ti/Ta₂O₅-SnO₂ electrodes. *Ultrasonics Sonochemistry*, 23, pp. 135-141.
- III. Shestakova, M., Graves, J., Sitarz, M. and Sillanpää, M. (2016). Optimization of Ti/Ta₂O₅-SnO₂ electrodes and reaction parameters for electrocatalytic oxidation of methylene blue. *Journal of Applied Electrochemistry*, 46, pp. 349-358.
- IV. Shestakova, M., Vinatoru, M., Mason, T.J., Iakovleva, E. and Sillanpää, M. (n.d.). Sonoelectrochemical degradation of formic acid using Ti/Ta₂O₅-SnO₂ electrodes. *Journal of XXX*. Submitted for publication 2016.

Author's contribution to publications I – IV

Marina Shestakova is the principal author and investigator in papers I – IV. Author performed literature survey, planned and conducted experiments, analysed the data and prepared the first draft of all the papers.

Other publications by the same author

- I. Shestakova, M. and Sillanpää, M. (2013). Removal of dichloromethane from ground and wastewater: A review. *Chemosphere*, 93, pp. 1258-1267.
- II. Shestakova, M. and Sillanpää, M. (2013). Electrocatalytic oxidation of organic compounds at Ti/Ta₂O₅-SnO₂ electrodes. In: *Proceedings of the 11th Finnish Conference of Environmental Sciences (FCES'13)*, pp. 27 -30. Tampere: Juvenes Print TTY.
- III. Vinatoru, M., Dukkanci, M., Shestakova, M., Mason, T.J. (2015). The use of ultrasounds for oxidation of water pollutants. In: *Proceedings of the 4th European Conference on Environmental Applications of Advanced Oxidation Processes – EAAOP4*, pp. B2-15. Athens.
- IV. Sampath, S., Shestakova, M., Maydannik, P., Ivanova, T.V., Brykvin, A., Sillanpää, M., Nagumothu, R. and Alagan, V. (2016). Photoelectrocatalytic activity of ZnO coated nano-porous silicon by atomic layer deposition. *RSC Advances*, 6, pp. 25173-25178.
- V. Sampath, S., Maydannik, P., Ivanova, T., Shestakova, M., Homola, T., Bryukvin, a., Sillanpää, M., Nagumothu, R. and Alagan, V. (2016). Efficient solar photocatalytic activity of TiO₂ coated nano-porous silicon by atomic layer deposition. *Superlattices and Microstructures*. In press.

Nomenclature

Latin alphabet

f	ultrasonic frequency	kHz
F	Faraday's constant	C·mol ⁻¹
$\Delta_r G^0$	standard free energy of the reaction	J·mol ⁻¹
h_{peak}	liquid height in sonochemical reactor	cm
E^0_a/E^0_c	standard anodic/cathodic equilibrium electrode potential	V
I	applied current	A
t	degradation time	min
T	temperature	°C
t_{el}	electrolysis time	h
U^0	theoretical decomposition voltage of water electrolysis	V
E_{el}	applied voltage at electrolysis	V
S	synergetic effect	%
k	rate constant	min ⁻¹
V_s	solution volume	L
p_g	gas pressure	Pa
p_v	vapour pressure	Pa
p_{hs}	hydrostatic pressure	Pa
γ	surface tension	dyn·cm ⁻¹
r	radius of cavitation bubble	m
D	transducer's diameter	m
c	sound velocity in water	m/s
N	near field distance	m

Abbreviations

AOP	advanced oxidation process
COD	chemical oxygen demand
CV	cyclic voltammetry
EO	electrochemical oxidation
EO/US	sonoelectrochemical degradation
DCN	Diamond coated niobium anode
FA	formic acid
FC	fractional conversion
M	metal electrode
MB	methylene blue
Ma	metal anode
MO	higher oxide anode
MMO	mixed-metal oxide electrode
NPOC	non-purgeable organic carbon
OER	oxygen evolution reactions
R	pollutant
SEM	scanning electron microscopy

TOC	total organic carbon
XRD	X-Ray diffraction spectrometry
US	ultrasonic/sonication/sonochemical

1 Introduction

Advanced oxidation processes (AOPs) are modern methods using highly reactive hydroxyl radicals for the oxidation of persistent organic (sometimes inorganic) compounds in aqueous phase [1]. The main advantage of radicals generation during sonochemical (US) and electrochemical (EO) degradation experiments is the ability to mineralize harmful pollutants into simple inorganic compounds such as H_2O or CO_2 , which are natural for the environment. Mineralization of organic pollutants is a generally better option than just transferring pollutants from one phase to another, which takes place in traditional water treatment methods such as for example adsorption, filtration or coagulation. The main advantage of AOPs over biological wastewater treatment is the ability of these methods to mineralize highly toxic compound, which are dangerous for microorganisms. Additionally, biological treatment requires a relatively large working area. Moreover, all conventional methods produce secondary wastes, including chemical sludge in coagulation and excess sludge in activated sludge processes or used adsorbents, which have to be disposed. The European Commission Council Directive 99/31 /EC prohibits direct landfilling of liquid sludge [2]. Since the dry matter content of original sludge is only about 1–5%, additional investments are required for its processing [3]. Among AOPs, sonoelectrochemical (EO/US) degradation is a technique employing electric energy as the main driving force during the degradation process without the need for additional chemicals like for example in Fenton process [4]. Moreover, it is suitable for turbid and coloured wastewater, which are challenging to treat by photocatalysis and photodegradation methods.

One of the main disadvantages of electrochemical method is the polarization and passivation of electrodes due to poor mass transfer. Polarization can be caused also by gas accumulation near to the electrode surface and as a result depletion of pollutant in the electrode's boundary layer [5]. Passivation can be caused by the deposition of reaction products on the surface of electrodes, which results in diminishing of the process efficiency. The most common electrodes used for water treatment in electrolysis are PbO_2 , BDD, $Ti/Ta_2O_5-IrO_2$, Ti/SnO_2-IrO_2 , Ti/RuO_2-IrO_2 , $Ti/Sb-SnO_2$, $Ti/SnO_2-Sb_2O_5-RuO_2$ and Ti/TiO_2-IrO_2 etc. [6] [7] [8] [9] [10]. As can be seen, all these electrodes contain either Sb or Pb, which are toxic to the environment, or expensive Pt, boron-doped diamond or Ir and Ru that are Pt group metals. In this regard, a search for new non-toxic and non-expensive electrode materials is of current importance, which could allow reducing the negative impact on the environment and production costs.

Ultrasound technology is non-selective, therefore it is suitable for the industrial wastewater treatment application. It does not require addition of chemicals to the treatment process and can be easily automated. However, ultrasonication alone often cannot achieve complete mineralization of organic pollutants and has low degradation rates. In order to provide a synergetic effects and better degradation efficiency of organic pollutants ultrasound is combined with other treatment methods such as Fenton, Fenton-like processes, ozonation, other oxidant addition, catalysis, photolysis, electrochemical remediation and others. Ultrasound combined with electrochemical degradation process eliminates electrode contamination because of the continuous mechanical cleaning effect

produced by the formation and collapse of acoustic cavitation bubbles near to the electrode surface [11]. Moreover, ultrasound can reduce polarization by enhancing mass transfer of electroactive species near to the electrode surface and can activate catalytic surface of electrodes. Another advantage of EO/US degradation method is the use of electricity as the main reactant. Addition of electrolyte to conduct electrolysis is not required in industrial treatment application due to high electrical conductivity of wastewater. The process is easy to automate. EO/US decomposition of organic pollutant is a developing method. In addition to active radicals it can provide the complete oxidation of pollutants by formed oxidative species and thermal decomposition.

It is known that dyes are widely used in a wide range of industrial applications including textile, pharmaceutical, plastic, rubber, pulp and paper, which produce enormous amount of coloured wastewater. Dyes are complex organic compounds that are difficult to mineralize. Formic acid (FA) in addition to broad industrial application is a final product of organic pollutants decomposition and resistant to many of the degradation processes. In this regards, methylene blue (MB) dye and FA were used as model pollutants in the research

Chapter 2 represents the state of the art research developments in the field of EO, US and EO/US oxidation of organic compounds. Chapter 3 defines the objectives of the work. Experimental work is described in Chapter 4. Results and discussion and conclusions along with further perspectives of the work are represented in Chapters 5 and 6 respectively.

As an environmental friendly approach and with the growing interest in Green Chemistry, EO/US treatment process holds a promising future perspective in improving industrial processes and cleaner production procedures over the reduction of chemical and energy consumptions. Extrapolation of research to higher volumes and reactors could allow reducing the operational cost of equipment and increasing its energy efficiency.

2 State of the art research developments in sonoelectrochemical oxidation of organic compounds

All organic pollutants in water can be divided into two size groups. The first group includes polymers having a particle size of about 10 - 100 nm. Polymers form heterogeneous mixture with water (colloidal solutions). Removal of high molecular weight organic pollutant from water usually achieved by their coagulation, flocculation, flotation, electrocoagulation electroflotation as well as micro and ultrafiltration. The second group includes small organic molecules with average size of 1 to 10 nm forming homogeneous mixture with water or molecular solution. The conventional water treatment methods allowing removing small organic molecules are adsorption, biological treatment, nanofiltration, AOPs, which include for example EO, US, Fenton process photocatalysis and photodegradation, ozonation, persulphate oxidation, radiolysis etc. Advantages and disadvantages of these methods are described in Table 2.1 [12] [13].

As it can be seen from the Table 2.1 EO and US methods do not generate secondary waste when compared to the nanofiltration, adsorption Fenton and biological treatment processes. Moreover, no auxiliary chemicals are needed in the case of industrial wastewater applications. EO and US processes are relatively safe for operating personnel, compared with the processes of radiolysis and ozonation. They are applicable for turbid and coloured wastewater, which cannot be treated by photodegradation methods. Combination of US and EO have prerequisites of EO enhancement due to the physiscal effect of US, which can activate electrocatalytic properties of electrodes and reduce their polarization. However, the main drawback of the combined EO/US process may be high energy consumption.

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Table 2.1: Advantages and disadvantages of different methods used for small molecules removal.

Treatment methods		Advantages	Disadvantages
Adsorption		Complete removal of pollutants is achievable Ease of implementation Widespread systems for different flow rates and concentrations Low operation costs	Regeneration of saturated and utilization of spent adsorbents Efficiency dependence on temperatures and pH Utilization of retentate is often required
Nanofiltration		Simultaneous water softening Systems are available for different flow rates Low investment costs	Membrane fouling Concentration polarisation Short service life of membranes Utilization of retentate and spent membranes is required
Biological treatment		Possibility to recycle anaerobic sludge High efficiencies of aerobic treatment Widespread method Low cost method	Large working areas Waste activated sludge of aerobic treatment should be disposed Efficiency depends on temperature Post-disinfection is often required Toxic compounds are dangerous for microorganisms Addition of nutrients is required
AOPs	EO	Complete decomposition and high mineralization is achievable Ease of implementation and automation No chemicals required in industrial wastewater applications	Energy-intensive process Electrodes polarization and contamination Electrodes corrosion
	US	Fast decomposition reactions No chemicals required Ease of implementation and automation Multicomponent degradation mechanism by $\cdot\text{OH}$ radicals, pyrolytic reactions, physical effect of bubble collapse.	Low mineralization and degradation rates Energy-intensive process Strong reproducibility dependence on reactor types Cooling is required Formation of toxic by-products is possible

Table 2.1 is continued on p. 17

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Table 2.1: Advantages and disadvantages of different methods used for small molecules removal.

Treatment methods		Advantages	Disadvantages
AOPs	Fenton	Complete mineralization is achievable Fast decomposition reactions No energy input required	Addition of chemicals is required pH-dependent degradation Ferric hydroxide sludge should be utilized
	Photodegradation and photocatalysis	Complete mineralization is achievable No chemicals required	Non-applicable for turbid and coloured wastewaters Separation of photocatalyst is required pH-dependent degradation
	Ozonation	High degradation efficiencies are achievable Fast decomposition reactions No chemicals required No pH changes in during the treatment Simultaneous disinfection effect	Energy-intensive process Ozone toxicity and fire hazards issues Formation of toxic by-products
	Radiolysis	Fast decomposition reactions Non-selective process	High investment cost of electron accelerator Hazards of radioactive personnel exposure High resistant materials are required

2.1 Electrochemical oxidation of organic compounds

To keep the environment clean and prevent natural resources depletion the technological processes should avoid the secondary contamination of the environment with harmful side products, improve the effective recycling of materials and use energy saving solutions. In wastewater treatment processes, electrochemical and particularly electrocatalytic oxidation of organic compound meets these requirements. The prevention of formation of secondary contamination with harmful side products in electrocatalytic oxidation is achieved both directly and indirectly. The direct averting of the contamination is due to the ability of this method to mineralize organic compounds to simple inorganic ones such as H_2O and CO_2 , which are natural for the environment. The indirect prevention is based on the rejection of the use of potentially toxic elements such as Pb or Sb in electrodes structure. Electrocatalytic oxidation can be attributed to the energy efficient processes, as it requires only insignificant amount of energy in the form of applied current or potential for catalytic electrodes activation and work. In addition to the mentioned points, electrocatalytic oxidation process has a benefit of easy automation and implementation. In real systems, electrochemical wastewater treatment methods have an advantage over traditional treatments methods and do not require addition of salts to maintain the process, which is due to high electric conductivity of industrial wastewater, which can exceed 10 mS/cm. Moreover, while comparing with biological treatment, EO has an ability to oxidize compounds, which are toxic and/or refractory in biological treatment. EO is not affected by toxic metals, which are dangerous for microorganisms. As all processes, electrocatalytic oxidation processes have disadvantages such as polarization of electrodes due to poor mass transfer and gases accumulation and as a result reagent/pollutant depletion in electrode's boundary layer or passivation of the electrodes surface by reaction products deposits [14]. The surface of electrodes is prone to foul with polymeric and oligomeric deposition products formed during electrode reactions. These however can be suppressed by powerful agitation generated for example by ultrasound. Another disadvantage of EO is corrosion of electrodes due to a use of improper materials or formation of corrosive product on the surface of electrodes. The solution of the problem is the careful selection of proper catalytic material applicable for the oxidation of specific pollutants and development of for example mixed-metal oxide (MMO) electrodes such as $\text{RuO}_2\text{-IrO}_2$ mixtures with decreased corrosion properties [15].

2.1.1 The theory and mechanism of EO of organics

EO of organic compounds in wastewater is carried out by means of electrolysis, i.e. the passage of electric current through the electrochemical system, which consist of two electrodes (anode and cathode) and an electrolyte solution (aqueous solution of salts, acids or bases).

There are direct and indirect mechanisms through which organic compounds can be oxidized in EO processes [16] [17] [18]. In indirect techniques oxidation of organic pollutants takes place by means reactions with different electrogenerated species such as

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for example hypochlorite [19] [20], hydrogen peroxide or electro-Fenton reaction [21], peroxodisulfate, peroxidiphosphate [22] and ozone [23].

Electro-Fenton is based on on-site electrogeneration of H_2O_2 at a cathode and further formation of $\bullet OH$ radicals by addition of iron catalyst to the working solution [21].

The main disadvantage of hypochlorite use is the formation of toxic chlorinated intermediates, which however can be reduced while working in alkaline media [24]. In addition, the concentration of chloride ions should be higher than 3 g/l to provide high degradation rates, which requires a significant addition of salt in the case of low concentration of chloride ion in wastewater [25].

Direct EO requires oxygen to be reacted with organic pollutants in order to oxidize them. Water molecules are the source of oxygen in wastewaters and water should be activated to produce an active oxygen. In acidic media, this is reached either by water dissociative adsorption below oxygen evolution reactions (OER) potential or by water electrolytic discharge above OER potential.

Dissociative adsorption of water can be achieved only at electrocatalytic electrodes when bond energy of M-OH and M-H is higher than dissociative energy of water to $H^{\bullet}$ and $HO^{\bullet}$ radicals. The dissociative adsorption can be described by the following equations

Electrolytic discharge of water leads to the formation of physically adsorbed reactive HO[•] radicals through the reaction represented below.

The further reaction depends on the electrode nature, which can be conditionally divided into “active” and “non-active” [26]. In the absence of organic pollution, adsorbed [•]OH radicals are further transformed releasing oxygen in accordance with the reaction 2.16.

Hydroxyl radicals adsorbed strongly on the active electrodes can interact with anode forming higher oxides (MO), which further react with pollutant forming pollutant oxidation products or release free oxygen [16].

Hydroxyl radicals weakly adsorbed on non-active anodes do not interact with anode material and directly react with organic pollutants mineralizing them (2.20). However, the reaction of full oxidation of organic pollutants competes with the oxygen evolution reaction (2.16).

Along with useful electrochemical reactions leading to organic pollutant oxidation, there are undesirable reactions causing the electrodes corrosion. They are for example, dissolution of the anode metal (2.21), anodic oxygen evolution (2.22 -2.23) or toxic chlorine gas evolution (2.1) in the case of chloride ions presence in the wastewater solutions (hereafter the “working solution”) [27]. Therefore, the better performance of EO requires corrosion resistant electrodes materials.

When considering the electrolysis it is important to remember that in addition to the organic pollutant molecules and ions of the electrolyte, working solution contains ions of H⁺ and OH⁻, which are the products of water dissociation. Thus, the electrolyte cations and hydrogen ions will be reduced at the cathode and electrolyte anions and hydroxide ions will be oxidized at the anode. Furthermore, water molecules can also be subjected to

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an electrochemical oxidation or reduction. The implementation of each specific reaction is associated to a minimum energy consumption. Electrochemical reactions of water decomposition into hydrogen (H_2) at cathode and oxygen (O_2) at anode depend on the pH value of working solution and described by reactions 2.22 – 2.25 [28] and standard electrode potential (E^0_a/E^0_c):

Reactions 2.22 – 2.25 described above compete with the reactions of pollutants oxidation. The total reaction of water decomposition is described by reaction 2.26 with theoretical decomposition voltage (U^0) [29]

Theoretically, according to thermodynamic law, any organic compound should be oxidized at small potentials before water oxidation. The standard thermodynamic potential of the cell is calculated based on standard free energy of reactant and product formation using Eq. 1 [30]

$$E^0 = \frac{-\Delta_r G^0}{nF} \quad (\text{Eq. 1})$$

where $\Delta_r G^0$ ($J \cdot mol^{-1}$) is the standard free energy of the reaction obtained from the tabulated data, n is a number of electrons participating in the reaction and F is the Faraday's constant ($C \cdot mol^{-1}$).

However, in real conditions the complete mineralization can be achieved only for simple C1 organic compounds using high quality electrocatalytic anodes such as Pt. Therefore, the main efforts in EO of organic compounds are focused on the search of new electrocatalytic materials able to provide oxidation of pollutants with an overpotential towards OER.

To be able to estimate the energy efficiency of EO, a number of parameters have been introduced. They are electrochemical oxidation index (EOI), total current efficiency (TCE, Eq. 2), the apparent current efficiency (ACE) and instantaneous current efficiency (ICE). The calculations of these parameters have the same nature based on COD reduction data during electrolysis process with applied value of current [31].

$$TCE, ICE = \frac{FV[(COD_{t_0}) - (COD_t)]}{8I\Delta t} \quad (\text{Eq. 2})$$

Where COD_{t_0} and COD_t are chemical oxygen demand at initial time (t_0) and time t after electrolysis process respectively, V is volume of electrolyte (m^3) and I is applied current (A) [32].

2.1.2 History of use of electrochemical methods for the destruction of organics and present situation

The first works on EO of organic compound started in the early 1970s from the trial research on phenolic compounds degradations on PbO_2 anodes [33]. However, the intensive work on EO of organic compounds in wastewaters started in the late 1980s beginning of 1990s from the work of Sharifian, Kirk, Comninellis, Stucki, Kötzt and others [34] [35]. One of the first studies on phenol removal in acidic media of packed bed reactor filled with PbO_2 pellets showed removal efficiency in the range of 72 – 100% depending on experimental conditions after 1.5 – 2.5 h. The initial concentration of phenol was $1.4 \cdot 10^{-4}$ M and current applied varied from 1 to 3 A [36]. The main metabolites of the oxidation process were benzoquinone, maleic acid and CO_2 . The similar study showed the similar results on EO of phenol on PbO_2 packed-bed anodes [37]. The complete degradation of treated solutions containing 93 - 1100 mg/L phenol at applied current of 10 A and pH 2.5 was achieved after 1.5 -2 h of electrolysis. Higher pH of the media reduced the efficiency of EO [37]. EO of a mixture of five monohydric phenols (phenol, p-cresol, o-cresol, 2,3-xyleneol and 3,4-xyleneol) on PbO_2 anodes promoted 57, 18 and 22% decrease of TOC, COD and BOD respectively within 3 h at $526 A/m^2$ applied current density. The degradation efficiency of phenols mixture however exceeded 98% [38]. It was shown that Ti/ SnO_2 anodes doped with Sb performed about 5 times better than Ti/ PbO_2 and Ti/Pt anodes [39]. For the same current density of 30 mA/cm^2 , more than 90% removal of benzoic acid was achieved at Ti/ SnO_2 anode while the acid removal at Ti/ PbO_2 and Ti/Pt anodes did not exceed 30%. The complete mineralization of 1000 mg/l phenol was observed on Ti/ SnO_2 - Sb_2O_5 anodes in alkaline media at applied current density of 300 A/m^2 . The same conditions but with Ti/ PbO_2 electrode provided 40% of TOC reduction [35]. It was shown that chemical oxidation of phenol can follow two ways at Pt anode. They are direct oxidation of adsorbed phenol and its intermediates such as maleic, fumaric oxalic acids to CO_2 and chemical oxidation through the generation of hydroxyl radicals [31]. Thus far, phenol and its derivatives are the most studied compounds in EO research.

2.1.3 Types of electrodes materials used in EO

There is a wide variety of catalytic materials used nowadays in electrochemical water treatment applications. However, neither of them are both sufficiently efficient and stable. As it has been mentioned above, the stronger the anode interactions with adsorbed hydroxyl radicals, the lower electrode efficiency towards organics mineralization and higher activity towards OER. This is usually applicable to the anodes with low

overpotential towards OER. On contrary, the weaker $\cdot\text{OH}$ radicals bond to an anode, the more efficient the anode towards complete mineralization of organic compounds and less sensitive towards OER. This statement is true for materials with high overpotential towards oxygen evolution. Thereby all electrodes used for organic compounds oxidation were divided on two categories, which were mentioned above. They are active and non-active electrodes. Carbon based electrodes, Pt, iridium oxide and ruthenium oxide electrodes are active ones and lead oxide, Sb doped SnO_2 and BDD are non-active [26].

Fig. 2.1 shows the range of onset potential of OER for different electrodes in acidic media. As it can be seen, the boron-doped diamond-based anode (BDD) along with $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ are the most effective in terms of complete oxidation of organic pollutants followed by Ti/PbO_2 and $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ electrodes. The smallest activity towards mineralization efficiency belong to Pt, $\text{IrO}_2\text{-Ta}_2\text{O}_5$ and $\text{RuO}_2\text{-TiO}_2$ electrodes. While analysing the electrodes composition, it can be seen $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ can be considered as economically and environmentally friendly and potentially effective for the complete oxidation of organics.

Nevertheless the lower efficiency of mineralization, metal electrodes have the longest history of use in water treatment applications and other chemical processes. Among catalytic materials, Pt and Pt-group metals are stable in a wide range of potentials and pH. However, these materials are expensive and cannot find a wide application for wastewater treatment in industrial scale. Nevertheless, they are intensively used in laboratory scale for new process investigations due to their excellent repeatability properties. It was found that Pt can completely degrade phenol to chlororganic compounds while applying only 1 mA/cm^2 current [7]. Pt anode could provide 96-98% malachite green oxalate dye decolourisation in 6 h of electrolysis while applying 66.7 mA/cm^2 current [40]. However, the mineralization efficiency after 6 h equalled only to 22%. As it is seen Pt anodes are not efficient in mineralization of organic compounds, since they have low overpotential towards OER. To enhance their oxidation efficiency, the electrodes are usually used in indirect oxidation processes coupled with other strong oxidants and their intermediates like for example H_2O_2 or electro-Fenton. In the case of malachite green oxalate dye, coupling of EO on Pt anode with electro-Fenton process increased mineralization efficiency of the dye up to about 97% after 3h of degradation process at the same working parameters [40]. Moreover, the mineralization of the dye reached nearly 85% after 2 h of degradation process while coupling Pt anodic oxidation with photo electron-Fenton process.

The second most studied anodic material is PbO_2 with the onset potential for OER lying in the range from 1.8 to 2 V vs. SHE (Fig. 2.1), thus suggesting a high efficiency towards the complete organics oxidation. It was shown that 55% TOC removal was achieved after 2 h of electrolysis in 0.25 mM solution of methyl orange dye at applied current of 1 A and pH 3 [41]. The removal efficiency of tetracycline reached 78% within 1 h of electrolysis at Pb/PbO_2 anode with applied current density of 25 mA/cm^2 [6].

Figure 2.1: The onset potential of OER for different anode materials in acidic media.

The mineralization efficiency of treated solution containing picloram herbicide reached 50% while using filter-press reactor with β -PbO₂ anode at applied current density of 30 mA/cm², pH 10 and initial herbicide concentration of 100 mg/L [42]. When conducting electrolysis of phenol solution (50 mg/L) at PbO₂ anodes at 50 mA/cm² applied current, TOC removal efficiency reached 90% after 3 h of degradation [43]. Despite the good performance of PbO₂ anodes in organic pollutants EO, the potential toxicity of Pb due to its leaching from the electrode limits the use of these electrodes in industrial application for water treatment.

Another group of catalysts used in wastewater treatment application are metals alloys (Pt-Au, Ru-Pd, Pt-Ru). The activity of this catalysts depends on the component ratio as well as surface properties. These catalyst are commonly used in fuel cell applications and rarely finds application in water treatment technologies.

Carbon-based anodes is another group of catalysts, which were tested in EO of organic compounds. However, the use of those materials is limited by high electrode corrosion rates at potential higher than 1.7 – 1.9 V vs. SCE [44]. The corrosion is always a disadvantage since it leads to the electrode material loss, which in turn causes increase of electrode resistance and loss of stability. It was shown that after 8 h of potentiostatic electrolysis at a constant voltage of 1.7 V, phenol degradation reached 50% [44]. The electrochemical treatment of textile effluents were tested in a square packed/bed reactor with graphite rod used as an anode [45]. About 95% TOC removal was obtained after 1 h of treatment at applied current density of 28 mA/cm².

Mixed-metal oxide catalyst are a broad group of materials both noble and base able to adsorb oxygen on their structure. Due to the possibility of complete or partial reduction of oxide at cathode and instability to acidic media, these materials are more suitable for

anodic oxidation of organic compounds in neutral and alkaline conditions. MMO electrodes include a wide range of materials such as Ti/TiO₂-RuO₂ [8], Ti/Ta₂O₅-IrO₂ [9], Ti/TiO₂-RuO₂-IrO₂ [46], Ti/IrO₂-RuO₂ [47], Ti/SnO₂-Sb₂O₅ [10] etc. The majority of MMO electrodes are prepared on Ti substrate, which is explained by its stability, conductivity properties and acceptable price. Ti-based mixed oxides anodes have corrosion resistant properties and persistent to dissolution. The commercial name for MMO anodes is dimensionally stable anodes (DSA), which was given to the materials because of their excellent properties. Comparing to the graphite, iron and lead anodes DSA preserve the structural integrity well and have much slower rate of degradation, which is usually attributed to the regenerative catalytic surface oxide coating. DSA invention was a breakthrough in electrocatalysis field, which allowed new cell engineering solutions with stable, inexpensive and long service life lasting electrodes (up to 10 years) [48]. DSA were found effective in mineralization of dyes, pesticides, herbicides, phenols and other toxic organic compounds [49] [24] [50] [51]. The doped IrO₂ and RuO₂ oxides at Ti substrate are the most studied DSA electrodes.

The efficiency of several DSA electrodes were tested for electrochemical degradation of glyphosate herbicide (1000 mg/l) in acidic medium (pH = 3) of NaCl (2662 mg/l) at 50 mA/cm² applied current. After 4 h of electrolysis Ti/Ru_{0.30}Pb_{0.70}O₂ electrodes showed the best removal efficiency of about 75% followed by Ti/Ru_{0.30}Ti_{0.70}O₂ (50%), Ti/Ir_{0.30}Sn_{0.70}O₂ (35%), Ti/Ru_{0.30}Sn_{0.70}O₂ (32%) and Ti/_{0.3}(RuO₂)_{0.7}(Ta₂O₅) (30%) electrodes. The best anodic mineralization of 24% was obtained for Ti/Ir_{0.30}Sn_{0.70}O₂ electrode [52].

Another DSA electrodes showed a good performance towards mineralization of rhodamine B dye, which was used as a model compound for degradation experiments. After 30 min of electrolysis with 20 mA applied current, Ti/TiO₂-PdO-RuO₂ provided 71.7% complete oxidation, Ti/TiO₂-PdO electrodes showed 61.7% mineralization and 50.1% mineralization was obtained on Ti/RuO₂ electrodes. Ti/TiO₂ electrode could provide only 15.2% of complete oxidation of rhodamine B. Ti/TiO₂-PdO-RuO₂ electrode was the most efficient among above tested electrodes for treated solution decolourisation, which reached 90.4% after 30 min [53].

SnO₂ anode with a small amount of dopant elements such as Sb showed catalytic behaviour of semiconductor. Ti/SnO₂-Sb₂O₅ electrode provided complete oxidation of 1000 mg/l phenol to CO₂ at pH = 12 while applying 300 A/m² current [35].

As it is seen from Fig. 2.1, BDD has a high overpotential for OER, which allows to suggest its high oxidation activity towards organic compounds [54] [55] [56] [57]. This fact was confirmed by a significant number of research [58] [59] [60]. It was found that the complete destruction of Reactive Orange 16 dye was achieved after 1 h of electrolysis using Ti/BDD anode and applied current density of 200 mA/cm² [61]. Despite of the high electrochemical stability of BDD electrodes and corrosion resistance, ability to completely mineralize pollutants by anodically formed hydroxyl radicals, excellent conducting properties even at low temperatures and low operation costs, BDD has

limitation preventing them from an extensive use [62]. Since BDD electrodes consists of diamond and boron doping, which are in the range from 10^{19} to 10^{21} atoms/cm³, the material becomes expensive for a widespread use [63] [64], however due to BDD excellent performance there are some attempts to implement these electrodes in industrial applications. However, it was found that BDD has a reduced efficiency towards organics mineralization in diluted solutions [63] and at increasing current density higher than a limiting current due to the consuming of $\cdot\text{OH}$ radicals for the side reactions [65].

Another study on ifosfamide (IF) and cyclophosphamide (CF) oxidation on BDD anodes, showed the complete drugs degradation after about 240 min of electrolysis at pH =6.5 and applied current density of 16 mA/cm². The initial concentration of pharmaceuticals was equal to 0.19 mM and degradation followed the pseudo-first order kinetic model [32].

The summary on performance of different electrode materials for oxidation of organic compounds by means of direct and indirect oxidation is listed in Table 2.2.

Table 2.2: Performance of different electrode materials in direct and indirect EO of organic compounds

Anode type	Targeted pollutant	Working parameters	Removal efficiency	Reference
Pt	Reactive Blue 109 (1000 mg/L)	NaCl (0.1 M) I = 20 mA/cm ² pH 4 t _{el} = 1.25 h	96% COD	[25]
	Dimethyl phthalate (0.03 mM)	Na ₂ SO ₄ (0.2 M) I = 20 mA/cm ² pH 7 t _{el} = 18 h	20% 10% COD	[66]
	Diethyl phthalate (0.03 mM)	Na ₂ SO ₄ (0.2 M) I = 20 mA/cm ² pH 7 t _{el} = 18 h	50% 30% COD	[66]
	Diheptyl phthalate (0.03 mM)	Na ₂ SO ₄ (0.2 M) I = 20 mA/cm ² pH 7 t _{el} = 18 h	100% 100% COD	[66]
Pt/MnO ₂	Methylene blue (40 mg/L)	Na ₂ SO ₄ (0.05 M) I = 7 mA/cm ² pH 8 t _{el} = 2 h	90% 70% COD	[67]
Ti/SnO ₂ -Sb-Mo	Phenol (100 mg/L)	Na ₂ SO ₄ (0.25 M) I = 10 mA/cm ² t _{el} = 3.5 h	99.6% 82.7% TOC	[68]
PbO ₂	Aniline (2.7 mM)	pH 2 I = 2 A t _{el} = 1 h	> 90%	[69]
Ti/Pt/PbO ₂	Sanitary landfill leachate (COD 6.2 g/L)	I = 0.3 A t _{el} = 6 h	40% COD	[70]
Ti/Pt/SnO ₂ -Sb ₂ O ₄	Sanitary landfill leachate (COD 6.2 g/L)	I = 0.3 A t _{el} = 6 h	40% COD	[70]
Ti/IrO ₂ -RuO ₂	4-chlorophenol (100 mg/L)	Na ₂ SO ₄ (0.1 mM) I = 39 mA/cm ² t _{el} = 2 h	100% >70% COD	[71]

Table 2.2 is continued on p. 28

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Table 2.2: Performance of different electrode materials in direct and indirect EO of organic compounds

Anode type	Targeted pollutant	Working parameters	Removal efficiency	Reference
Carbon black diamond	2-chlorophenol (200 mg/L)	Na ₂ SO ₄ (0.25 M) I = 30 mA/cm ² pH 3 t _{el} = 6 h	96% 82.5% COD	[72]
Ti/IrO ₂ /RuO ₂ /TiO ₂	2,4-dichlorophenol (80 mg/L)	Na ₂ SO ₄ (0.05 M) pH 9 E _{el} = 1.8 V t _{el} = 4 h	100%	[73]
Ti/SnO ₂ -Sb	Pretilachlor (60 mg/L)	Na ₂ SO ₄ (0.1 M) I = 20 mA/cm ² pH 7.2 t _{el} = 1 h	98.8% 43.1% TOC	[74]
	Phenol (100 mg/L)	Na ₂ SO ₄ (0.25 M) I = 10 mA/cm ² t _{el} = 6 h	95.5% 74.5% TOC	[75]
	Pyridine (100 mg/L)	Na ₂ SO ₄ (10 g/L) I = 30 mA/cm ² pH 3 t _{el} = 3 h	98%	[76]
	Perfluorooctanoic acid (100 mg/L)	NaClO ₄ (10 mM) I = 10 mA/cm ² t _{el} = 1.5 h	90.3%	[77]
Ti/SnO ₂ -Sb/PbO ₂	Perfluorooctanoic acid (100 mg/L)	NaClO ₄ (10 mM) I = 10 mA/cm ² t _{el} = 1.5 h	91.1%	[77]
Ti/TiO _x H _y /Sb-SnO ₂	Aniline (500 mg/L)	Na ₂ SO ₄ (5 wt.%) I = 20 mA/cm ² t _{el} = 5 h	85% 71% COD	[78]
PbO ₂ -ZrO ₂	Methylene blue (30 mg/L)	Na ₂ SO ₄ (0.2 M) I = 50 mA/cm ² t _{el} = 2 h	100% 72.7% COD	[79]

Table 2.2 is continued on p. 29

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Table 2.2: Performance of different electrode materials in direct and indirect EO of organic compounds

Anode type	Targeted pollutant	Working parameters	Removal efficiency	Reference
Ti/SnO ₂ -Sb/MnO ₂	Perfluorooctanoic acid (100 mg/L)	NaClO ₄ (10 mM) I = 10 mA/cm ² t _{el} = 1.5 h	37.1%	[77]
Sn _{0.86} -Sb _{0.03} -Mn _{0.10} -Pt _{0.01} -oxide/Ti	4-chlorophenol (8 mM)	H ₂ SO ₄ (0.5 M) I = 30 mA/cm ² t _{el} = 10 h T = 23 °C	100%	[80]
Stainless Steel/SnO ₂ -CeO ₂	Dye wastewater (Colour, 1565 PCU; COD, 188.94 mg/L)	E _{el} = 5 V t _{el} = 2 min	83% colour 48.6% COD	[81]
Ti/RuO ₂ -IrO ₂ -SnO ₂ -TiO ₂	Phthalic anhydride (2 g/L)	Na ₂ SO ₄ (0.1 M) I = 5 A/dm ² pH 3 t _{el} = 4 h	88% COD	[82]
BDD	Phenol (100 mg/L)	Na ₂ SO ₄ (0.25 M) I = 10 mA/cm ² t _{el} = 6 h	100% 95.4% TOC	[75]
	Sanitary landfill leachate (COD 6.2 g/L)	I = 0.3 A t _{el} = 6 h	40% COD	[70]
	Dimethyl phthalate (0.03 mM)	Na ₂ SO ₄ (0.2 M) I = 20 mA/cm ² pH 7 t _{el} = 0.5 h	100% 50% COD	[66]
	Diethyl phthalate (0.03 mM)	Na ₂ SO ₄ (0.2 M) I = 20 mA/cm ² pH 7 t _{el} = 0.5 h	100% 50% COD	[66]
	Diheptyl phthalate (0.03 mM)	Na ₂ SO ₄ (0.2 M) I = 20 mA/cm ² pH 7 t _{el} = 0.5 h	50% 10% COD	[66]

2.2 Sonochemical destruction methods of organic pollutants

2.2.1 The theory and mechanism

Ultrasound is sound waves having a frequency above the audible sound typically higher than 20 kHz and up to 10^6 kHz. Ultrasound in a medium is transmitted via series of compression and rarefaction cycles, which lead to formation of high and low pressure zones in the medium respectively [83]. In rarefaction cycle when high power of the cycle exceeds the attraction forces of the liquid molecules cavitation bubbles filled with saturated liquid vapour are formed [84]. Bubble undergo a continuous grow and compression during subsequent cycles in a process called rectified diffusion (Fig. 2.2). Stable cavitation bubbles will reach an equilibrium size and continue to vibrate producing acoustic micro-flows. Transient cavitation bubbles will continue to grow in size and then collapse violently generating tremendous pressures up to 400 MPa and temperatures of gases inside the bubbles (2000 – 5000 K) and in the liquid surrounding the cavity (1500 – 2000 K) [85]. Immediately after collapse, spherical shock waves are transmitted in the liquid rapidly attenuating. Static equilibrium of bubbles in water is described by the equation 3 [86].

$$p_g + p_v = p_{hs} + \frac{2\gamma}{r} \quad (\text{Eq. 3})$$

where p_g and p_v are pressure of gas and vapour inside the bubble respectively, p_{hs} is the hydrostatic pressure, γ is the surface tension, r is the bubble radius.

A sudden drop in hydrostatic pressure in the liquid below a certain value cause the formation of cavitation bubbles as a result of rupture of fluid continuity.

Pure liquids without bubbles inclusions have a high tensile strength. For example, in order to form a cavity in water with a radius of 10^{-10} m at 293 K, it is necessary to apply a negative pressure $p = 2\gamma/r = 2 \times 0.073/10^{-10} = 1.46 \text{ GPa}$. However, it is a very difficult task to obtain a pure liquid without heterogeneity. The presence of gas bubbles and gas nuclei trapped in suspended solid particles create “weak spots” in the liquid, which consequently reduce tensile strength of the liquid. As a result, significantly less pressure (about 10^3 - 10^4 times) is required to initiate cavitation [87].

The cavitation bubble growth depends on ultrasonic frequency. Higher ultrasonic frequencies promote faster bubble collapse thus producing smaller cavitation bubbles [88]. External conditions and fluid properties influence the cavitation development and intensity (the amount of energy passed per unit time per unit area perpendicular to the ultrasound beam, $\text{J/s/m}^2 = \text{W/m}^2$). Degassing of the liquid reduces cavitation and increases the intensity of the shock waves created by cavitation bubble. The higher the heat capacity and solubility as well as the lower thermal conductivity of the ambient gas, the better cavitation is induced [89] [90]. While increasing the medium temperature, the pressure inside the bubble increases and the fluid viscosity decreases.

Figure 2.2: The mechanism of cavitation bubbles formation and collapse

These conditions promote more ease cavitation occurring at lower powers and less violent bubble collapse [91]. The minimum ultrasonic intensity required for initiation of cavitation is called cavitation threshold, which depends on many factors such as ultrasonic frequency, liquid properties, ambient temperature etc. [92].

The asymmetric bubbles collapse (Fig. 2.3) on/or close to a solid surface provoke the generation of liquid microjets directed towards the surface with speeds up to few hundred meters per second [93] [85]. The presence of solid particles or other foreign liquids in the area of liquid microjets action lead to their active degradation due to high pressures at bubble collapse. The physical effect of ultrasound on compound degradation is also based on formation of liquid microjets in addition to shock waves, acoustic streaming and shear forces.

Acoustic cavitation in liquids initiate various physical and chemical phenomena such as sonoluminescence, sonochemical reactions, solid surfaces erosion, mixing and homogenization of immiscible liquids etc. Because imploding bubbles can produce excited molecules in high-energy-states, these molecules emit visible light when returning to ground state, a phenomenon known as sonoluminescence [94]. Sonochemical reactions depend on many parameters including ultrasonic frequency and power, pH, temperature, materials types etc.

Figure 2.3: Asymmetric cavitation bubble collapse near a solid surface producing a liquid microjet.

It was shown in many studies that higher frequency, generate higher amount of $\cdot\text{OH}$ radicals, which are the main reactants in chemical transformations [95] [96]. At the same time, collapse that is more violent is produced at lower frequencies providing higher temperatures and pressures [97]. This is explained by long acoustic cycles and as a result larger bubble sizes. Violent cavitation bubbles collapse is also formed at higher ultrasonic intensities [98]. It should be noted that, unlike most chemical reactions, sonochemical reactions decrease with increasing ambient temperature. This is because the higher the ambient temperature the greater will be the extra vapour intake inside the cavity, which cushions the implosion of the cavity and lowers the temperature of its collapse [88]. A summary of different parameters on cavitation process is listed in Table 2.3.

In addition to the described parameters, transducer placement within the reactor and reactor geometry influence the distribution of ultrasonic field and as a result, efficiency of sonochemical reactions. However, the modern ultrasonic systems are equipped with amplitude unit control, which allow automatic adjustment of amplitude to a constant value, and a unit for automatic overlapping ultrasonic waves, which is achieved by sweeping the frequency in the range of ± 1 kHz, which eliminates the formation of dead zones and hot spots [99] [100].

Table 2.3: The main parameters that influence the cavitation

Parameter	Effect of different parameters of cavitation process
Frequency	Higher frequency leads to shorter acoustic cycles, smaller cavitation bubble size, shorter bubble collapse time, higher $\cdot\text{OH}$ formation. Lower frequencies provide more violent collapse.
Dissolved gases	Reduced tensile strength of the liquid initiates the cavitation process at lower pressures. The more gas nuclei in the liquid the lower intensity of generated shock waves. Monatomic gases generates more energy on collapse than multiatomic gases, which is related to the heat conductivity of gases.
Intensity	There is a minimum level of intensity, which is required to initiate cavitation. Higher intensity generates more bubbles. However, too many bubbles may prevent the distribution of ultrasonic power into entire solution, therefore an optimal level of intensity should be found.
Temperature	Higher ambient temperature reduces viscosity of the liquid and surface tension, which results in cavitation threshold decrease and higher bubbles formation, however bubble collapse is less violent. Too many bubbles may reduce the distribution of ultrasonic power into entire solution. Temperatures above the boiling point of the media significantly reduces the effect of sonochemical reactions.
Pressure	Higher ambient pressure reduces the number of bubble collapses at the same intensity, however collapses are more violent.

There are three theories explaining cavitation bubble collapse. These are i) electrical, where electrical discharge is produced during asymmetric bubble implosion [101]; ii) plasma theory implying microplasma formation inside the cavitation bubble [102] and iii) hot-spot theory, which is the most used due to its simplicity and the fact that other theoretical approaches could not describe various findings. [98]. In the hot-spot theory there are three regions where chemical reactions take place (Fig. 2.4). A hot spot hydrophobic gaseous nucleus (1), which is created due to the compression of gases and liquid vapours inside the cavity initiates high local temperatures inside the cavity and in interfacial region (2). Since temperature of hot-spot is enormously high, the heat disperses rapidly and warms up the bulk solution (3). It was suggested that degradation of compounds inside the cavity (hot-spot) including solvent decomposition occurs through the thermal decomposition mechanism. Pyrolysis and hydroxylation are the main pathways of compounds decomposition in interfacial region. Decomposition of compounds in the bulk solutions occurs by hydroxylation and reactions with hydroxyl radicals [103].

Figure 2.4: The hot-spot model of cavitation.

Energy released during the collapse of the bubble is enough to excite, ionize and dissociate water molecules, gases and substances. At this stage, any gas present in the liquid is an active component participating in the transfer of excitation energy, recharging and other processes. The oxidation of organic species presenting in those three areas occurs through reaction with $^\bullet\text{OH}$ radicals produced during water thermolysis and H_2O_2 obtained from the recombination reaction of $^\bullet\text{OH}$ radicals [104] [105].

The action of reactive gases as for example O_2 and H_2 inside the cavitation bubble is ambivalent. H_2 and O_2 are involved in radical transformation reactions (2.31 and 2.34)

Additionally, inert and noble gases participate in transfer of electron excitation energy to water molecules. The presence of gas, salts or nanoparticles in treated solution can enhance the degradation rates of pollutants due to availability of additional centres for the cavitation or the formation of additional radicals. Persulphate and periodate ions can be considered as an example of high reactive secondary radicals formation [106] [107] [108].

The addition of carbon tetrachloride was found to enhance sonodegradation of organic pollutant through the degradation of organic compounds through the formation of chlorine-containing radicals and recombination with $H\cdot$, which prevents $\cdot OH$ recombination with $H\cdot$ [109] [110] [111].

2.2.2 Sonochemical degradation of organic compounds

The first reports on the effect of ultrasound on the course of chemical reactions were published by Wood R. W. and A. L. Loomis [112]. In 1929 A. L. Loomis and E. N. Harvey showed the effect of ultrasound on deactivation of luminous bacteria [113]. In 1950 Miller was one of the first suggesting formation of reactive species from the disruption of water molecules during acoustic cavitation [114]. A few years later Henglein and Weissler showed that hydrogen peroxide was generated during the sonication of water [115] [116]. In 1950 Weissler also found that the addition of CCl_4 enhances the

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degradation of KI and generating free chlorine under at CCl_4 sonication [117]. The first works confirming the direct generation of $\cdot\text{OH}$ and $\text{H}^\cdot$ radicals and their effect on ultrasonic degradation of organic compounds were conducted in 1970s – 1980s [118] [119]. For the first time the mechanism of thymine degradation at 450 kHz ultrasonication was described through radical formation and degradation products were identified [118]. Creation of inexpensive ultrasonic generators in the 1980s promoted further studies on organics remediation using ultrasound [88].

Despite the considerable amount of research conducted on the sonochemical degradation of organic compounds, comparison of different studies provides a random error due to the different transducers geometry and spartial set-up used in the studies.

For the last 30-40 years of intensive development of ultrasonic technologies, sonochemical remediation have been found effective in a wide range of applications as an individual process and assisting other water treatment technologies such as EO, photodegradation, chemical oxidation, adsorption, membrane filtration, biological treatment, coagulation etc. The individual ultrasound remediation techniques use the energy of ultrasound as a main reactant for pollutants degradation.

Degradation of organic compounds such as pesticides, dyes, pharmaceuticals, herbicides surfactants, solvents and industrial chemicals is the most studied field in ultrasonic wastewater treatment [120] [121]. However, dyes are the leaders among other pollutants investigated in sonochemical degradation. The recent study of the degradation of rhodamine B, acid orange 7 and malachite green dyes at 300 kHz (0.085 W/mL output power) sonication provided 85, 80 and 95% dyes degradation efficiency of 5 mg/L dyes respectively after 1 h at 25 $^\circ\text{C}$ treated solution temperature [122]. The mechanism of pollutant degradation was the reaction with $\cdot\text{OH}$ radicals. Degradation experiments were conducted in a cylindrical glass reactor with a transducer incorporated into the bottom of the reaction vessel. The increase of liquid temperature up to 55 $^\circ\text{C}$ significantly approved dyes degradation, which was explained by the fact that $\cdot\text{OH}$ radicals formation and number of cavitation bubbles increase with the temperature rise. The degradation efficiency of magenta dye equal to 80% was obtained in ultrasonic bath after 3 h sonication at pH 7.2 of 30 mg/L dye solution [123]. The ultrasonic frequency used in the study was 50 kHz with output power of 0.085 W/mL. Addition of NaCl to the treated solutions slightly enhance the degradation efficiency of the dye till 85% while applying the same working parameters.

It was found that the thermal decomposition mechanism is responsible for the degradation of hydrophobic compounds such as for example trichloroethylene, tetrachloride, chlorobenzene etc., which occurs mostly inside the cavitation bubble [124] [125]. Degradation of hydrophilic compounds occurs in water phase mostly through their reactions with formed radicals generated by gaseous vapours thermolysis [95] [126]. It was shown that phenol decomposition occurs through the reaction with hydroxyl radicals resulting in genaration of phenoxy radical, which react with $\text{HO}^\cdot$ once again forming nonradical degradation products [127].

The degradation of phenol (1100 mol/L initial concentration) using 28 kHz ultrasonic bath followed by the zero-order kinetics model and efficiency of degradation after 3 h of sonication did not exceed 25% [127].

Most of the studies applied ultrasound of low to medium frequency which was found effective for example for dyes decomposition [89] [128] [97], however, the most used frequencies are between 20 and 100 kHz, which is explained by the availability of low ultrasonic frequency devices on the market. Only a few studies used ultrasound frequency higher than 1000 kHz [129] [130] [131] [132]. Thus it was shown that irradiation of solution containing 10 mol/L MB dye in ultrasonic bath type reactor with 1640 kHz frequency (0.08 W/mL actual power) for 1 h provided 25% of dye degradation efficiency [133]. To the best of our knowledge, 1640 kHz was the highest frequency tested in MB degradation. However, while comparing the sonication of MB solution at 1640 kHz with applied frequencies of 22.8, 127, 490 and 970 kHz, the highest degradation of about 50% was achieved using 490 kHz. So, once again the necessity of careful optimization of ultrasonic working parameters was shown. At the same time the higher ultrasonic powers applied showed the better degradation rates of MB at every studied frequency.

The positive effect of the pulsed mode, especially over longer period of sonication, was also confirmed in some studies [134] [135]. Sonication of high-molecular-weight polysaccharide extracted from *Phellinus linteus* mycelia at 20 kHz and 10 – 30 W/mL output power in a pulsed mode (2 s on – 2 s off) provided 64 - 93% molecular weight removal with higher decrease at higher output powers. The initial molecular weight of $3.1 \cdot 10^8$ g/mol in 5% w/v polysaccharide solution dropped to about 0.2 and 1.1 g/mol for 10 and 30 W/mL respectively after 3 h of sonication [136].

It was found that the use of multiple frequencies of (20 + 30 + 50) kHz allowed enhancing the degradation of formic acid by nearly 50% comparing with single sonication of 100 ppm FA solution at 30 kHz [137]. Multiple and single frequency experiments were carried out in a hexagonal flow cell with each set of transducers incorporated into each side wall of the reaction vessel. In the same study, it was shown that higher volumes of treated solutions with the same pollutant concentration of 100 ppm provided higher degradation efficiency of FA of 9% using 1700 ml solution against 4% while sonicating 750 ml of the treated solution. This was explained by the fact of standing wave formation at higher volumes, which lead to higher ultrasonic intensity generated at higher volumes. Another study conducted on the degradation of rhodamine B dye using simultaneous irradiation of solution with double frequency mode (25 + 40 kHz) showed the degradation efficiency be equal to a sum of efficiencies of singular degradation processes at 25 and 40 kHz [138]. Reaction was conducted in a cylindrical cell with 3 set of transducers for each frequency fixed at opposite walls of the reactor. Degradation of FA at 20, 200 and 607 kHz frequencies showed 6 and 8 times higher degradation of the pollutant at higher

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frequencies of 200 and 607 kHz (transducers incorporated at the bottom of the reactor) respectively comparing to 20 kHz (ultrasonic probe system) sonication [139]. The mechanism of sonochemical degradation of FA showed to be complicated with formation of different intermediates such as CO₂, H₂O, H₂C₂O₄, CO [139]. However, the main degradation occurs through FA decarboxylation shown in reaction 2.49 – 2.51 [139].

Mechanical stirring (200 rpm) of treated solution could improve the FA degradation by a factor of 3 from 2 to 6% compared to sonication without stirring when using 590 kHz ultrasonic frequency with output power intensity of 0.13 W/mL in degradation of 1000 mg/L FA in a cup-horn reactor with a transducer fitted at the bottom of the vessel. [140]. The further increase of rotation speed decreased the efficiency of the process thus showing a need for stirring conditions optimization. Addition of 4% NaCl to the treated solution enhanced the efficiency of FA degradation, which was explained by creation of additional centres of cavitation and concentration of pollutant in the hot-spot of cavitation bubbles. Higher amounts of salt decreased the efficiency of the process that was attributed to the fact of surface tension and vapour pressure changes preventing the formation of cavitation effect.

The more detailed information on different organic compounds degradation by sonication is represented in Table 2.4.

Table 2.4: Efficiency of ultrasonication in degradation of different organic compounds in water

Pollutant	Initial concentration /Comments	Working parameters			Removal efficiency	Reference
		Power, W/mL	Frequency kHz	Time, min		
Bisphenol A	0.228 mg/L	0.2	28 580	30	61% 93%	[141]
Bisphenol A	26.9 mg/L pH3; O ₂	0.27	300	90	100%	[142]
Bisphenol A	2 mg/L 50 mg/L	1	130	180	47% 30%	[143]
Dextran 1000 (MW 1.2·10 ⁶)	10-20 mg/L	12	20	60	83% depolymerisation	[144]
Diazinon	2.4 mg/L	0.6-1.8	20	60	42-58%	[145]
Dichlorvos	110 mg/L O ₂	0.201	500	100	97%	[146]
Diclofenac	8.88 mg/L	0.2	20 577 861 1145	60	50% 90% 95% 88%	[147]
Diclofenac	40 mg/L	0.1	20	60	30%	[148]
Diethyl phthalate	45 µM	0.065	283	120	5% _{TOC}	[149]
Dinitrotoluenes	450 mg/L (TOC)	126	20	360	13% _{TOC}	[150]
Formic acid	100 mg/L 1000 mg/L	4.8	22.7	120	8% 14%	[137]
Guar gum	27.93 mL/g intrinsic viscosity	0.67	36	30	95.6% intrinsic viscosity	[151]
Linuron	10 mg/L	1	200	20	79%	[152]

Table 2.4 is continued on p. 40

Table 2.4: Efficiency of ultrasonication in degradation of different organic compounds in water

Pollutant	Initial concentration /Comments	Working parameters			Removal efficiency	Reference
		Power, W/mL	Frequency kHz	Time, min		
Low-density poly-ethylene	1.4% 60 mL/g intrinsic viscosity	2.4	22.5	6	7.5%	[153]
Malachite Green	2 mg/L 10 mg/L 150 rpm	0.17	35	200	63% 91%	[154]
Methomyl	25 mg/L	1	20	75	30%	[155]
Methylene Blue	50 mg/L	0.5	42	60	10%	[156]
Methyl Orange	10 mg/L	0.36	20	90	8%	[157]
Methyl parathion	20 mg/L	0.072	20	60	8%	[158]
Methyl parathion	50 mg/L	1	40	80	16%	[159]
Oxalic acid	210 mg/L	0.35 0.56	40	60	3% 13%	[160]
Reactive Brilliant Red K-2BP	20 mg/L pH3	4	20	40	12%	[109]
Sulfamethazine	9 µM	0.2- 0.5	800	60	41-95%	[161]
2,4,6-trichlorophenol	100 mg/L	1.8	20	150	25%	[162]
17α-ethinylestradiol	296 µg/L	0.2	28 580	30	67% 98%	[141]
2,4-dichlorophenol	50 mg/L pH 2-11; O ₂	0.4	489	60-120	100%	[163]
2,3,7,8-TeCDD	20 ng/L pH 2	1.5	20	60	100%	[164]

2,3,7,8-TeCDD 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin

2.3 Sonoelectrochemical destruction methods

EO/US degradation of organic compounds is a relatively new developing technique, which shows high mineralization rates in degradation of organic compounds. EO/US degradation methods are based on the synergetic effect of separate mechanism of EO and US degradation, which were described in section 2.1 and 2.2. The effects of sonication involving shock waves, shear forces promote almost all electrochemical processes. Acoustic streaming and liquid microjets activate an electrode surface by removing passivating impurities from the electrodes surface, enhancing electrolytic current mode and facilitating mass transfer of electroactive species [165]. Degassing effect of ultrasound can reduce polarization of electrodes by removing the generated gases from the electrodes surface. The extreme conditions generated at cavitation bubbles collapse provide additional mechanisms of pollutant degradation through generation of hydroxyl radicals and thermal decomposition. However, free radicals produced during EO/US process can be also consumed by recombination reactions. When summarizing the advantages and disadvantages of EO and US treatments it can be concluded that combined EO/US treatment is suitable for the degradation of highly toxic compounds regardless of their concentration and turbidity at ambient conditions. Moreover, electrical energy is used as the main reactant in the process and no additional chemicals are required.

The synergetic effect of combined EO and US processes can be calculated using Eq. 4 [166]

$$S = \frac{k_{US/EO}}{k_{EO} + k_{US}} \quad (\text{Eq. 4})$$

Where S is the synergetic index; k_{EO} , k_{US} and $k_{EO/US}$ are rate constants in EO, US and EO/US processes respectively.

The one of the main disadvantages EO/US is potential enhanced electrodes corrosion at combined sonication and electrolysis, which instead of increase can decrease the degradation process efficiency. Higher electrolysis currents lead to higher gas evolution such as oxygen and toxic chlorine gas (generated from the presence of Cl^- ions in the electrolyte solution). The produced gases can initiate corrosion of the electrodes. At the same time, ultrasound is known for its cleaning effect due to the formation of liquid microjets and shock waves during the cavitation bubbles collapse, which can assist the initiated corrosion of electrodes at higher currents. In this regards, the working parameters such as applied current or voltage in electrochemical experiments and actual power, reactor geometry in sonochemical experiments, which were effective in singular processes, need a careful optimization (often decrease for voltage and US powers) to be applied to sonoelectrochemical processes. A spatial set-up of electrodes and transducer in the reaction vessel significantly influence sound distribution and a result has an effect on pollutant degradation efficiencies and electrode deterioration. The effect of ultrasound on decrease of decomposition voltage can be explained by the fact of reducing anodic reactions overpotential and increasing cathodic reactions overpotentials. This was shown on the example of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}/\text{Ag}$ redox couple where shift of anodic potentials was

observed at 20 and 500 kHz sonication of different intensity [167]. Cathodic polarization depression was obtained also in chromium deposition process under continuous acoustic irradiation [168]. The two-sided effect of ultrasound, which can both promote and suppress the corrosion of metals and metal alloys was reported in a number of works [169] [170] [171].

Some of the first uses of ultrasound in electrochemistry were for the removal of any passivation layer from electrode surfaces, for the homogenization of electrolytes and for the improvement of structural properties in films deposited during electroplating [172] [173] [174]. The degradation of phenol at applied current of 6.8 mA/cm^2 and ultrasonic irradiation at 20 and 500 kHz was the pioneering work [175]. Ti/Pt grid was used as an anode in the study and Ni form was cathode. EO/US showed the enhanced degradation rates comparing to US alone and higher frequency provided faster degradation, which were equal to 95% after 10 minutes of treatment comparing with 75% within the same time when using 20 kHz sonication. Moreover, 20 kHz sonication combined with EO contributed to the formation of toxic decomposition product such as quinones, which were absent in 500 kHz/EO degradation with acrylic and chloroacrylic acids as the main decomposition products.

The intensive studies related to the use of sonoelectrochemical methods in pollutant degradation date back to the turn of the 21st century [4] where ultrasound assisted the electrochemical degradation of diuron herbicide, Procion Blue dye and N,N-dimethyl-p-nitrosoaniline [176] [177] [178]. It was found that procion blue can be directly oxidized in US field on BDD anodes at potentials below 2.5 V vs. SCE in acidic conditions since contamination of electrodes was enhanced in alkaline solutions [176]. US-assisted EO was conducted to decompose diuron herbicide using glassy carbon plate anode and applying 35 and 20 kHz ultrasonic irradiation [178]. Glassy carbon anode was subjected to polarization at potentials higher than 1.4 V, therefore the electrolysis was conducted at lower potential of 1.16 V. After 8 h of EO/US process, the degradation of diuron was equal to 72%. When conducting electrolysis in 35 kHz ultrasonic bath at 1.3 V applied voltage, the degradation efficiency did not exceed 43%. That was explained by the fact that cleaning efficiency of the US horn is higher than in US bath thus preventing the passivation of the electrodes.

2.3.1 Reactor types used in EO/US degradation

All EO/US methods can be set up in three major types depending on ultrasonic reactor type. The first type is an ultrasonic bath type with working electrodes immersed into the reactor. The distribution of acoustic field in bath type reactors is considered to be even [4]. The second group consists of working electrodes and ultrasonic horn placed in the reactor volume. Both set ups are used in this study and will be discussed in the Chapter 4. The third set up uses a combination of working electrode and sonotrode in one device, which is shown in Fig. 2.5 [179].

Figure 2.5: Schematic representation of sonoelectrochemical reactor with working electrode acting as a sonotrode.

The first study on EO/US reduction of benzaldehyde and benzoquinone in different solvents using the working Ti cathode combined with 20 kHz sonotrode was conducted in 1996 [179]. It was shown that US increased the current intensity at constant voltage applied and consequently enhanced the reduction rates of studied compounds. EO/US process conducted within 2 h provided 84% of benzoquinone reduction, which was 7 times higher when using electrolysis alone. Ultrasonic enhancement of reduction rates left mechanism of reduction unchanged, but changed the behavior of electroactive species. One of the drawbacks of combined ultrasonic emitter and working electrode use is the necessity for a precise potentiostatic control, which can allow the electron transfer control on such electrodes [180].

A special attention should be paid to the distance between ultrasound source in the case of horn type sonotrodes and electrodes since it influences the intensity of mass transfer, etching of electrode surfaces, polarization intensity etc. [181]. The approximate liquid height (h_{peak}) in sonochemical reactor where the maximum sonochemical efficiency is produced can be calculated using equation 5 [182]:

$$h_{peak} = \frac{23400}{f} - 22.9 \quad (\text{Eq. 5})$$

where f is the ultrasonic frequency.

Another approach to calculate an approximate distance from the transducer to the vicinity of reactor where the maximum peak of US pressure occurs is described by equation 6 [183]:

$$N = \frac{D^2 f}{4c} \quad (\text{Eq. 6})$$

where N is near field distance, D is transducer's diameter, f is frequency and c is sound velocity in water.

It is worth to notice that lower ultrasonic frequencies promote higher cleaning and mechanical effect of ultrasound in enhancement of degradation processes with a domination of turbulent acoustic streaming [184]. Higher frequencies have major contribution to the degradation through free radicals formation [185].

Cyclic voltammograms recorded in ultrasonic field proved the significant enhancement of anodic currents and decrease in diffusion layer thicknesses especially at close ultrasonic emitter-working electrode distances [184]. The fact of increased anodic current can be attributed to the enhanced mass transfer due to reduction of diffusion layer thickness caused by cavitation in the case of higher frequencies. [186]. Enhanced mass transfer can assist the EO efficiency of pollutants especially at their low concentrations.

2.3.2 Dyes degradation

Over the last few years, ultrasonically assisted electrochemical methods were tested for the degradation of a range of different compounds such as pesticides, dyes, pharmaceuticals etc. [187] [174] [188] [189] [190]. Table 2.5 contains a summary of extended works conducted in the field of EO/US degradation of organic pollutants. Degradation of dyes remains the most studied in EO/US treatment processes.

Amaranth dye degradation on BDD anode in alkaline media provided 98% dye mineralization after 1.5 h when coupling US at 20 kHz (523 W/cm²) and electrolysis at 50 mA/cm² [191]. The degradation followed the pseudo-first order kinetic model with rate constant equal to 0.035 min⁻¹. The lower applied current of 35 mA/cm² showed a slightly lower TOC removal, which reached 90% after 1.5 h. The initial concentration of dye in treated solution was equal to 100 mg/L and K₂SO₄ (0.05 mol/L) was used as an electrolyte. The proposed dye degradation mechanism involves the rupture of azo bond by cathodic reduction on the first stage. The next step is the reaction with 'OH radicals, consistent elimination of sulfonic acid and NH₂ groups and cleavage of carbon bonds in aromatic ring, decarboxylation, hydroxylation and the formation of CO₂ and H₂O final products. The main intermediates of the amaranth decomposition are naphthalenediol, tautomers, phthalic acid, phthalic anhydride, benzoic acid, phenol fumaric and aliphatic acids.

Table 2.5: Efficiency of EO/US in degradation of different organic compounds in water

Pollutant/ Initial concentration	Working parameters		Removal efficiency	Time/ Conditions	Reference
	Electrochemical	Sonochemical			
Amaranth dye 100 mg/L	BDD anode $I = 35 \text{ mA/cm}^2$	20 kHz 523 W/cm ²	95.1% TOC	1.5 h	[192]
Cl reactive black 8 100 mg/L	Ti/RuO ₂ -IrO ₂ anode $I = 31.7 \text{ A/cm}^2$	20 kHz 100 W/L	32.4% COD	1.5 h pH 5.4	[193]
Pentachloro- phenol 2 mg/L	Pt anode $E_{el} = 30 \text{ V}$	22.5 W/L 35 kHz 170 kHz 300 kHz 500 kHz 700 kHz	75% 65% 50% 45% 40%	1 h	[194]
Perchloro- ethylene; 60 mg/L	PbO ₂ anode $I = 3.5 \text{ mA/cm}^2$	20 kHz 0.27 W/mL	100% FC 56%	6 h	[195]
Phenol 0.5 mM	Stainless steel anode $E_{el} = 30 \text{ V}$	850 kHz 170W	98%	1h	[196]
Sandolan Yellow; 50 mg/L	Pt anode $I = 60 \text{ mA}$	40 kHz 0.011 W/mL	75% decolour.	80 min	[187]
Reactive Blue 19 dye 50 mg/L	PbO ₂ anode $E_{el} = 10 \text{ V}$	80 kHz 0.3 W/mL	90% decolour. 56% TOC	2h pH 8	[189]
Diuron 18 – 26 mg/L	BDD anode $I = 60 \text{ mA/cm}^2$	20 kHz 750 W	100% 43% TOC	8 h 10 °C pH 12	[197]
Rhodamine B 5 mg/L	Pt anode $E_{el} = 4 \text{ V}$	22 kHz 400 W	91% decolour.	6 min pH 6.5	[190]

Table 2.5 is continued on p. 46

Table 2.5: Efficiency of EO/US in degradation of different organic compounds in water

Pollutant/ Initial concentration	Working parameters		Removal efficiency	Time/ Conditions	Reference
	Electrochemical	Sonochemical			
Lissamine Green B 20 mg/L Acid Black 24 75 mg/L Methyl Orange 20 mg/L Reactive Black 5; 65 mg/L Trupocor Red 50 mg/L	Graphite anode $E_{el} = 5 \text{ V}$	20 kHz 1.05 W/mL	95% decolour. 60% COD 50.2% decolour. 19% COD 84% decolour. 27% COD 73% decolour. 22% COD 78% decolour. 24% COD	2 h	[198]
Methyl paraben 100 mg/L	BDD 21.6 mA/cm ²	20 kHz 523 W/cm ²	50% TOC	2 h pH 5.7 T = 25 °C	[199]
Methylene blue 200 mg/L	Ti/TiO ₂ -IrO ₂ - RuO ₂ anode I = 11 mA/cm ²	45 kHz 0.42 W/mL	92% TOC	1 h	[200]
Trichloroacetic acid 0.005 M	Pt/Ti anode I = 4 mA/cm ²	24 kHz 0.032 W/mL	96%	6 h	[188]
Triclosan 10 mg/L	$E_{el} = 10 \text{ V}$ DCN anode Silicon carbide Stainless steel	850 kHz 0.425 W/mL	67% 61% 81%	15 min	[201]
2,4-dihydroxybenzoic acid 300 mg/L	Ti/Pt electrodes I = 300 A/m ²	500 kHz 0.75 W/mL	47% TOC	1.5 A·h	[202]

Novel Ti/SnO₂-Sb₂O₃/PTFE-La-Ce-β-PbO₂ anodes were tested in EO/US degradation of 200 mg/L cationic gold yellow X-GL dye in acidic media. The maximum removal efficiency of the dye was about 99.95% and COD removal was 74% under 50 kHz (36.71 W/cm²) US irradiation and electrolysis with applied current density of 71 mA/cm² after 2 h treatment [203]. The same working parameters of EO/US process tested with different anodes modifications (Ti/SnO₂-Sb₂O₃/PTFE-β-PbO₂, Ti/SnO₂-Sb₂O₃/PTFE-La-β-PbO₂, Ti/SnO₂-Sb₂O₃/PTFE-Ce-β-PbO₂) provided about 10% lower removal efficiency towards the dye and COD. The synergetic effect of sonication and electrolysis in EO/US process was confirmed in the study.

Reactive red 195 was completely decolourized at MMO electrodes when assisting EO with 20 kHz (0.04 W/mL output power) US [204]. For comparison, EO degradation provided 90% decolourization and only 3% of colour removal was obtained in US degradation after 2 h of treatment. The initial dye concentration was 100 mg/L and 2 g/L NaCl was used as supportive electrolyte. The COD removal was below 30%. Better hydrodynamics and mass transfer explained the improvement in dye decolourisation in EO/US compared to EO and US processes. Among different electrolytes tested in the degradation of the dye, KCl and NaCl showed the best effect on reactive red 195 degradation. When using Na₂SO₄ and Na₂CO₃ as electrolytes, colour removal did not exceed 50% and COD removal was below 10%. The better results obtained in KCl and NaCl electrolyte solution is explained by generation in situ of chlorine and hypochlorite, which are strong oxidizing agents. The higher powers of ultrasonic irradiation was found to be less efficient in dye decolourisation. This fact is explained by degassing of formed chlorine thus preventing the formation of hypochlorite (2.46).

2.3.3 Removal of phenolic compound

Degradation of phenolic compounds is the second most studied after dyes. Ultrasound was found to increase significantly the current efficiency of EO. It was shown that combination of EO with 20 mA/cm² current density and 33 kHz US (50 W output power) for phenol degradation promoted increase in current efficiency by 100% on BDD electrode and by 49% on Pt anode [56]. Moreover, US enhanced the degradation of phenol in EO/US process by 301% on BDD electrode and by 51% on Pt one. The difference in degradation efficiencies on BDD and Pt electrodes was explained by mechanism of the pollutant decomposition and adsorption. Thus in the case of BDD electrode, US provided 79% decrease of phenol adsorption on the surface of the electrode versus 56% adsorption decrease obtained on Pt anode. BDD provided higher degradation rates of phenol and less variety of intermediate products generated at pollutant decomposition. When applying ultrasonic irradiation, significant enhancement in diffusion coefficients by 375% and 42% was observed for both BDD and Pt anodes respectively.

Nitroaromatics are recalcitrant compounds, which are hardly degradable by conventional wastewater treatment methods. In this regard, AOPs including EO/US method could be potentially effective for their degradation. It was shown that US enhanced the electrochemical degradation of 1,3-dinitrobenzene (DNB) and 2,4-dinitrotoluene (DNT) [205]. The cathodic reduction of DNB and DNT to less toxic dihydroxylamines using combined Ti ultrasonic horn and cathode reached 60 and 50% respectively after 30 min EO/US with 50 mA applied current. Even though the parameters for electrolysis were not optimized, however the enhancement in DNB and DNT oxidation were 3-fold and 2-fold higher in EO/US respectively compared to single electrochemical degradation.

A novel alternated pulsed ultrasound and EO process provided 94.1% of p-nitrophenol removal after 2 h of degradation in a dual-pulse EO/US mode in acidic media (pH 3) [206]. The increase of the pH of treated solution to 11 reduced the degradation efficiency to 35%. The pulse time of potentiostatic EO at 10 V was set to 50 ms. The pulse time of sonication at 22 kHz (48.8W output power) was equal to 100 ms. After 2 h of degradation continuous EO/US process could provide only 89% efficiency versus 58.9 and 2.4% obtained at degradation of 100 mg/L p-nitrophenol in pulsed EO and pulsed US processes respectively. The degradation of the pollutant fitted to the pseudo-first order kinetic model for every degradation process. Ti/Sb-SnO₂ dimensionally stable anode (DSA) was used as a working electrode.

2.3.4 Removal of pharmaceuticals

One of the recent studies on degradation of refractory pharmaceutical cephalosporin wastewater showed that low frequency ultrasound (45 kHz) can enhance the catalytic activity of nano-coated Ti/RuO₂-IrO₂ anode by promotion of [•]OH radicals formed at the electrode surface to the bulk solution without radicals adsorption step on the electrode. Moreover, facilitated chlorine production was obtained in the process [207]. The initial COD of wastewater was equal to 17 630 mg/L and TOC to 7340 mg/L. Stainless steel cathode was used in the study. While applying 8 mA/cm², 45 kHz frequency with output power of 100W for 20 min, complete decolourisation of wastewater was obtained with COD removal efficiency equal to 80% and TOC reduction to around 67% at pH 5. Comparing the degradation of cephalosporin wastewater to single electrolysis and sonication processes, COD reduction in electrochemical treatment did not exceed 40% and was below 3% in sonication alone. While conducting the treatment at the same conditions for 1 h, 94% of COD removal was achieved.

Sonoelectrochemical degradation of commonly used ibuprofen on Pt anodes at constant voltage of 30 V and 1000 kHz (100 W/L) ultrasonic irradiation for 1 h provided 89.3% drug removal in alkaline media [208]. The initial concentration of ibuprofen used in the treatment was equal to 2 mg/L, stainless steel electrode was used as a cathode. The degradation followed the pseudo-first kinetics model. Low ultrasonic frequencies provided low ibuprofen degradation rates, which reduced from 0.027 min⁻¹ when sonicating at 1000 kHz to 0.022, 0.018 and 0.014 min⁻¹ at 500, 300 and 35 kHz respectively. Moreover the highest energy efficiency of 0.062 mmol/kWh was observed

for 1000 kHz frequency. A general trend of higher degradation efficiencies at higher ultrasonic powers was observed.

Removal of anti-inflammatory drug diclofenac exceeded 90% at pH 5.8 when using EO/US process for 5 min [166]. The initial concentration of the drug was 50 $\mu\text{g/L}$ and reaction followed the pseudo-first order kinetics with the rate constant of 0.505 min^{-1} . Kinetic rate of the drug decomposition reduced at lower applied voltage. The potentiostatic electrolysis (7.2 V) on BDD electrodes immersed on 12.1 cm was combined with 850 kHz (94.1 W/L) sonication. Smaller applied voltage of 2.8 V at the same ultrasonic conditions provided only 54% diclofenac removal. The influence of immersion depth on the pollutant removal was insignificant while the effect of electrodes distance was prominent at higher voltages. The smaller distance (1 cm) between the electrodes provided higher degradation rates (93%) compared to the degradation efficiency of 75% at higher distance (3 cm) when using 7.2 V voltage. The removal was dependent on the media pH and decreased from 96.8% at pH 4 to 85.1% at pH 9.9.

3 Objectives of the work

The aim of this research was to develop novel environmentally and cost-effective electrodes working as electrocatalysts and test their activity in the electrocatalytic oxidation of organic compounds such as dyes and organic acids. Moreover, the goal of the research was to enhance the efficiency of electrocatalytic degradation processes by assisting it with ultrasound in order to eliminate the main drawbacks of a single electrochemical oxidation such as electrodes polarization and passivation.

The specific aims were:

1. To prepare novel Ti/Ta₂O₅-SnO₂ electrodes, which would not contain toxic or expensive Pt-group metals in their composition and optimize the electrodes bulk composition and number of active oxide layers for coating (Paper I).
2. To characterize the obtained electrodes structurally and electrochemically. The goal of structural characterization was to study the electrodes crystal structure (Paper I and Paper III), their surface topography and the bulk composition of the obtained oxide films (Paper I). Electrochemical investigation was conducted to find out the electrodes electrocatalytic properties towards methylene blue (MB) oxidation and applicability for water oxidation.
3. To optimize the annealing temperature of Ti/Ta₂O₅-SnO₂ electrodes and compare the surface area properties of electrodes annealed at different temperatures with the surface area properties and commercially available Au electrode (Paper III).
4. To check the electrodes performance towards MB oxidation under continuous agitation fields (Paper III) and reproducibility of electrodes activity after applying different post-treatment procedures (Paper I).
5. To test the electrodes performance in electrochemical MB dye and formic acid oxidation experiments and find the best media conditions for the electrolysis process (Paper II, III and IV).
6. To estimate the effect of a wide range of ultrasonic frequencies and powers on MB degradation efficiency (Paper II).
7. To improve the efficiency of MB and formic acid degradation by assisting electrochemical oxidation of model pollutants with ultrasound and study the synergetic effect of electrolysis and sonication in sonoelectrocatalytic degradation experiments (Paper II and IV).
8. To investigate the energy efficiency of electrochemical (Paper II and III), sonochemical and sonoelectrochemical (Paper II and IV) degradation experiments using model organic pollutants.

4 Experimental work

4.1 Ti/Ta₂O₅-SnO₂ electrodes preparation

Preparation of novel Ti/Ta₂O₅-SnO₂ electrodes is described in details in Papers **I**, **II** and **III**. Briefly, electrodes were first prepared by drop casting technique and thermal decomposition using Ti substrates and organic solvent based metal chlorides precursor. All chemicals required for precursor and pretreatment solutions preparation were of analytical grade and used without further purification.

The electrode composition was modified by changing the concentration of tantalum and tin in the precursor solution and keeping the total metal ion concentration constant at 0.04 M. The atomic content of Ta in the prepared electrodes varied from 0 to 50%. The amount of active layers deposited on Ti substrate were ranged from one to ten. Annealing of electrodes was conducted for 10 h at temperatures of 450, 550, 650 °C in muffle furnace.

4.2 Physicochemical and electrochemical characterization of the electrodes

The surface microstructure and composition of electrodes was determined by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy for elemental analysis of microareas (**Paper I and III**). X-ray diffraction spectrometry (XRD) was used to analyse the crystal structure of the electrodes (**Paper I and III**).

The electrochemical characterization of electrodes was conducted by Potentiostat/Galvanostats PGSTAT12 (**Paper I and III**) and PGSTAT 30 (**Paper I**) using cyclic voltammetry (CV) technique with scan rates between 5 and 100 mV/s in a conventional three electrode cell. Solution of 0.1 mM methylene blue (MB) and 0.1 M Na₂SO₄ was used for the detection of electrocatalytic activity of Ti/Ta₂O₅-SnO₂ electrodes at different pH media, which was controlled by H₂SO₄ or NaOH. Solution of 0.1 M Na₂SO₄ was used as reference solution. To estimate the active surface of prepared electrodes and compare it with common available electrodes, CV measurements were conducted in 0.5 mM potassium hexacyanoferrate (II) trihydrate and 0.1 M Na₂SO₄ solution using Ti/Ta₂O₅-SnO₂ electrodes (**Paper I and III**) and gold disk electrode (**Paper III**) as working electrodes.

In **Paper I** the reproducibility of electrocatalytic activity of Ti/Ta₂O₅-SnO₂ electrodes with Ta chosen nominal content of 25 and 37.5 at.% was checked by applying different post treatment procedures such as ten voltammetric cleaning cycles between 0.2 and 2.5 V in 0.1 M Na₂SO₄, annealing for 1 h at 550 °C and cleaning in ultrasonic bath for 30 minutes. To prove the ability of mechanical agitation of the solution to improve and maintain a constant mass transport of electroactive species near to the electrode surface CV measurements in magnetic stirring and ultrasonic irradiation field were carried out (**Paper III**).

4.3 Experimental set-up in degradation experiments

Fig. 4.1 shows a general experimental set-up used in sonication, electrolysis and sonoelectrochemical degradation experiments. Power amplifier, ultrasonic sinus wave generator and transducer were used for sonication part and power supply was used in electrochemical experimental part. Electrolysis was conducted using two electrodes set-up with Ti/Ta₂O₅-SnO₂ electrode as an anode and Ti plate as a cathode. While carrying out sonication or electrolysis alone, either sonochemical or electrochemical part worked. In the case of sonochemical experiment, electrodes were withdrawn from the reaction vessel. Combined EO/US experiments were conducted with a simultaneous work of sonication and electrolysis parts. In all experiments, a glass beaker played a role of reaction chamber. The majority of sonication experiments were conducted using indirect ultrasonic irradiation. In **Paper II** the decolourisation of dye was controlled online using a peristaltic pump for solution circulation through a UV-Vis spectrophotometer (Fig. 4.1c). In **Papers II and IV** when conducting indirect sonication of solutions containing synthetic pollutant, the beaker was placed into a jacketed ultrasonic bath with water circulation for cooling (Figure 4.1b and c). Direct sonication was conducted in **Paper II** using low frequency 20 kHz ultrasonic probe which was placed in the beaker with working solution (Fig. 4.1a). Working parameters of degradation experiments are listed in Table 4.1. The actual ultrasonic power generated within the working solution were determined by calorimetry measurements.

Table 4.1: Experimental parameters for pollutants degradation

Paper No.	Type of degradation experiment	Pollutant and pollutant concentration	Volume of working solution, ml	Applied current density, mA/cm ²	Ultrasonic frequency, kHz	Supporting electrolyte and its concentration
II	EO/US	MB 0.025 mM	50	9.1	380, 850	Na ₂ SO ₄ , 0.1 M
	US	MB 0.025 mM	50	-	20, 40, 380, 850, 1000, 1176	Na ₂ SO ₄ , 0.1 M
	EO	MB 0.025 mM	50	9.1	-	Na ₂ SO ₄ , 0.1 M
III	EO	MB 0.1 mM	30	9.1	-	Na ₂ SO ₄ , 0.1 M
IV	EO	FA, 250 mg/l	40	4.5; 9.1; 13.6	-	NaCl, 3 g/L
	US	FA, 250 mg/L	40	-	381	NaCl, 3 g/L
	EO/US	FA, 250 mg/L	40	-	381, 863, 992, 1176	NaCl, 3 g/L

Figure 4.1: Experimental set-up (a) in **Paper II** using 20 kHz ultrasonic probe (Sonics and Materials Inc., VCX 600, 600W of max output power, 12.5 mm tip) and Thulby PL320 DC power supply; (b) in Paper IV using ultrasonic bath (Meinhardt, Ultraschalltechnik, 250 W of maximum output power) with transducer type E/805/TM, (75 mm diameter) fitted at the bottom of cylindrical jacketed glass reactor [100] and programmable power supply GW Instek, PSP-405; (c) in Paper II using 40 kHz ultrasonic bath (Langford Electronics, Sonomatic 375TT, 300W of output power), 850 kHz bath (Meinhardt, K80-5, 140W of max output power, 69.6 mm transducer diameter fitted at the bottom of cylindrical reactor) and multi-frequency bath operated at 380, 1000 and 1176 kHz (Meinhardt, M11, 250W of max out power, 52 mm transducer diameter fitted at the bottom of cylindrical reactor) and Thulby PL320 DC power supply.

4.4 Analysis of liquid samples

The decolourisation efficiency of MB was controlled by UV-Vis spectrophotometer (Lambda 45, UV-2450, Perkin Elmer Instruments in **Paper II** and **III**) through the monitoring light absorbance by MB at 664 nm in neutral and acidic media and at 591 nm in basic one. Chemical oxygen demand (COD) was controlled by Dr. Hach Lange 2800 (Paper II) and 200 (Paper III) systems. Mineralization efficiency of pollutant was controlled by measuring total organic carbon (TOC) and non-purgeable organic carbon (NPOC) by TOC analyser (Sartec Limited DC190, Sartec Group in **Paper II** and TOC-Vcpn, Shimadzu in **Paper III and IV**). Shimadzu LC-20 high performance liquid

chromatograph (HPLC) using Shodex RSpak KC-811 column and UV-Vis detector SPD-20AV measured FA concentration in the working solutions.

4.5 Energy efficiency control and kinetics

The energy consumption (EC, kWh/m³) per volume of working solution and current efficiency (CE, %) in electrolyses processes were calculated using Eq. 7-8:

$$EC \text{ (kWh/m}^3\text{)} = IVt/V_s \quad (\text{Eq. 7})$$

$$CE \text{ (\%)} = ((\Delta COD)FV_s/8It) \times 100 \quad (\text{Eq.8})$$

where I is the average applied current (A), V is the average cell voltage (V), t is the electrolysis time (h in the case of EC) or time of the COD decay (s in the case of CE), V_s is the solution volume (dm³), ΔCOD is the COD reduction (g/dm³) at time t , F is the Faraday constant (96487 C/mol) and the constant 8 is the oxygen equivalent mass (q/equiv).

The EC for the sonication process was estimated from the actual ultrasonic powers determined by calorimetry measurements and sonication time. The EC for sonoelectrochemical process was determined by summarizing the EC of electrolyses and sonication processes.

Kinetics rate constants derived from the plot of natural logarithm versus degradation time were best fitted to the first-order kinetic model represented by Eq. 9:

$$\ln C_t = \ln C_0 - kt \quad (\text{Eq. 9})$$

where C_0 is the initial concentration of pollutant, C_t is the concentration of pollutant at time t and k is the first-order rate constant which was estimated from the slope by plotting.

5 Results and discussion

5.1 XRD analyses

XRD analysis was used to identify the crystal structure of the prepared thin films of Ti/Ta₂O₅-SnO₂ electrodes in **Papers I and III**. All patterns of prepared electrodes for the exception of electrodes annealed at 650 °C contained intense peaks of hexagonal Ti substrate corresponding to the (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) crystal orientations of titanium. XRD patterns on Fig. 5.1a contained additional peaks associated to the (0 0 4) and (1 0 4) planes which can be explained by a wider range of 2-Theta scale applied in the studies. XRD patterns of Ti/Ta₂O₅ - SnO₂ electrodes annealed at 650 °C contained only the one clear pick of hexagonal Ti appearing at $2\theta = 40.141^\circ$ (Fig. 5.1b) which could be explained by high crystallinity of thin films formed at 650 °C and dense Ta₂O₅ - SnO₂ coating obtained. The presence of low intensity tetragonal rutile (TiO₂) peaks corresponding to the (101), (111) and (211) main atomic planes in the electrodes films annealed at 550 °C except those with Ta content of 50 and 7.5% (8 layers) can be explained by the oxygen solubility in the metal lattice of the titanium substrate. Tantalum XRD patterns showed the reflections corresponding to the (0 0 1), (1 1 1 0), (2 8 0), (1 1 1 1), (0 0 2), (3 10 1) atomic planes (Fig. 5.1a) and (0 0 1), (1 1 0), (2 0 0), (1 1 1), (2 0 1), (0 0 2), (3 1 0), (2 0 2), (3 1 2), (4 0 2) planes (Fig. 5.1b) typical of orthorhombic β -Ta₂O₅. Electrodes containing 8 active layers of Ta₂O₅-SnO₂ films and annealed at 550 °C contained peaks corresponding to the (0 0 1), (1 0 0), (1 0 1) planes (Fig. 5.1a) and (0 0 3), (2 0 0), (2 0 3), (0 0 6) and (2 2 0) planes (Fig. 5.1b), which are typical of hexagonal δ -Ta₂O₅. Tin was represented by tetragonal rutile SnO₂ with main peaks corresponding to the (1 1 0), (1 0 1) and (2 1 1) atomic planes (Fig. 5.1a and b) and minor peaks corresponding to the (1 1 1), (3 1 0), (3 0 1), (2 0 2), (3 2 1), (4 0 0) and (3 3 0) reflections.

Even though electrodes annealed at 650 °C revealed the highest crystallinity, annealing temperatures higher than 550 °C had insignificant effect of electrodes electrocatalytic efficiency towards MB degradation (see below). Ti/Ta₂O₅ - SnO₂ electrodes annealed at 450 °C as well as Ti/Ta₂O₅, Ti/Ta₂O₅-SnO₂ ($x = 7.5$ at.%, 4 layers) and Ti/Ta₂O₅-SnO₂ ($x = 50.0$ at.%) electrodes annealed at 550 °C revealed the low intensity of metal oxides peaks and a high intensity hexagonal Ti peaks, which can be explained by a low crystallinity of the film formed at this temperature. Ta₂O₅ peaks were absent in the diffractograms of Ti/Ta₂O₅ and Ti/Ta₂O₅-SnO₂ ($x = 7.5$ at.%, 4 layers) electrodes. Ti/Ta₂O₅-SnO₂ (450 °C annealing) and Ti/Ta₂O₅-SnO₂ ($x = 50.0$ at.%) electrodes did not contain SnO₂ peaks.

5.2 SEM and EDX analyses

Fig. 5.2 shows SEM images of Ti/Ta₂O₅, Ti/SnO₂ and Ti/Ta₂O₅-SnO₂ of different annealing temperature and nominal composition. EDX element mapping of the Ti/Ta₂O₅-SnO₂ electrodes annealed at 450, 550 and 650 °C with Ta content of 7.5 at.% represented on Fig. 5.2 (n-o, q-r, t-u). In general, the surface structure of electrodes prepared at different annealing temperatures and with different nominal composition is slightly cracked which is typical of many MMO electrodes [209] [210] [211]. The surface of Ti/Ta₂O₅ electrode (Fig. 5.2a) was porous in contrast to the surface of Ti/SnO₂ electrode (Fig. 5.2b), which was clogged. The addition of Ta to the SnO₂ coating partly recovers the roughness of electrode surface due to the formation of Ta₂O₅ oxides (Fig. 5.2c –g). Among annealing temperatures of 450, 550 and 650 °C the surface of the electrode prepared at 550 °C (Fig. 5.2p) is rougher with cavities and pin holes on it. This allows assuming a potentially larger active surface area available for mass transfer at electrolysis. The influence of surface roughness and porosity on diffusion to the electrode surface will be discussed below.

The element distribution over the surface of Ti substrate was studied using EDX mapping. As it can be seen from Fig. 5.2o, r, u Sn distribution over Ti substrate is nearly homogeneous with a greater content on electrodes annealed at 550 °C and smaller accumulation on the surface of electrodes annealed at 450 and 650 °C. Distribution of Ta over Ti substrate and SnO₂ films is less uniform (Fig. 5.2 n, q, t) with formed Ta₂O₅ particles varying in a size from a few nanometers (dots on the mapping images) to a few micrometers (bright blue agglomerates on the mapping images).

Paper I contains more detailed information on experimental bulk composition and Sn/Ta atomic ratios of the Ti/Ta₂O₅-SnO₂ electrodes, which were determined by EDX microanalysis. Shortly, the electrodes containing 8 active Ta₂O₅-SnO₂ catalytic oxide layers showed the best agreement between nominal and prepared Sn/Ta atomic ratios. The surface texture of the Ti/Ta₂O₅-SnO₂ electrodes annealed at 550 °C and containing different number of active metal oxide layers is investigated in the **Paper I**. The dependence of porosity on the number of active layers was insignificant.

Fig. 5.2: SEM images of (a) Ti/Ta₂O₅, (b) Ti/SnO₂, and Ti/Ta₂O₅-SnO₂ electrodes of different nominal composition for 550 °C annealing temperature: (c) 50.0 at.%, (d) 25.0 at.%, (e) 12.5 at.% and (g) 7.5 at.%; different annealing temperatures of 450 °C (m-o), 550 °C (p-r), 650 °C (s-u) and element-mapping for the electrode with x = 7.5 at.%, (n, q, t). Ta mapping and (o, r, u) Sn mapping.

5.3 Cyclic voltammetry

5.3.1 Characterization of electrodes

Cyclic voltammetry was chosen to characterize electrodes annealed at different temperatures. To compare the electrodes relative surface area, the cyclic voltammograms (CVs) were taken in a simple ferrocyanide-ferricyanide redox couple solution. Figure 5.3 shows CVs run in aqueous solution of 0.5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.1 M Na_2SO_4 at different potential scan rates for $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrode annealed at 550 °C. The process was classified as quasi-reversible with well-formed oxidation and reduction peaks. The separation between the peaks (Table 5.1) was varying from 98 mV at the scan rate of 5 mV/s to 129 mV at the sweep rate of 100 mV/s which is greater than 60 mV/s for an ideal reversible process. This could be explained by a high resistance of prepared electrodes. The diffusion coefficient was estimated from the linear dependence of the anodic peak current I_p on the square root of the sweep rate using the Randles-Sevcik equation. The value of diffusion coefficient were equal to $9.2 \cdot 10^{-6} \text{ cm}^2/\text{s}$, which is in good correspondence with literature data [212] [213].

Table 5.1 demonstrates the peak current densities for the oxidation of 0.5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ obtained at $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrodes of different annealing temperatures, Pt deposited on vitreous carbon electrode and commercial gold disc electrode. The CVs were recorded at a potential scan rate of 5 mV/s.

Figure 5.3: CVs $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrode annealed at 550 °C in 0.5 mM $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and 0.1 M Na_2SO_4 at different scan rates v.

Table 5.1: Peak currents for the oxidation of 0.5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in 0.1 M Na_2SO_4 for Ti/Ta₂O₅-SnO₂ electrodes, gold disk electrode and Pt deposited on vitreous carbon at a scan rate of 5 mV/s.

Electrode	Annealing temperature	Peak Current Density/ $\mu\text{A}/\text{cm}^2$
Ti/Ta ₂ O ₅ -SnO ₂	450	41.2
	550	35.4
	650	32.8
Au disc electrode	-	22.1

As it is seen from Table 5.1, Ti/Ta₂O₅-SnO₂ electrodes annealed at different temperatures had anodic oxidation peak of about the same order of magnitude with the highest value observed for the electrode annealed at 450 °C and the lowest one for the electrode annealed at 650 °C. These values were compared to the values obtained from commercial Au disc electrode and Pt deposited on vitreous carbon. In both cases oxidation peak currents from Ti/Ta₂O₅-SnO₂ electrodes were 1.5 – 2 times higher. This proves the resulting surface roughness of prepared electrodes shown on Fig. 5.2 and active working area of about 1.5 – 2 times higher than that for Au disc and Pt on vitreous carbon electrodes. The decrease of peak current density with the annealing temperature increase could be explained by formation of poorly conductive oxide layer between the coating and Ti substrate which was observed by other workers (**Paper III**) [214].

5.3.2 Water and MB oxidation

Fig. 5.4 shows the results on optimization of Ta content in Ti/Ta₂O₅-SnO₂ electrodes with Ta(x) - Sn(100-x) nominal composition of metal ions in the precursor solution. CV measurements run on the electrodes with x atomic content varied from 0 to 100 % in a blank solution of 0.1 M Na_2SO_4 are shown on Fig. 5.4a. As it was expected, Ti/SnO₂ and Ti/Ta₂O₅ electrodes could not produce a significant anodic current up to 2.5 V which is explained by a wide band gap of n-type semiconductors. While increasing the amount of Ta in the precursor solution from 0 to 2.5 at.%, the anodic current density corresponding to the OER increased from 34.5 at Ti/SnO₂ electrode to 115 $\mu\text{A}/\text{cm}^2$. When raising Ta content to 5 at.% anodic current density increased by the factor of 72 to $2.5 \cdot 10^3 \mu\text{A}/\text{cm}^2$ showing the highest performance of this electrode towards water oxidation. Further increase of Ta content led to lowering of anodic current densities of OER until it dropped to the level of Ti/SnO₂ and Ti/Ta₂O₅ electrodes at x = 50 at.%. This could be explained by improvement of carrier density and lowering the resistivity of SnO₂ films owing to Ta doping effect.

Figure 5.4: Cyclic voltammograms of Ti/SnO_2 , $\text{Ti/Ta}_2\text{O}_5$ and $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ electrodes of 8 active oxide layers in (a) $0.1 \text{ M Na}_2\text{SO}_4$ and (b) $0.1 \text{ M Na}_2\text{SO}_4$ and 0.1 mM MB ; $\nu = 50 \text{ mV/s}$.

To determine a possible applicability of $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ electrodes for organic compounds electrocatalytic oxidation, CVs were run in $0.1 \text{ M Na}_2\text{SO}_4$ and 0.1 mM MB aqueous solutions. As it can be seen from Fig. 5.4b all voltammograms for the exception of those obtained on Ti/SnO_2 and $\text{Ti/Ta}_2\text{O}_5$ electrodes contained a new anodic oxidation peak with a peak maximum at $1.1 - 1.2 \text{ V vs. SCE}$. The peak was attributed to MB oxidation and $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ electrodes were proved to have electrocatalytic activity towards MB oxidation. In order to find the highest electrocatalytic activity of the electrodes, their nominal composition was modified by addition of Ta. The addition of Ta in the amount of 5 at.% gave a significant increase in an anodic current of MB oxidation. However, the maximum of electrocatalytic activity was reached at Ta content of 7.5 at.%. Since $\text{Ta}_2\text{O}_5\text{-SnO}_2$ films with a nominal composition of $x = 7.5$ at.% were constituted only by

hexagonal δ -Ta₂O₅, it was suggested that hexagonal δ -Ta₂O₅ enhanced the electrocatalytic activity of the films (see (0 0 1), (1 0 0) and (1 0 1) atomic planes on Fig. 2). Further rise of Ta content in oxide films decreased the electrocatalytic activity of the electrodes and shifted the onset potential of OER to more positive values. That could be explained by the enhanced adsorption of MB on Ta₂O₅ active centers, which blocks the catalytic activity of the electrodes with Ta content higher than 7.5 at%. Relatively reversible anodic current at potential of 0.2 – 0.5 V which was absent on CVs obtained in the blank solution was attributed to pseudo/capacitive process of MB adsorption/desorption. The second anodic oxidation peak on voltammogram of Ti/Ta₂O₅-SnO₂ electrode with x = 7.5 at.% at potential of 1.6 V was assigned to the oxidation of potentially formed oxidation products caused by nascent oxygen generation at films surface.

To estimate the effect of the Ta₂O₅-SnO₂ film thickness on the electrocatalytic properties, several Ti/Ta₂O₅-SnO₂ electrodes were prepared with a different number of active oxide layers and tested in the blank solution of 0.1 M Na₂SO₄ and working solution of 0.1 M Na₂SO₄ and 0.1 mM MB. The results on CVs run are presented on Fig.5.5.

As the number of layers increases, the onset potential for the OER shifts to more negative values, and the currents generated by OER increase. Fig. 5.5a shows that for one and two active layers the potentials needed to generate for example a 100 μ A/cm² current density are the most positive ones (2.6 – 2.7 V) while increasing the number of active layers reduces the required potential from 2.6 -2.8 V to less than 2 V for 6 – 10 layers. For current density equal to 250 μ A/cm² the overpotential of OER decreased by 110 mV for ten-layer electrodes compared to the one layer electrode. The activity of the electrodes also increased with the number of layers at constant potential, which could be explained by the influence of underlying Ti substrate clearly detected during SEM and XRD measurements (**Paper I**).

The maximum current reached 1430 μ A/cm² for 10 active layers of Ta-doped SnO₂ electrode at 2.5 V. On the other hand, its electrocatalytic activity for MB oxidation (Fig. 5.5b) was similar to that of the 8-layer electrode. However, the peak profiles of the MB oxidation process are different for the 8 and 10-layer electrodes, indicating slight differences in their electrocatalytic activity. The current generated at potentials more positive than 1.6 V was mainly used for water oxidation. While running CVs with this electrode in the working solution, the height of the anodic peaks decreased with each scan (see inset in Fig. 5.5b). It can be explained by poor mass transfer at the surface of the electrode derived from the low concentration of the dye. During the first scan the MB coverage on the electrode surface was high, and thus the oxidation current was also high. However, with each subsequent scan, the coverage of MB decreased together with the anodic oxidation peaks. Moreover, the CV profiles corresponding to the OER recorded in the working solution were shifted towards positive potentials with respect to those of the blank solution. Therefore, poor mass transfer was also aggravated by fouling the electrode with degradation products of MB leading to the formation of organic films on the electrode surface, as is frequently the case for MMO [215] [216].

Figure 5.5: CVs of Ti/Ta₂O₅-SnO₂ electrodes of nominal composition $x = 7.5$ at.% and different number of active layers in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ and 0.1 mM MB; $\nu = 50$ mV/s. Inset Fig. 4b: Different voltammetric cycles for Ti/Ta₂O₅-SnO₂ electrodes with eight active layers in 0.1 M Na₂SO₄ and 0.1 mM MB (scan 1-3) and third scan in 0.1 M Na₂SO₄ (blank); $\nu = 50$ mV/s.

Figure 5.6: CV of Ti/Ta₂O₅-SnO₂ electrodes prepared at different temperatures (Fig. 4a) and run in different media (Fig. 4b) in working solution of 0.1 mM MB and 0.1 M Na₂SO₄ (Fig 4b) adjusted to of pH = 2 and pH = 12 (Inset Fig. 4b) with H₂SO₄ or NaOH respectively for Ti/Ta₂O₅-SnO₂ electrode annealed at 550 °C. $\nu = 50$ mV/s.

To prove the best performance of Ti/Ta₂O₅-SnO₂ electrodes for MB oxidation, the annealing temperatures and media for conducting electrolyses experiments were optimized. Fig. 5.6a shows the CV results of prepared Ti/Ta₂O₅-SnO₂ electrodes annealed at different temperatures and recorded from a working solution of 0.1 mM MB and 0.1 M Na₂SO₄. The voltammograms of electrodes annealed at 550 and 650 °C contain an

anodic current peak of MB oxidation with a maximum at potential of 1.1 V. Anodic current of $60 \mu\text{A}/\text{cm}^2$ at potential of 1.1 V is 3 and 8 times higher for the electrode annealed at 550°C than for electrodes annealed at 650°C and 450°C respectively. The higher capacitance current observed at potentials between 0.2 and 0.5 V from the electrode annealed at 550°C also confirms a greater microroughness. Therefore, it was confirmed that annealing temperature of 550°C for tantalum/tin oxide coating shows promise as a non-precious metal electrode for the electrocatalytic oxidation of MB.

To optimize an electrochemical behaviour of $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrodes for MB oxidation at different pH, CVs were conducted in the working solutions of 0.1 M Na_2SO_4 and MB at pH 2, 6.5 and 12 (Figure 5.6b). Anodic current density peaks of MB oxidation with the values of 60 and $30 \mu\text{A}/\text{cm}^2$ were recorded on voltammograms at pH 6.5 and at pH = 2 respectively. However, no anodic current of MB oxidation was observed at pH value of 12, (Inset Fig. 5.6b). The absence of MB oxidation peak is explained by a significant shift of the OER onset potential to more negative values from about 1.8 V to 1.4 V and overlapping the MB oxidation peak. Once more it was confirmed that alkali media is therefore more favourable for OER rather than MB oxidation.

To check the reproducibility of these results and the ability of electrodes to recover their electrocatalytic activity some post treatment procedures were applied to the Ta-doped SnO_2 electrodes of nominal composition $x = 25 \text{ at\%}$ and $37.5 \text{ at\%}$. The chosen electrodes were: i) submitted to 10 voltammetric cycles between 0.2 and 2.5 V in the blank solution, ii) annealed at 550°C for 1 h, iii) cleaned in a ultrasonic bath (FinnSonic M08, 200 W, 40 kHz) for 30 minutes. CVs were recorded after each treatment both in the blank solution and in the working solution. All the treatment applied to the electrodes demonstrated either a partial or a complete recovery of the electrocatalytic activity towards MB oxidation. Annealing at 550°C was found the most effective way to recover the electrodes electro-activity towards water oxidation. Electrochemical cleaning had either insignificant or no effect on the recovery of electrodes activity for water electrolysis and oxidation of MB. Ultrasonic treatment appeared to be a good way to clean the electrode due to the increase of electrode films electro-activity towards both water oxidation and MB oxidation. For more information, please refer to **Paper I**.

To avoid depletion of mass transfer near to the electrode surfaces, a continuous agitation of working solution should be maintained. Typically, this is achieved on an industrial scale by a number of techniques for example rapid stirring, pumping or using turbulence promoters [217]. Ultrasound can also be applied to enhance mass transport of electroactive species to the electrode surface. Moreover, the sonication can initiate the generation of hydroxyl radicals increasing the oxidation rates of organic pollutants. Figure 5.7 shows the first and sixth scans from the CV measurements using a magnetic stirrer (Fig. 5.7a) and with a 30 kHz ultrasonic field applied (Fig. 5.7b). The cyclic voltammogram exposed to continuous stirring and ultrasonic irradiation showed no change in the current density response. This means that MB is replenished as fast as it is consumed at the electrode surface. Therefore, applying ultrasonic irradiation to electrolyses processes can provide good electrolyte movement and accelerate the MB oxidation of MB through hydroxyl radical generation.

Figure 5.7: Different CV scans of Ti/Ta₂O₅-SnO₂ electrodes made in the working solution of 0.1 mM MB and 0.1 M Na₂SO₄ in acidic media (pH = 2) under the influence of ultrasonic field (Fig. 9a) and with magnetic stirrer (Fig. 9b). $\nu = 50 \text{ mV s}^{-1}$

5.4 Electrochemical degradation

5.4.1 MB degradation

Electrocatalytic activity of Ti/Ta₂O₅-SnO₂ electrodes was tested in electrochemical degradation experiments using 0.1 mM MB in 0.1 M Na₂SO₄ as a model pollutant. A series of electrolysis experiments was conducted in different media at pH 2, 6.5 and 12 using magnetic stirring of 1000 rpm (Fig. 5.8).

Figure 5.8: Colour removal efficiency after 8 h of electrolysis of 0.1 M Na₂SO₄ and 0.1 mM MB working solution.

According to Fig. 5.8 decolourisation efficiencies of 95% were obtained in original media of the working solution (pH 6.5) followed by 80% achieved in acidic media and 78% in basic conditions after 2 h of degradation. The lower degradation efficiency achieved in basic conditions was explained by low overpotential towards OER and was confirmed by CV measurements. The complete decolourisation of MB solution regardless the medium acidity was obtained after 6 h of oxidation process. The COD decrease obtained at pH 2, 6.5 and 12 was equal to 70, 85 and 26% respectively after 2 h of oxidation (**Paper III**). Decolourisation and COD removal efficiencies obtained after 2 h of MB electrolysis at Ti/Ta₂O₅-SnO₂ electrodes was comparable to MB degradation efficiencies obtained in other studies at Pb/MnO₂, PbO₂-ZrO₂ and TiO₂-NTs/Co-PbO₂ electrodes [79] [67] [218]. As it is seen, all mentioned electrodes contain potentially toxic Pb in the structure thus emphasizing the advantages of Ti/Ta₂O₅-SnO₂ electrodes to be environmentally friendly. NPOC reduction data obtained during electrolysis showed that MB mineralization reached 71, 74 and 76% at pH of 12, 6.5 and 2 respectively after 8 h of degradation for the electrodes annealed at 550 °C (**Paper III**).

5.4.2 FA degradation

To estimate the effect of applied current on FA removal efficiency galvanostatic electrolysis was conducted at applied currents of 10, 20 and 30 mA (4.5, 9.1 and 13.6 mA/cm² respectively). Figure 5.9 shows the dependence of FA removal efficiency and its kinetic behaviour (Inset Fig. 5.9) from the electrolysis time with currents applied. The degradation followed the first-order kinetic model. The first-order kinetic rate constants were estimated from the slope by plotting the logarithm of FA concentration versus time for the degradation experiments.

Figure 5.9: Effect of the current applied on FA removal efficiency and variation of the kinetic behaviour with the applied current (Inset Fig. 5.9).

The slowest kinetics of FA degradation was obtained at 10 mA applied current (0.0079 min^{-1}) with the maximum FA removal efficiency of 64% after 2 h of electrolysis. When increasing current densities to 9.1 and 13.6 mA/cm^2 , the kinetic rate constants increased more than 2-fold to 0.0185 and 0.0207 min^{-1} showing nearly the same FA removal efficiencies of 92 and 92.8% respectively after 2 h of degradation. NPOC removal reached 58.6, 74.6 and 77.7% after 2 h of electrochemical degradation experiments using 4.5, 9.1 and 13.6 mA/cm^2 current densities respectively. This can be explained by mass transfer limitations in the process and higher electrode polarization at higher current densities [219]. For this reason it was considered that 9.1 mA/cm^2 was the best current density to employ because 13.6 mA/cm^2 provided only a slight improvement in rate constant and a negligible increase in removal efficiency. It was decided to conduct further studies of the sonoelectrochemical experiments at a constant current density of 9.1 mA/cm^2 .

The direct mechanism of FA degradation was suggested taking into account the chemical structure of the acid and relatively high degradation efficiency and was similar to that introduced elsewhere for BDD electrode [220]:

5.5 Sonochemical degradation

5.5.1 MB degradation

Sonochemical MB degradation was conducted in a range of different frequencies (20, 40, 380, 850, 1000 and 1176 kHz). The values of the real power entering into the reaction vessel were calculated using calorimetrically technique and can be found in **Paper II**. To estimate the effect of ultrasound on MB decolourisation a detailed examination of dependency of colour removal efficiency on different frequencies and powers was conducted.

Fig. 5.10 shows the decolourisation removal obtained during the sonication of the working solution at different ultrasonic frequencies. The ultrasonic frequency of 1000 (0.8 W) kHz did not have any effect on the dye degradation. The frequency of 1176 kHz (0.4 W) had a slightly better efficiency giving about 6% of MB colour removal. The low efficiency at 1000 and 1176 kHz frequencies is explained by low actual ultrasonic powers generated by the equipment thus producing lower cavitation effect. The complete decolourisation of solution was achieved using 380 (2.7 W) and 850 kHz (9.3 W) after 3 and 1.5 h of sonication respectively. When applying 20 kHz (8.8 W) and 40 kHz (4.9 W) ultrasonic irradiation for 3 h the colour removal reached only 58 and 19% respectively. Despite the higher powers employed at 20 and 40 kHz comparable with those produced at 380 and 850 kHz baths, the higher frequencies provided better degradation rates. This was explained by the higher production of hydroxyl radicals at higher frequencies as a result of a shorter cavitation bubbles lifetime and increased bubbles collapse per a unit of time [45–47]. While making a general comparison of a direct (ultrasonic probe is immersed into solution) and indirect (ultrasonic energy is transmitted to the working solution through an intermediate media; water in our case) sonication, direct system transmit more ultrasonic energy directly to the working solution. It is possible to proceed smaller volumes with higher ultrasonic intensities in direct set-ups. In the case of indirect sonication, significant amount of energy is reflected from the intermediate liquid/reactor vessel walls interface. However, the main advantages of indirect set-up is applicability to sterile solutions as well as the elimination of sample lost and solution foaming. Effect of different ultrasonic frequencies on dye decolourisation was further analysed using about the same ultrasonic powers for the treated solution irradiation (**Paper II**). The results did not show any clear dependence of decolourisation rates on ultrasonic frequencies. In this regards a careful optimization of working parameters is required in sonication processes, which was confirmed by a number of studies [221] [222].

The effect of different ultrasonic powers on MB decolourisation was studied using ultrasonic irradiation at 850 kHz (Fig. 5.11), which has the highest efficiency towards MB degradation. Fig. 5.11 shows a general trend of higher degradation rates at higher powers, which can be attributed to an increased number of cavitation bubbles produced at higher powers leading to enhanced hydroxyl radicals formation [208].

Figure 5.10: Effect of sonication at different frequencies upon decolourisation of 0.025 mM MB and 0.1 M Na₂SO₄ solution.

Figure 5.11: Effect of different ultrasonic powers at constant frequency on decolourisation efficiency of 0.025 mM MB and 0.1 M Na₂SO₄ solution.

5.5.2 FA degradation

Ultrasonic irradiation of 250 mg/L FA in 3 g/L NaCl at 1176, 992, 862 and 381 kHz provided a negligible effect on pollutant degradation with a maximum degradation efficiency of 2.5% obtained after 2 h sonication at 381 kHz (Fig. 5.12). Taking into account resistivity of FA to treatment processes and low oxidation efficiency of MB in the previous studies, it was decided to change electrolyte from Na₂SO₄ to NaCl since chloride ions facilitate the indirect oxidation of pollutants by means of electrogeneration of strong oxidizing agent such as hypochlorite. The degradation followed the first-order kinetic model with kinetic rate constants within the range from 0.00004 to 0.0001 min⁻¹ (**Paper IV**). When comparing the sonochemical degradation of FA with electrochemical treatment, electrolysis provided 90% removal of FA in the same time.

Based on literature data, it was reported that 22.7 kHz horn and 20 kHz ultrasonic bath can provide 14 and 6% degradation of 250 mg/L FA [137]. When using direct sonication (590 kHz) for degradation of 1000 mg/L FA without stirring, the maximum degradation efficiency of 3% can be achieved in 1.5 h [140]. When applying 200 rpm mechanical stirring the degradation efficiency increased more than twice up to 6%. The increase of degradation rate at stirring can be explained by improved compound distribution in the reactor, which enhances degradation rates. The low degradation efficiencies obtained in this work is probably attributed to the low powers used, indirect sonication and absence of stirring in the reactor. When conducting indirect sonication only around 37% of energy is transmitted across water/pyrex glass reactor and about 63% is lost due to reflection interface (based on acoustic impedance data).

Figure 5.12: Effect of ultrasonic frequencies on removal of 250 mg/L FA in 3 g/L NaCl in sonochemical degradation experiments.

5.6 Sonoelectrochemical degradation

5.6.1 MB degradation

Fig. 5.13 shows the dependence of MB decolourisation upon the time of degradation in EO, US and EO/US experiments. Ultrasonic frequencies of 380 (0.054 W/mL) and 850 kHz (0.186 W/mL) were used in combined EO/US process due to their high efficiency obtained in sonication. As can be seen in Fig. 5.13 electrolysis and sonication applying 380 kHz irradiation provided almost complete decolourisation of the working solution in three hours of degradation. Combined electrolysis and sonication provided complete decolourisation of MB in 45 minutes compared to 90 and 180 minutes obtained in independent sonication and electrolysis respectively while using 850 kHz frequency and 20 mA current (see vertical lines in the figure). When combining 380 kHz sonication and 20 mA electrolysis the complete decolourisation rate increased by a factor of 3 and was achieved in one hour versus three hours in separate processes of sonication and electrolysis (Inset Fig. 5.13).

Figure 5.13: Comparison of electrochemical, sonochemical and sonoelectrochemical decolourisation of 0.025 mM MB and 0.1 M Na₂SO₄ solution.

COD and TOC reduction values confirmed the obtained improvement of MB degradation rates (**Paper II**). The COD removal efficiency of combined sonication at 850 kHz and electrolysis at 20 mA achieved 85.4% after 2 h of degradation compared to 40.4 and 78.5% obtained after separate sonication and electrolysis respectively. In order to investigate a contribution of EO/US process to mineralisation efficiency, TOC data were investigated. The TOC removal efficiency achieved 38.4% in 2 h of sonoelectrolysis versus 3.6 and 26% obtained in sonication and electrolysis respectively within the same degradation time.

5.6.2 FA degradation

In order to confirm the choice of optimal current, EO/US degradation of FA was conducted using 10, 20 and 30 mA applied currents (4.5, 9.1 and 13.6 mA/cm² current densities) and 381 kHz (0.02 W/cm³) frequency (Fig. 5.14). The kinetic rate constant increased twice from 0.0185 min⁻¹ in 9.1 mA/cm² electrolysis to 0.0374 min⁻¹ in combined use of sonication and electrolysis and almost 200-fold comparing with sonication alone (**Paper IV**). The kinetic rate constants obtained in this study for EO and EO/US processes of FA degradation were among the highest values when comparing with different AOPs [223] [137] [140]. The higher kinetic rate constant of 955 min⁻¹ was observed while using photocatalytic degradation over Fe/TiO₂ catalyst [224]. However, the initial concentration of FA used in photocatalytic degradation was equal to 2.3 mg/L and considered to be negligible comparing with this study. Photocatalytic degradation of FA of higher concentration (103 mg/L) provided only 6.29·10⁻⁴ min⁻¹ kinetic rate constant [225]. The time required for 90% FA degradation reduced from 2 h in electrolysis to 1.1 h in sonoelectrolysis. A combination of 4.5 and 13.6 mA/cm² electrolysis 381 kHz sonication had no significant effect on kinetic rate constants improvement compared to separate electrochemical oxidation. EO/US decomposition process slightly improved the removal efficiency of FA from 64 to 78%, 92 to 99% and 93 to 97% for 4.5, 9.1 and 13.6 mA/cm² applied current densities respectively compared to single electrochemical oxidation after 2 h of treatment. It should be noticed that combined 13.6 mA/cm² electrolysis and 381 kHz sonication provided lower degradation of FA comparing with EO/US process, which could be explained by higher corrosion of the electrodes. Increased currents enhance the gas evolution such as oxygen and toxic chlorine gas (generated from the presence of Cl⁻ ions in the electrolyte solution), which can initiate the corrosion of electrodes. The known cleaning effect of ultrasound due to the formation of liquid microjets and shock waves during the cavitation bubbles collapse can assist the initiated corrosion of electrodes at higher currents. Moreover, it was reported that ultrasound can both promote and suppress the corrosion of metals and metal alloys [169] [170] [171]. Comparable degradation rates (over 99%) of FA was obtained in photocatalytic and wet oxidation method combined with the use of catalyst within one and 8.3 h respectively [226] [225]. The same behaviour was obtained while comparing mineralization efficiencies of EO/US treatment, which were equal to 75, 95 and 92% after 2 h of degradation process at 381 kHz (0.02 W/cm³) irradiation and at 4.5, 9.1 and 13.6 mA/cm² applied currents respectively. In this regard, the careful optimization of working parameters should be done for both EO, US and EO/US processes.

Figure 5.14: Effect of applied current densities on sonoelectrochemical degradation of 250 mg/L FA in 3 g/L NaCl at a constant ultrasonic frequency of 381 kHz (0.02 W/cm³ power)

Among tested currents in EO/US degradation experiments, 9.1 mA/cm² was found optimal, which was confirmed by electrolysis experiment (Fig. 5.9). In this regard, the further studies on EO/US degradation of FA was carried out using 9.1 mA/cm² current.

Fig. 5.15 shows the effect of ultrasonic irradiation at 381 (0.02 and 0.007 W/cm³), 863 (0.0067 W/cm³), 992 (0.003 W/cm³) and 1176 kHz (0.003 W/cm³) frequencies on the EO/US degradation of FA. The highest degradation efficiency (99%) and kinetic rate constant (0.0374 min⁻¹) were obtained after 2 h of sonoelectrolysis while irradiating the working solution with 381 kHz, which also provided the highest power of 0.02 W/cm³. The lowest degradation efficiency of 91% and kinetic rate constant of 0.0184 min⁻¹ was obtained after 2 h of sonication at 992 kHz combined with 9.1 mA/cm² electrolysis. The same low degradation efficiency of 0.8% was also obtained in a separate sonication at 992 kHz irradiation. The removal of FA for 2 h of EO/US experiments at frequencies of 381 (0.007 W/cm³), 863 (0.0067 W/cm³) and 1176 kHz (0.003 W/cm³) were approximately at the same range of 96 – 97%.

Figure 5.15: Effect of different ultrasonic frequencies on FA degradation in sonoelectrochemical experiments.

As it seen from Fig. 5.15 the efficiency of FA degradation after 2 h of sonoelectrochemical experiments is comparable to the degradation efficiency obtained in singular electrochemical decomposition. Therefore, it is difficult to compare these processes and estimate the effect of US on the degradation of FA. In this regard, comparison of synergetic indexes of combined sonochemical and electrochemical degradation rates calculated by Eq.4 could allow better understanding of degradation process. The data on kinetic rate constants and synergetic indexes are listed in Table 5.2. Table 5.2 shows a clear synergy between the sonochemical and electrochemical degradations of FA in sonoelectrochemical process for all tested ultrasonic frequencies except 992 and 1176 kHz. The highest S index equal to 2 was obtained for combined sonication at 381 kHz (0.02 W/cm^3) and electrolysis at 9.1 mA/cm^2 followed by S index of 1.63 obtained while sonicating the working solution at the same frequency of 381 kHz and actual power of 0.007 W/cm^3 with applied 9.1 mA/cm^2 current density. The value of synergetic index significantly above 1 for 381 and 863 kHz indicated the enhancement of electrochemical decomposition of FA by US. This can be caused by the improved mass transfer near to the electrode surface or activation of electrode's electrocatalytic properties and cleaning of the electrode surface by ultrasound. When combining sonication at 992 and 1176 kHz with electrolysis at 9.1 mA/cm^2 applied current density, no synergetic effect was observed. It can be speculated that generated power at these frequencies is too low to generate sufficient cavitation effect.

Table 5.2: Rate constants and synergetic index obtained for sonoelectrochemical decomposition of FA.

The type of degradation experiment	Working parameters		The first-order kinetic rate constant, k , min^{-1}	Synergetic index, S
	Ultrasonic frequency, kHz (actual power W/cm^3)	Applied current density, I , mA/cm^2		
Sonication	381 (0.02)	-	0.0002	-
	381 (0.007)	-	0.0002	-
	863 (0.0067)	-	0.0001	-
	992 (0.003)	-	0.00004	-
	1176 (0.003)	-	0.00005	-
Electrolysis	-	4.5	0.0079	-
	-	9.1	0.0185	-
	-	13.6	0.0207	-
Combined electrolysis and sonication	381 (0.007)	9.1	0.0304	1.63
	381 (0.02)	9.1	0.0374	2
	381 (0.02)	4.5	0.0097	1.2
	381 (0.02)	13.6	0.0273	1.31
	863 (0.0067)	9.1	0.0234	1.26
	992 (0.003)	9.1	0.0184	0.99
	1176 (0.003)	9.1	0.0201	1.08

A smaller amount of cavitation bubbles is formed at lower powers, which means fewer cavitation bubble collapses in the unit of time and lower physical effect of US. The best mineralization efficiency was obtained in EO/US processes ($9.1 \text{ mA}/\text{cm}^2$) at the highest frequency of 1176 kHz (97%) followed by 381 kHz ($0.02 \text{ W}/\text{cm}^3$) and 863 kHz having similar mineralization efficiency of 94.7%. Overall the NPOC reduction data in EO/US degradation experiments with 20 mA constant current can be placed in series with increasing mineralization at 381 kHz ($0.007 \text{ W}/\text{cm}^3$) < 992 kHz < 381 kHz ($0.02 \text{ W}/\text{cm}^3$) < 863 kHz < 1176 kHz. Based on the results of literature search FA haven't been studied before in EO/US degradation processes. Therefore the obtained results provide a valuable contribution to overall understanding and further development of these methods in environmental remediation of organic pollutants. High mineralization efficiency and kinetic rate constants of EO/US FA degradation make the process competitive among other AOPs. Moreover, the majority of studies on organic pollutants degradation by AOPs contain the information on compounds degradation rates and do not provide data

on pollutants mineralization. However, the degradation does not necessarily mean remediation since organic pollutants can be just transformed from one state to another leading often to formation of more toxic compounds. Formation of toxic quinones intermediates during EO/US phenol degradation can serve as an example of pollutants adverse transformation [175].

5.7 Energy consumption estimation required for the oxidation processes

In order to compare the energy efficiency of studied degradation processes, the EC was estimated. In the case of MB degradation, EC was calculated using actual powers entering the system (**Paper III**). In the case of FA degradation, EC was estimated using the power consumed from the grid by electrochemical and sonochemical equipment (**Paper IV**). In any approach electrochemical degradation process at 20 mA applied current was the most energy efficient for both MB and FA degradation. Neutral media for MB oxidation showed the best performance in terms of EC (9.3 kWh/m³ for 80% of COD reduction) and CE (10.1%). Acidic conditions provided the fastest MB degradation and thus the lowest EC for complete MB decolourisation (7.7 kWh/m³). Alkaline medium showed the highest EC and the lowest CE (1%) values which was attributed to oxygen evolution being the favored reaction. Comparing the EC values of electrochemical degradation of FA conducted at applied currents of 10, 20 and 30 mA, 20 and 30 mA electrolysis were found to be optimal with 675 and 700 kWh/m³ grid energy consumed for 90% pollutant degradation (**Paper IV**). The highest EC required for the complete decolourisation of MB was consumed in sonication process thus making it the least energy-efficient (**Paper II**). US degradation had no significant influence on FA degradation. Therefore EC values were not estimated for the process.

As it was mentioned in the Chapter 5.6 that EO/US oxidation of MB at 850 kHz provided a complete decolourisation of working solution within 45 min while using the 380 kHz irradiation provided the complete colour removal in 1 h. Despite an insignificant improvement in time EO/US degradation of MB dye at 380 kHz and 20 mA enhanced the EC 2.5-fold comparing to the combined sonication at 850 kHz and 20 mA electrolysis (**Paper II**).

Among FA EO/US degradation experiments combined sonication at 381 kHz (0.007 W/mL) and 20 mA electrolysis was most energy-efficient process with EC equal to 1785 kWh/m³ and required for 90% pollutant degradation. Ultrasonic irradiation at 863 and 1176 kHz combined with 20 mA electrolysis was the least energy-efficient process requiring 4399 and 4346 kWh/m³ energy for 90% of FA degradation. Notwithstanding the significantly higher EC values required for EO/US FA degradation compared to electrochemical oxidation combined sonication and electrolysis reduced the time of degradation (**Paper IV**). The same effect was observed for MB degradation. In this regard a careful optimization of the degradation process is required depending on whether the requirement is for fast degradation or cost efficiency.

6 Conclusions and further perspectives

During this study, the following research results were obtained:

1. Novel Ti/Ta₂O₅-SnO₂ electrodes for water and organic compounds oxidation were developed.

The electrodes were prepared by thermal decomposition technique. The small amount of Ta and presence of Sn in oxide coating structure was cost-effective and environmentally friendly replacement of expensive Pt-group metals such as Ir or Ru and potentially toxic for the environment compounds such as Sb or Pb commonly used in MMO electrodes. Ti/Ta₂O₅-SnO₂ electrodes were found to be electrocatalytically active towards water and organic compounds oxidation and therefore can be applicable in both environmental and energy fields.

2. An optimal nominal composition of Ti/Ta₂O₅-SnO₂ electrodes and number of active thin oxide layers were determined.

The electrocatalytic properties were found to be significantly influenced by the nominal composition of metal ions in the precursor solution showing the effect of metal oxides doping as well as by the number of active oxide layers in the coating. The nominal composition of electrodes annealed at 550 °C with Ta content of 5 at.% and 10 active oxide layers thickness were found the most preferable for conducting water oxidation experiments since showing high current values and low overpotential of OER. The electrodes containing 7.5 at.% of Ta and coated with 8 active film layers of Ta₂O₅-SnO₂ oxides showed the highest electrocatalytic activity towards MB oxidation.

3. Electrochemical and physical characterization of novel Ti/Ta₂O₅-SnO₂ electrodes were conducted.

The enhanced electrocatalytic activity towards organic compounds oxidation was suggested to be a result of hexagonal δ -Ta₂O₅ presence in the electrodes structure. The electrodes had a slightly cracked surface, which is typical for many MMO electrodes. In general, the lower annealing temperatures of Ti/Ta₂O₅-SnO₂ electrodes provided a slightly higher peak for the oxidation of 0.5 mM K₄Fe(CN)₆ and as a consequence a slightly higher electrodes surface roughness. According to CV measurements, the surface area of Ti/Ta₂O₅-SnO₂ electrodes at all annealing temperatures was found about 1.5-2 higher than the surface area of Au electrode. The annealing temperature of 550 °C was found optimal for electrocatalytic MB oxidation.

4. Recovery methods of the electrocatalytic properties of electrodes were investigated.

The electrodes were found susceptible to fouling by decomposition products of MB. Thermal, ultrasonic and electrochemical post-treatments completely recovered the

electrodes performance towards organics oxidation and improved the electrocatalytic activity of electrodes towards OER shifting the onset potential to more negative values. The continuous agitation of working solution using stirring and ultrasonic irradiation allowed to keep the activity of electrodes in a steady state through the enhanced mass transfer of electroactive species near to the electrode surface which was supported by the data on diffusion controlled process.

5. Optimization of the working parameters for electrolysis process was conducted.

The original media (pH 6.5) of treated solution provided the highest anodic peaks towards OER, MB oxidation, decolourisation, COD and TOC removal efficiencies and was analogous to the acidic media, which however was the most energy-effective for MB decolourisation. Decreased efficiency of electrodes in basic media was due to the OER onset potential shift to more negative values and as a result of useful current loss for water oxidation. An applied current of 20 mA was found to be the most energy-efficient for the electrochemical degradation of FA.

6. Sonochemical degradation of model pollutant was carried out.

Among tested 20, 40, 380, 850, 1000 and 1176 kHz ultrasonic frequencies, the best performance was achieved using 850 kHz frequency leading to complete decolourisation of MB in 1.5 h. Ultrasonic irradiation of FA solution provided insignificant FA degradation not exceeding 3%. There was no a clear dependence of pollutants degradation rates on applied ultrasonic frequencies and therefore optimal frequency had to be found experimentally. In the case of MB decolourisation a general trend of higher degradation rates at higher powers was observed.

7. Ultrasonically-assisted electrochemical degradation of model pollutants using novel Ti/Ta₂O₅-SnO₂ electrodes was conducted.

The synergetic effect of combined electrolysis and sonication was found while conducting EO/US degradation of MB and FA. The colour removal of MB was enhanced twice and four times at 9.1 mA/cm² applied current density and 850 kHz frequency comparing to sonication and electrolysis alone. The COD removal efficiency increased twice in sonoelectrolysis comparing to sonication alone. TOC reduction of the joint sonication and electrolysis was 1.5 and 10.5 times higher than in the process of separate electrolysis and sonication respectively. The joint electrolysis at 9.1 mA/cm² applied current density and ultrasonic irradiation at 381, 863 and 1176 kHz provided over 94% mineralization efficiency of FA comparing to 75% TOC decrease in electrolysis process and less than one percent in sonication alone.

8. Energy efficiency of sonochemical, electrochemical and sonoelectrochemical degradation experiments was evaluated.

In general, electrochemical oxidation of tested organic pollutants was the most-energy efficient consuming the least amount of energy required for reaching the same degradation efficiency of pollutant than in US or EO/US processes. However, EO/US degradation provided higher degradation kinetic rate when comparing with electrolysis and sonication. Thereby a careful optimization of cost and time efficiency should be implemented depending on the requirements.

The preparation method of Ti/Ta₂O₅-SnO₂ electrodes can be further improved using atomic layer deposition techniques, which would provide higher reproducibility of electrodes coating properties. A relatively high OER overpotential makes the electrodes potentially effective in applications of electrocatalytic organic pollutants oxidation. However, the mechanism of organics oxidation on the electrodes surface should be studied in detail in order to determine the electrode class (“active” or “non-active”). The mechanism of the pollutants degradation and by-product determination in sonication process should be done.

The electrodes activity towards water oxidation could be further investigated since they can compete with more expensive metal oxides of RuO₂ and IrO₂, which are widely used catalysts in water oxidation applications. Testing the electrodes in different electrolytes including organic solvents is required to determine the electrolyte potential window. Corrosion tests are required to determine the stability of Ti/Ta₂O₅-SnO₂ electrodes. The electrodes can be further tested in the degradation of different organic pollutants in comparison with other commercially available electrodes like for example BDD. Experiments on the electrode’s service life, brittleness, hardness (cavitation resistance) and evaluation of their cost are required in order to determine the competitive market for these materials. Further investigation of the effect of ultrasonic low and high frequencies, amplitude, current density, electrodes distance etc. on the synergy of sonochemical and electrochemical experiments in sonoelectrolysis is of great interest.

High degradation kinetic rates and mineralization efficiencies of model pollutants obtained in EO/US experiments provide the preconditions for further extrapolation of this treatment method to pilot scale studies with industrial wastewaters.

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Publication I

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Novel Ti/Ta₂O₅-SnO₂ electrodes for water electrolysis and electrocatalytic oxidation of organics

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Novel Ti/Ta₂O₅-SnO₂ electrodes for water electrolysis and electrocatalytic oxidation of organics

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ABSTRACT

Mixed metal oxide (MMO) electrodes have been applied to different technologies including chlorine production, organic compounds oxidation, water electrolysis, electroplating, etc. due to their catalytic, optical and electronic properties. Most of the existing MMO electrodes contain either toxic metals or precious metals of the platinum group. The aim of this study was to develop environmentally friendly and cost-effective MMO electrodes for water and organic compounds oxidation. Ti/Ta₂O₅-SnO₂ electrodes of different nominal composition were prepared, and electrochemically and physically characterized. For water oxidation, Ti/SnO₂ electrode with 5 at.% of Ta produced the highest electroactivity. Ti/SnO₂ electrode with 7.5 at.% of Ta showed the best performance for the oxidation of methylene blue (MB). The electrocatalytic activity of the Ti/Ta₂O₅-SnO₂ electrodes increased with the number of active layers. The maximum current of water oxidation reached 3.5 mA at 2.5 V when the electrode was covered with ten layers of Ta₂O₅. In case of the oxidation of 0.1 mM MB, eight and ten active layers of Ta₂O₅ significantly increased the electrode activity. The prepared electrodes have been found applicable for both water electrolysis and organic compounds oxidation.

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1. Introduction

Mixed metal oxide (MMO) electrodes occupy an important place in many technological processes. They are widely used for the production of chlorine and oxygen and find extensive applications in electroplating, solar cells and supercapacitors [1–8]. For example, they are efficient electrodes for sustaining the oxygen evolution reaction (OER), which is of great importance in water electrolyzers, rechargeable batteries, and zinc, copper, cobalt and nickel electrowinning processes. MMO electrodes have also been applied for electrochemical and, in particular, electrocatalytic oxidation of refractory organic compounds in wastewaters [9–13].

The conventional composition of MMO electrodes consist of a base metal substrate, a protective passivating layer and the actual electrocatalyst [14]. The most common electrodes for water and organic compounds oxidation are Ti/Ta₂O₅-IrO₂, Ti/SnO₂-IrO₂, Ti/IrO₂-SnO₂-Sb₂O₃, Ti/RuO₂-IrO₂, Ti/Sb₂O₃-SnO₂, Ti/SnO₂-Sb₂O₃-RuO₂, and Ti/TiO₂-IrO₂ [15–20]. All these

electrodes have a Ti substrate, because of its mechanical stability and uniform current distribution. In addition, they contain either a significant amount of platinum-group metal oxide electrocatalysts, such as IrO₂ and RuO₂, which are expensive or the Sb₂O₃ electrocatalyst, which is toxic to the environment. Refractory metal oxides such as Ta₂O₅ and TiO₂ are often used as passivating layers. Thus, the development of cost-effective and environmentally friendly metal oxide electrodes for water and organic compounds oxidation is desirable. To the best of our knowledge, there are no reports on the electrochemical oxidation of water and organic compounds on Ti/Ta₂O₅-SnO₂ electrodes. Therefore, in this study, several Ti/Ta₂O₅-SnO₂ electrodes were prepared and structurally characterized. Water electro-oxidation was investigated in sodium sulfate solutions. In the same way, the electro-oxidation of methylene blue (MB) was studied as an example of organic compounds oxidation. Na₂SO₄ was chosen as the supporting electrolyte because of its neutral and non-corrosive properties in aqueous medium. MB was selected for the investigation of the catalytic oxidation activity of Ti-supported Ta₂O₅-SnO₂ electrodes because it is a typical representative of complex organic compounds with aromatic structure, which in addition is extensively used as a food and paper colorant, textile dye and bacteriology stain in human and veterinary medicine [21,22].

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Fig. 1. SEM images of (a) $\text{Ti/Ta}_2\text{O}_5$, (b) Ti/SnO_2 , and $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ electrodes of different nominal composition: (c) 50.0 at.%, (d) 25.0 at.%, (e) 12.5 at.% and (f)–(l) 7.5 at.% with different number of active deposited layers: (f) 4 layers, (g) 8 layers and (h) 10 layers; element-mapping for the electrode with $x = 7.5$ at.%, (i) total mapping, (j) Ta mapping, (k) Sn mapping and (l) Ti mapping.

2. Experimental

2.1. Electrode preparation

Several $\text{Ti/Ta}_2\text{O}_5\text{-SnO}_2$ electrodes were prepared by thermal decomposition of precursor solutions on titanium substrates [23]. The nominal composition $\text{Ta}(x)\text{-Sn}(100-x)$ of electrodes was modified by changing the x value from 0 atom (at.%) till 50 at.% Ta. The total concentration of metal ions was kept constant and was equal to 0.04 M.

In the preparation of the precursor solutions, stoichiometric amounts of tantalum (V) chloride (99.99% trace metal basis,

Sigma-Aldrich) and tin (II) chloride 2-hydrate (pro analysis, Panreac) were dissolved in 10 ml of absolute ethanol (pro analysis, Panreac), stirred and refluxed for one hour at 80 °C. Titanium plates (99.7% trace metals basis, Sigma-Aldrich) were pretreated by degreasing in 10 wt% NaOH for 15 s, etching in boiled 18 wt% hydrochloric acid (pro analysis, Fluka) for 10 min, and rinsing with ultrapure water (18.2 MΩ·cm, Millipore). The precursor solution was applied on the pretreated dry substrates by drop casting. A volume of 80 μL of the precursor solution was dropped on the titanium surface, dried at 80 °C for 5 min, allowing for the complete solvent evaporation, and finally annealed at 550 °C for 5 min. This procedure was repeated for both electrode sides. In the following, the

term layer will be employed to refer to the ultrathin film deposited on the titanium substrate upon the application and thermal decomposition of 80 μ L drop of the precursor solution. This procedure was repeated until the desired number of layer was reached. After the last layer formation, each electrode was additionally annealed at the same temperature for 10 hours in order to generate Ta₂O₅-SnO₂ composite oxide structures on the electrode surface.

2.2. Physicochemical and Electrochemical Characterization of the Electrodes

The crystal structure of the electrodes was analyzed by X-Ray diffraction (XRD) spectroscopy. Scanning electron microscopy (SEM Hitachi S-3000 N) coupled to X-ray detector (Bruker XFlash 3001) for energy-dispersive X-Ray (EDX) microanalysis and mapping was used to study the surface texture and bulk composition of the electrodes.

The electrochemical characterization of Ti/Ta₂O₅-SnO₂ composite electrodes was conducted by using cyclic voltammetry (CV) measurements. All the experiments were performed in a three electrode cell (200 ml) with computer-controlled Autolab PGSTAT30 and PGSTAT12 potentiostats. Both potentiostats were controlled by GPES EcoChimie software. A coiled platinum wire was used as a counter electrode and an Ag/AgCl/KCl (sat) electrode as a reference electrode. Unless otherwise stated, all the potentials are quoted versus this reference electrode. CV measurements were performed between 0.2 and 2.5 V potential limits at a scan rate of 50 mVs⁻¹. Before each measurement, working electrodes were electrochemically pretreated by conditioning them at potentials of 0.2 V for 15 s and 1.2 V for 5 s. All the working electrodes had the same surface area of 2.4 cm², which was controlled with Teflon ribbon.

CV was carried out at room temperature in supporting electrolyte solutions (blank solution) of 0.1 M Na₂SO₄ (anhydrous ACS reagent, Sigma-Aldrich) and in aqueous solutions of 0.1 M Na₂SO₄ and 0.1 mM MB (Certistain, Merck) hereafter referred to as the working solution. Solutions were deoxygenated by argon bubbling before every CV measurement.

3. Results and discussion

3.1. SEM and EDX analyses

SEM images of Ti/Ta₂O₅, Ti/SnO₂ and Ti/Ta₂O₅-SnO₂ electrodes and EDX element mapping of the electrode with a nominal composition x = 7.5 at.% Ta are shown in Fig. 1. As can be seen from Fig. 1k, in the case of 7.5 at.% Ta electrode, Sn uniformly covers the Ti substrate (Fig. 1l), while Ta deposition (Fig. 1j, 1i) is less homogeneous. The size of the resulting Ta₂O₅ particles varied from a few nanometers (particles regularly distributed on the SnO₂ films) to a few micrometers forming islands (bright white spots) on the electrodes surface. The surface of the electrodes had a slightly cracked structure as is the case for many MMO electrodes [24–26]. In the absence of Sn (Fig. 1a), the surface of the electrode was porous and rough, whereas in the absence of Ta (Fig. 1b), the surface was flattened and pores were clogged. As expected, when the number of active layers of Ta additive increases, the density of Ta₂O₅ crystals on the surface also increases, resulting in partial roughness recovery (Fig. 1c–1e, g). The porosity of the electrodes was influenced by the number of deposited active oxide layers, although a tendency was not clearly observed (Fig. 1f–h).

The bulk composition of Ta₂O₅-SnO₂ thin films was determined by EDX microanalysis. Table 1 represents the data comparing atomic ratios obtained by EDX analysis with the nominal atomic ratios. Most of the analyzed electrodes consist of eight Ta₂O₅-SnO₂ oxide layers. These electrodes show a reasonably good agreement

Table 1
Comparison of nominal and experimental atomic ratios of Ti/Ta₂O₅-SnO₂ electrodes.

Ta at. %	Number of active layers	Sn/Ta atomic ratio	
		EDX	Nominal
50.00	8	0.68	1
25.00	8	2.14	3
12.50	8	5.55	7
7.50	4	6.41	12.33
7.50	8	12.05	12.33
7.50	10	15.78	12.33

between EDX and nominal Sn/Ta atomic ratios. When increasing the amount of Ta in thin films, Sn/Ta ratio decreased. It seems that films became enriched with Sn when the electrode had ten oxide layers while a significant enrichment in Ta was observed for the 4-layer electrode.

3.2. XRD analysis

XRD analysis was used to study the crystal structure of obtained thin films electrodes. XRD patterns of Ti/Ta₂O₅-SnO₂ thin films are shown in Fig. 2. All patterns contained intense peaks corresponding to the hexagonal Ti substrate appearing at $2\theta = 38.422, 40.171, 53.005, 62.951, 70.663, 76.221, 77.370, 82.292$ and 92.732° associated to the (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 1), (0 0 4) and (1 0 4) crystal orientations of titanium. TiO₂ was evidenced through the presence of (1 1 0), (0 0 4), (-1 -1 2), (-1 -1 4), (3 0 0) and (3 0 4) reflections. It was formed due to the oxygen solubility in the metal lattice of the substrate [27]. All the electrodes except those with x = 50.0 and 7.5 at.% (8 layers) revealed the presence of tetragonal rutile with peaks corresponding to (1 1 0), (1 0 1), (1 1 1) and (2 1 1). The low intensity of the TiO₂ peaks can be attributed to a low crystallinity of the formed TiO₂. The absence of TiO₂ in the electrodes of nominal composition x = 50.0 and 7.50 at.% could be explained by the dense Ta₂O₅-SnO₂ coating obtained (see

Fig. 2. X-Ray diffractograms for Ti/Ta₂O₅, Ti/SnO₂, and Ti/Ta₂O₅-SnO₂ thin film electrodes.

Fig. 3. Cyclic voltammograms of Ti/SnO₂, Ti/Ta₂O₅ and Ti/Ta₂O₅-SnO₂ electrodes in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ and 0.1 mM MB; $\nu = 50 \text{ mVs}^{-1}$. The amount of active oxide layers is eight. Inset Fig. 3a: Cyclic voltammetry current at 2.5 V vs. atomic Ta content for Ti/Ta₂O₅-SnO₂ electrodes. Inset Fig. 3b: Cyclic voltammograms of Ti/SnO₂, Ti/Ta₂O₅ and Ti/Ta₂O₅-SnO₂ electrodes of nominal composition $x = 2.5 \text{ at}\%$ in 0.1 M Na₂SO₄.

Fig. 1c, 1f), which prevented extensive Ti oxidation and as a result improved electrocatalytic activity of Ti/Ta₂O₅-SnO₂ electrodes (see below).

XRD patterns also showed the reflections corresponding to the (1 1 0), (1 0 1) and (2 1 1) atomic planes typical of the tetragonal rutile SnO₂ structure [28]. Tantalum was mostly represented by orthorhombic Ta₂O₅ with main peaks corresponding to the (0 0 1), (1 11 0), (2 8 0), (1 11 1), (0 0 2) and (3 10 1) planes. However, the electrode of nominal composition $x = 7.5 \text{ at}\%$ (8 layers) contained only hexagonal δ -Ta₂O₅ with peaks corresponding to the (0 0 1), (1 0 0) and (1 0 1) planes. The absence of Ta₂O₅ peaks in the XRD diffractograms of the Ti/Ta₂O₅ and Ti/Ta₂O₅-SnO₂ ($x = 7.5 \text{ at}\%$, 4 layers) electrodes and that of SnO₂ peaks in the diffractograms of Ti/Ta₂O₅-SnO₂ ($x = 50.0 \text{ at}\%$) is probably attributed to the low crystallinity of the formed oxides.

3.3. Cyclic voltammetry

Fig. 3a shows the CV results of prepared Ti/Ta₂O₅-SnO₂, Ti/SnO₂ and Ti/Ta₂O₅ electrodes in a 0.1 M Na₂SO₄ solution. It is found that both Ti/Ta₂O₅ and Ti/SnO₂ electrodes do not have enough conductivity to generate significant currents associated to the OERs in the potential range of 0.2 to 2.5 V. This is because both Ta₂O₅ and SnO₂ are wide band gap n-type semiconductors, i.e. no anodic reactions occur up to several volts versus SHE [29,30].

When the amount of Ta (V) ions was increased to 2.5 at.% in the precursor solution, the OER current increased by a factor of 3.5 (from 0.08 mA to 0.27 mA at 2.5 V). A rise of Ta content till a nominal composition of $x = 5 \text{ at}\%$ increased the OER current by a factor of 75, and thereby showed the highest electroactivity toward water oxidation. As it is seen in the inset of Fig. 3a, 7.5 Ta at.% apparently yielded a very low current of 2 mA after 5 at.%. At about 25 at.%, the current decreases to half the maximum value. At 50 at.%, no significant OER current is observed. This behavior suggests that Ta addition to a limited extent improves the carrier density and decreases the resistivity of SnO₂ films [31,32].

Fig. 3b presents CVs (third cycles) recorded on Ti/Ta₂O₅-SnO₂, Ti/SnO₂ and Ti/Ta₂O₅ electrodes in 0.1 M Na₂SO₄ + 0.1 mM MB aqueous solutions. All voltammograms show anodic current peaks or shoulders which were absent in the blank voltammograms (Fig. 3a). At the same time, Ti/SnO₂ and Ti/Ta₂O₅ electrodes did not produce anodic currents except for those corresponding to the OER (see inset in Fig. 3b). However, the inclusion of Ta in SnO₂ films with Ta in an amount of 5 at.% enhanced the electrode activity towards MB oxidation. Anodic currents at potentials more positive than 1 V

were observed due to the oxidation of MB. The oxidative activity of the electrodes reached a maximum at a Ta content of 7.5 at.%. The corresponding film was constituted only by δ -Ta₂O₅ as deduced from the appearance of the (0,0,1), (1,0,0) and (1,0,1) diffraction peaks (Fig. 2). Therefore, it can be speculated that the presence of hexagonal δ -Ta₂O₅ enhances the electrocatalytic activity of the Ta₂O₅-SnO₂ electrode film.

The increase of the oxidative activity coincides with a split of the MB oxidation peak. The first peak at 1.15 V is considered to display the electrocatalytic properties of the prepared electrodes and to correspond to the initial MB oxidation. At this potential electro-oxidation of MB perhaps occurred by the generation of nascent oxygen on the oxide surface, which would cause the formation of oxidation products [33]. These initial oxidation products would be further oxidized at potentials around 1.6 V. Electrochemical reactions taking place at potentials more positive than 1.6 V vs. Ag/AgCl were probably assisted by OER.

The relatively reversible currents at potentials 0.3–0.5 V are assigned to pseudo-capacitive processes. Comparing Figs. 3a and 3b, it may be concluded that the appearance of these currents is connected to the MB adsorption/desorption process on the electrodes surface. Further increase of Ta dopant in the thin films of SnO₂ over 7.5 at.% gradually decreased the electrocatalytic oxidation activity of the electrodes and shifted the onset potential for the OER to higher values. In this regard, we speculate that Ta₂O₅ could be responsible for both the electrocatalytic activity of the electrodes (anodic peaks at potentials more positive than 1 V) and the adsorption of MB (voltammetric signals at potentials in the range 0.3–0.5 V). The strong adsorption of MB on Ta₂O₅ active centers induced by a high Ta content in the surface films would block the catalytic activity of the electrodes with nominal composition $x > 7.5 \text{ at}\%$. Moreover, the XRD analysis of the electrodes with nominal composition $x > 7.5 \text{ at}\%$ (Fig. 2) showed a low content of hexagonal δ -Ta₂O₅, which may be related to their low electrocatalytic activity.

Several electrodes with a nominal composition of 7.5 Ta at.% were prepared with different number of oxide layers to assess the impact of the coating thickness on the electrocatalytic activity of the electrodes. Fig. 4 shows CVs for electrodes with different numbers of oxide layers in the absence and in the presence of MB. As the number of layers increases, the onset potential for the OER shifts to more negative values, and the currents generated by OER increase (see inset Fig. 4a). The inset of Fig. 4a shows that for one active layer the potential needed to generate a 0.25 mA current is the most positive one (2.6 V) while increasing the number of active layers reduces the required potential from 2.6 V to less than 2 V. For currents equal

Fig. 4. Cyclic voltammograms of Ti/Ta₂O₅-SnO₂ electrodes of nominal composition $x = 7.5$ at.% and different number of active layers in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ and 0.1 mM MB; $\nu = 50$ mV s⁻¹. Inset Fig. 4a: Cyclic voltammetry potential required for attaining different currents by Ti/Ta₂O₅-SnO₂ electrodes with different number of active layers in 0.1 M Na₂SO₄; $\nu = 50$ mV s⁻¹. Inset Fig. 4b: Different voltammetric cycles for Ti/Ta₂O₅-SnO₂ electrodes with eight active layers in 0.1 M Na₂SO₄ and 0.1 mM MB (scan 1–3) and third scan in 0.1 M Na₂SO₄ (blank); $\nu = 50$ mV s⁻¹.

Fig. 5. Cyclic voltammograms of Ti/Ta₂O₅-SnO₂ electrodes of the nominal composition $x = 37.5$ at.% in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ and 0.1 mM MB (1) before and after cleaning by (2) cycling in the blank solution, (3) ultrasonic irradiation or, (4) annealing; $\nu = 50$ mV s⁻¹. Insets: Cyclic voltammetry current produced by Ti/Ta₂O₅-SnO₂ electrode of nominal composition $x = 37.5$ at.% in (a) 0.1 M Na₂SO₄ at 2.5 V and (b) 0.1 M Na₂SO₄ and 0.1 mM MB at 1.2 V after different treatment.

to 0.5 and 0.8 mA the overpotential of OER decreased by 110 mV for ten-layer electrodes compared to the one layer electrode. Obviously at constant potential, the activity of the electrodes also increased with the number of layers.

The maximum current reached 3.5 mA for 10 active layers of Ta-doped SnO₂ electrode at 2.5 V. On the other hand, its electrocatalytic activity for MB oxidation (Fig. 4b) was similar to that of the 8-layer electrode. However, the peak profiles of the MB oxidation process are different for the 8 and 10-layer electrodes, indicating slight differences in their electrocatalytic activity. The current generated at potentials more positive than 1.6 V was mainly used for water oxidation. While running CVs with this electrode in the working solution, the height of the anodic peaks decreased with each scan (see inset in Fig. 4b). It can be explained by poor mass transfer at the surface of the electrode derived from the low concentration of the dye. During the first scan the MB coverage on the electrode surface was high, and thus the oxidation current was also high. However, with each subsequent scan, the coverage of MB decreased together with the anodic oxidation peaks. Moreover, the CV profiles corresponding to the OER recorded in the working solution were shifted towards positive potentials with respect to those of the blank solution. Therefore, poor mass transfer was also aggravated by fouling the electrode with degradation products of MB leading to the formation of organic films on the electrode surface, as is frequently the case for MMO [34,35].

To check the reproducibility of these results and the ability of electrodes to recover their electrocatalytic activity some post treatment procedures were applied to the Ta-doped SnO₂ electrodes of nominal composition $x = 25$ at.% and 37.5 at.%. The chosen electrodes were: i) submitted to 10 voltammetric cycles between 0.2 and 2.5 V in the blank solution, ii) annealed at 550 °C for 1 hour, iii) cleaned in a ultrasonic bath (FinnSonic M08, 200 W, 40 kHz) for 30 minutes. CV measurements were recorded after each treatment both in the blank solution and in the working solution. Since both electrodes showed a similar trend of the recovery of electrocatalytic activity, the post-treatment measurements are shown only for Ta 37.5 at.%.

Fig. 5 shows the effect of different treatment methods on the electroactivity recovery. All the treatment applied to the electrodes demonstrated either a partial or a complete recovery of the electrocatalytic activity towards MB oxidation. As can be seen on Fig. 5a, in the blank solution, the onset potential for water oxidation shifted by 10 mV to less positive values after cleaning in the blank solution or applying the ultrasonic treatment and by 130 mV after the thermal annealing procedure. The Fig. 5b shows that onset potentials of anodic oxidation process shifted to more negative values by up to 400 mV, showing a significant activation of the MB oxidation process and hence improvement of the electrocatalytic properties of the electrode. Insets in Fig. 5 show that electrode annealing at 550 °C is the most effective way to recover the electrode. The electro-activity towards water electrolysis (Fig. 5a) of the electrode

increased five times from 0.7 mA to 3.5 mA and more than two times towards MB oxidation (Fig. 5b). Electrochemical cleaning in the blank solution slightly increased OER currents. However, it did not recover the electrocatalytic activity towards MB oxidation and cannot be recommended as a treatment procedure. Ultrasonic treatment appears to be a good way to clean the electrode due to increase of electro-activity towards both water oxidation and MB oxidation.

4. Conclusions

New Ti/Ta₂O₅-SnO₂ electrodes were developed and the electrocatalytic activity of Ta₂O₅ in synergy with SnO₂ was revealed. It is interesting to notice that changes in both metal concentration in the precursor solutions and number of active electrocatalytic layers strongly affects the electrochemical properties of the MMO electrodes, demonstrating the effect of doping on metal oxides. Hexagonal δ -Ta₂O₅ was suggested as the phase responsible for the enhanced electrocatalytic activity towards the organic compounds oxidation process, whereas Sn is a cost-effective replacement of Ir in Ti/Ta₂O₅-IrO₂ electrodes. Moreover, the amount of Ta used in the electrodes is relatively small. The electrodes showed good regeneration of their activity after thermal, ultrasonic and electrochemical treatment procedures. Besides, thermal treatment improved the electrochemical properties of the electrodes towards water oxidation by shifting potential of OER to more negative values. Therefore, Ti/Ta₂O₅-SnO₂ electrodes have been found applicable for both OERs and electrocatalytic oxidation of organic compounds and may further find application in the environmental protection and energy sectors.

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Publication II

Shestakova, M., Vinatoru, M., Mason, T.J. and Sillanpää, M.

Sonoelectrocatalytic decomposition of methylene blue using Ti/Ta₂O₅-SnO₂ electrodes

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Sonoelectrocatalytic decomposition of methylene blue using Ti/Ta₂O₅–SnO₂ electrodes

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ABSTRACT

Sonoelectrochemical decomposition of organic compounds is a developing technique among advanced oxidation processes (AOPs). It has the advantage over sonication alone that it increases the efficiency of the process in terms of a more rapid decrease in chemical oxygen demand (COD) and in total organic carbon (TOC) and accelerates electrochemical oxidation which normally requires a lengthy period of time to achieve significant mineralisation. Moreover the use of an electrocatalytic electrode in the process further accelerates the oxidation reaction rates. The aim of this study was to improve the decomposition efficiency of methylene blue (MB) dye by sonoelectrochemical decomposition using environmentally friendly and cost-effective Ti/Ta₂O₅–SnO₂ electrodes. Decolourisation was used to assess the initial stages of decomposition and COD together with TOC was used as a measure of total degradation. The effect of a range of sonication frequencies 20, 40, 380, 850, 1000 and 1176 kHz at different powers on the decolourisation efficiency of MB is reported. Frequencies of 850 and 380 kHz and the use of higher powers were found more effective towards dye decolourisation. The time for complete MB degradation was reduced from 180 min using electrolysis and from 90 min while carrying out sonolysis to 45 min when conducting a combined sonoelectrocatalytic experiments. The COD reduction of 85.4% was achieved after 2 h of combined sonication and electrolysis which is a slightly higher than after a single electrolysis (78.9%) and twice that of sonolysis (40.4%). A dramatic improvement of mineralisation values were observed within 2 h of sonoelectrocatalytic MB degradation. The TOC removal efficiency increased by a factor of 10.7 comparing to sonication alone and by a factor of 1.5 comparing to the electrolytic process. The energy consumption (kWh/m³) required for the complete degradation of MB was evaluated.

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1. Introduction

Dyes are widely used in a range of industries including textile, pulp and paper, pharmaceutical, tannery, rubber and plastic. The annual worldwide production of dyes is estimated to be 7×10^5 tonnes of which up to 15% are directly discharged as effluent into waste streams from dyeing operations. Worldwide wastewater generation from dyeing facilities from the textile industry alone is estimated to be equal up to 8000 m³/day [1,2]. Waste water discharges without appropriate treatment cause a rise of COD and biological chemical demand (BOD) which in turn leads to eutrophication of water bodies. Moreover dyes are often toxic for aquatic organisms and harmful to humans. It has been reported that benzidine based dyes have carcinogenic effects on the human urinary bladder [3–5]. For these reasons there have been many attempts to remove dyes from wastewater including traditional treatment

techniques such as adsorption, coagulation and chemical oxidation. The use of such techniques is often restricted due to the formation of secondary wastes such as spent adsorbent which should be regenerated or disposed of as is the case with coagulation and excess activated sludge [6–8]. In addition the European Commission Council Directive 99/31/EC bans landfilling of liquid waste and the dry matter content of original sludge is only about 1–5%, so additional investments are required for the processing of sewage sludge [9,10]. Biological treatment methods are inefficient for dye decolourisation and degradation due to the stability of these compounds towards microorganisms attack [11]. Dyes are recalcitrant compounds which are only slowly biodegradable mostly due to their aromatic structure and have a half-life time in the aquatic environment under ambient conditions of up to several years [12,13].

Recently advanced oxidation processes (AOP) have become of great interest as they have the potential for the complete mineralisation of organic pollutants to CO₂ and H₂O without production of secondary wastes [14–16]. Within the range AOPs

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electrocatalytic and sonochemical treatments have a wide range of applications for decomposition of different organic compounds such as pharmaceuticals, chlorinated hydrocarbons and dyes [17–21].

Electrochemical decomposition of organic compounds via direct electrolysis on the surface of high O_2 overvoltage anodes (M) occurs by means of oxidation with hydroxyl radicals generated through Reaction 1 [22,23]:

Hydroxyl radicals are also produced in ultrasonic irradiation by water cleavage occurring during cavitation bubbles collapse when enormous temperatures and pressures are reached (Reaction 2) [24]:

It was found that more than 90% of color removal of 200 mg/L Novacron Yellow C-RG dye in 0.25 M Na_2SO_4 solution is achieved within 7 h in direct electrolysis on Pt/Ti anodes and within 3 h on BDD electrodes when applying 50 mA/cm² current density [25]. However, the lower color removal efficiency of 80% was achieved in 6 h of electrolysis on Pt/Ti and BDD electrodes while applying current density of 10 mA/cm². The maximum TOC removal after 9 h of electrolysis was in the range 15–30% for Pt/Ti electrodes and 80–90% for BDD electrodes. Another study reported a 95% decolourisation and 70% TOC removal of 100 mg/L opaque methylene blue and 0.1 M Na_2SO_4 solution within 8 and 6 h of electrolysis respectively using Sb-doped SnO_2/TiO_2 electrodes and applying 30 mA/cm² current density [26]. Ti/PbO₂-ZrO₂ nanocomposite electrodes with $SnO_2-Sb_2O_3$ interlayer could provide 100% color removal and about 82% of COD removal during 2 h of electrolysis with applied current density of 50 mA/cm² [27]. In addition to the above mentioned electrodes, Ti/ SnO_2-SnO_2 , Ti/ $Ta_2O_5-IrO_2$, Ti/ RuO_2-IrO_2 electrodes are commonly used for the oxidation of organic compounds [28–30].

A decolourisation efficiency of 23% was obtained after 4 h of sonication of 10 mg/L reactive brilliant red solution using a JSC-204 ultrasonic reactor (20 kHz) with an output power of 150 W [31]. Other studies compared degradation rates of MB at 22.8, 127, 490, 940 and 1640 kHz at different actual powers [32,33]. It was shown that the highest color removal efficiency of 90% could be achieved at a power of 8 W and a frequency of 490 kHz for the sonication of 0.1 L of 0.01 mM MB solution for 1 h. Sonochemical studies of the color removal of a solution of 50 mg/L orange II using 20, 40, 380, 850, 1000 and 1176 kHz frequencies found that 850 kHz frequency was the most effective [34,35]. Further an increase in sonication power from 2.04 to 22.07 W, increased color removal efficiency from 4.1% to 49% after 2 h.

From the examples quoted the electrolysis time required for the complete color removal of dyes using different electrodes varies from 2 to more than 9 h. In terms of degradation 80% TOC removal takes at least 6–9 h of even when highly active BDD electrodes are used. Less active electrodes give less than 30% TOC removal in the same time. To date all of the electrodes used for the oxidation of organic compounds contain either expensive platinum-group metals like Ir, Ru and Pt or diamond films or sometimes compounds like Sb that are toxic for the environment. It has also been reported that the activity of different electrodes towards organic compounds during oxidation decreases with electrolysis time due to passivation of the electrode surfaces [25].

Although there is a significant amount of published work on sonochemical dye decolourisation [31–35] these results do not directly reflect a complete mineralisation of the compounds. Indeed there is a lack of information on the effects of sonication on chemical oxygen demand (COD) and mineralisation which are

very important as they allow assessing the real efficiency of ultrasound in water treatment. In simple terms dye decolourisation is certainly of aesthetic value i.e., color removal but decolourisation may only mean a transformation of colored compounds to colorless intermediates which in practice could be more toxic than the dyes themselves.

The goal of this study was to improve degradation rates of MB dye in water by combining sonochemical and electrocatalytic processes and using environmentally friendly and economical Ti/ $Ta_2O_5-SnO_2$ electrodes for sono-electrocatalytic treatment. The advantages of combining ultrasound with electrochemistry has been known for many years and is based upon a combination of effects induced by cavitation bubble collapse [36]. These include micro jet formation, acoustic streaming and shear forces all of which are useful for surface cleaning and activation. It is expected that combined sonication and electrolysis will enhance the mass transfer of pollutants on the electrodes surface, create initiation sites for catalysts activation and remove passivating impurities from the electrodes surface and thereby considerably increase decomposition of pollutants and speed up decomposition rates. In addition to this and especially important for oxidation, acoustic cavitation in water can also produce highly active hydroxyl radicals. The link between mechanical and chemical effects of cavitation collapse depends upon the frequency of ultrasound with mechanical effects being favored at the lower end and chemical effects at higher frequencies [37].

Even though there are some studies on sonoelectrochemical decomposition of dyes there is a lack of information on its effect on COD and mineralisation [38–40]. Furthermore, to the best of our knowledge, there are no studies on Ti/ $Ta_2O_5-SnO_2$ electrodes use in sonoelectrochemical experiments. Novel Ti/ $Ta_2O_5-SnO_2$ electrodes have been recently developed, they are relatively inexpensive and do not contain any compounds which are toxic for the environment [41].

2. Experimental

2.1. Electrodes and solutions preparation

Ti/ $Ta_2O_5-SnO_2$ electrodes with the Ta content of 7.5 at.% were prepared by thermal decomposition and drop casting technique of the precursor solution on a titanium substrate [42]. The detailed preparation is described elsewhere [41]. The total concentration of $SnCl_2$ ($\geq 99.99\%$ trace metals basis, Sigma-Aldrich) and $TaCl_5$ (99.99% trace metal basis, Sigma-Aldrich) salts in precursor solution were kept at 0.04 M. Absolute ethanol (Baker Analyzed' VLSI grade, J.T. Baker) was used as a solvent. Ti plates were pre-treated in 10 wt.% NaOH ($\geq 98\%$ anhydrous, Sigma-Aldrich) and 18 wt.% boiled hydrochloric acid (pro analysis, Fluka) before precursor solution deposition.

A stock solution of 0.025 mM methylene blue (technical dye) and 0.1 M Na_2SO_4 (99.5% anhydrous, BDH AnalaR) were prepared and kept in a dry dark place and further used as a working solution for degradation experiments. To provide the highest compatibility of sonolysis and electrolysis processes Na_2SO_4 was used both in electrochemical oxidation experiments as an electrolyte and in sonochemical degradation experiments. Double distilled water was used for the stock solution preparation.

2.2. Experimental set-up, sonication and electrolysis

Sonoelectrochemical degradation of MB in electrolyte solution was conducted by means of direct electrolysis and indirect sonication (exception is 20 kHz ultrasonic probe which was directly placed in a beaker containing the working solution).

Fig. 1. Experimental set-up.

The experimental arrangement employed was similar to that used elsewhere with an addition of the electrochemistry component [35]. Fig. 1 shows a schematic illustration of the set-up for combined sonochemical and electrochemical degradation of MB working solution. The sonochemical section consisted of an ultrasonic generator, transducer and jacketed water bath. The ultrasonic probe was placed directly into the beaker containing the MB working solution (dashed line box in the upper left corner of Fig. 1). Sonication was carried out using a 20 kHz ultrasonic probe (Sonics and Materials Inc., VCX 600, 600 W of max output power, 12.5 mm tip diameter), 40 kHz ultrasonic bath (Langford Electronics, Sonomatic 375TT, 300 W of output power), 850 kHz bath (Meinhardt, K80-5, 140 W of max output power, 69.6 mm transducer diameter) and multi-frequency bath operated at 380, 1000 and 1176 kHz (Meinhardt, M11, 250 W of max out power, 52 mm transducer diameter). The actual powers entering the system from different ultrasonic devices were determined by calorimetric measurements [43]. A beaker with 50 ml of stock solution was placed in a jacketed reactor with circulating cooling water which in turn was positioned on ultrasonic transducer. Temperature during the degradation processes was kept at 25 ± 2 °C. In the case of conducting sonolysis alone the electrochemical part of the set-up was disconnected and electrodes were withdrawn from the working solution. In the case of the single electrolysis process the sonochemical parts were shut down. Electrodes were positioned in a beaker with 50 ml of stock solution with an inter electrode gap of 1 cm. Ti/Ta₂O₅-SnO₂ electrode with the surface area of 2.2 cm² was used as an anode. A Ti plate of the same surface area was used as a cathode. Electrolysis was carried out at a constant current of 20 mA delivered by a Thulby PL320 DC power supply.

The decolourisation efficiency was monitored online using a UV-Vis spectrophotometer (Lambda45, UV-2450, Perkin Elmer Instruments) by monitoring light absorbance of the working solution at a wavelength of 664 nm. A peristaltic pump was used for the working solution circulation through the system. Chemical oxygen demand (COD) was determined using a Dr. Hach Lange 2800 system. The total organic carbon (TOC) content was measured with a high temperature TOC analyzer (Sartec Limited DC190, Sartec Group). Color removal efficiency was calculated using Eq. (1).

$$\text{Colour removal efficiency (\%)} = (1 - C/C_0) \times 100 \quad (3)$$

where C_0 is the initial concentration of MB, C is the concentration of MB after sonolysis, electrolysis and joint sonolysis and electrolysis.

The energy consumption (EC) required for the electrolysis process per volume of treated working solution (kWh/m³) was calculated using Eq. (2) [44]

$$EC = IVt/V_s \quad (4)$$

where I is the average applied current (A), V is the average cell voltage (V), t is the electrolysis time (h) and V_s is the solution volume (dm³).

The EC for the sonolysis process was estimated through the sonolysis time and the calorimetry measurements.

3. Results and discussions

3.1. The effect of ultrasound on dye decolourisation

To estimate the effect of ultrasound on dye decolourisation a detailed examination of dependency of color removal efficiency on different frequencies and powers was conducted. The values of real power (calorimetrically determined) entering into the reaction mixture are presented in the Table 1.

The volume used in calorimetric measurements was 50 ml, i.e., the same as that used for the degradation experiments. As seen from Table 1, the highest power of 0.186 W/cm³ calorimetrically measured was produced by 850 kHz bath at a power setting of 4 and was followed by 0.176 W/cm³ actual power of 20 kHz probe at a power setting of 15%. The lower powers of 0.006 and 0.008 W/cm³ were generated by 850 kHz bath at a power setting of 1 and 1175 kHz multi-frequency bath at a power setting of 80%, respectively.

Fig. 2 compares changes in the decolourisation efficiency during the sonication of the working solution at different ultrasonic frequencies. It can be observed in Fig. 2a that the higher frequencies of 380 and 850 kHz were more efficient towards color removal comparing with the lower frequencies of 20 and 40 kHz. Complete color removal was reached in 1.5 and 3 h when the working solution was sonicated at 380 and 850 kHz respectively. Over the same

Table 1
Average real power of ultrasonic devices.

Type of ultrasonic device	Power settings	Actual power (W/cm ³)
20 kHz Probe	15%	0.176
40 kHz cleaning bath	100%	0.098
Multi-frequency bath	380 kHz	0.054
	1000 kHz	0.016
	1176 kHz	0.008
850 kHz bath	1	0.006
	2	0.032
	3	0.062
	4	0.186

Fig. 2. Effect of sonication at different frequencies upon decolourisation of 0.025 mM MB and 0.1 M Na₂SO₄ solution at different (a) and about the same (b) powers.

time the 20 kHz ultrasonic probe and 40 kHz cleaning bath provided only 58 and 19% of color removal efficiency respectively within 3 h of sonication despite the higher powers employed of 0.176 and 0.098 W/cm³ comparable with those produced at sonication with 380 and 850 kHz baths. This can be explained by the higher production of hydroxyl radicals at higher frequencies originated from a shorter lifetime of cavitation bubbles and increased bubbles collapse per a unit of time [45–47]. In contrast a less effective decolourisation effect was obtained by sonication at 1000 and 1176 kHz is probably explained by lower powers (0.016 and 0.008 W/cm³ respectively, which was the upper limit of the ultrasonic apparatus) entering into the systems. That is related to the fact that more power is required to create the same cavitation effect at higher frequencies than at lower ones [24].

Fig. 2b shows the relationship between MB degradation during sonolysis at different frequencies at approximately the same

Fig. 3. Effect of different ultrasonic powers at constant frequency on decolourisation efficiency of 0.025 mM MB and 0.1 M Na₂SO₄ solution.

powers. Comparing the data on color removal efficiency obtained at sonication with 380 (0.054 W/cm³ actual power) and 850 kHz (0.062 W/cm³ actual power) it is seen that the final decolourisation obtained in both cases was equal to 97% after three hours of irradiation regardless the frequency. Moreover as can be seen from the inset of Fig. 2b, ultrasonic irradiation at 850 kHz (0.006 W/cm³ actual power) showed a slightly better result towards MB degradation than ultrasonic irradiation at 1176 kHz (0.008 W/cm³ actual power). In spite of the common fact that higher radical formation is observed at higher frequencies, the highest frequencies did not ensure the best degradation rates of MB and an optimal frequency must be carefully chosen which was observed in a number of other studies [45,48,49].

To check the effect of different ultrasonic powers on the degradation efficiency of MB, a series of experiments were conducted using ultrasonic irradiation at 850 kHz (Fig. 3a) which has the highest efficiency towards MB degradation. While comparing data of real power from Table 1 and color removal efficiency in Fig. 3, a general trend of higher degradation rates at higher powers was observed which can be attributed to an increased number of cavitation bubbles produced at higher powers leading to enhanced hydroxyl radicals formation [34,50].

3.2. The effect of combined electrocatalytic oxidation and ultrasonic irradiation on the decomposition of MB

In order to estimate the contribution of the electrolysis process in the decolourisation and decomposition rates of MB by a combination of sonochemical and electrochemical decomposition experiments, a single electrocatalytic oxidation of MB was conducted using a novel Ti/Ta₂O₅-SnO₂ electrode. As can be seen in Fig. 4, almost complete decolourisation of the working solution is obtained in three hours of electrolysis. The behavior of decolourisation is similar to that using sonication at 380 kHz with 0.054 W/cm³ actual power. According to Fig. 2 ultrasonic irradiation at 850 (power setting of 4) and 380 kHz (power setting of 80%) showed the best performance towards MB degradation. Therefore, these frequencies and powers have been chosen for sono-electrocatalytic degradation experiments. A positive synergistic effect leading to the enhanced degradation efficiency of MB was observed when combining electrolysis and sonolysis processes. When using ultrasonic irradiation at 850 kHz (power setting of 4) and electrolysis with the applied current of 20 mA, the complete decolourisation of working solution was achieved in 45 min comparing with 90 and 180 min while using independently sonolysis and electrolysis respectively (see vertical lines in the figure). In the case of combination of ultrasonic irradiation at 380 kHz

Fig. 4. Comparison of sonolysis, electrolysis and combined sonolysis processes and electrolysis on the decolourisation of MB solution.

Fig. 5. COD (a) and TOC (b) reduction during electrolysis sonolysis and combined electrolysis and sonolysis, $i = 20$ mA, frequency: 850 kHz; power setting 4.

(power setting of 80%) and electrolysis (input current of 20 mA) the rate increased by a factor of 3 and complete decolourisation was achieved in one hour versus three hours in separate processes of sonolysis and electrolysis (Inset Fig. 4).

If we look to COD and TOC values for separate and combined processes similar effects were observed (Fig. 5a and b).

Fig. 5 shows decreases in both TOC (corresponding to 4.675 mg/l TOC of stock solution) and COD (corresponding to 9.82 mgO₂/l

COD of stock solution) during the degradation of 0.025 mM MB solution in 0.1 M Na₂SO₄. These results allow us to estimate and compare the oxidation power of the three methods: sonication (frequency of 850 kHz with an actual power of 0.186 W/cm³), electrocatalytic (input current of 20 mA) and sono-electrocatalysis (input current of 20 mA and frequency of 850 kHz with an actual power of 0.186 W/cm³). According to Fig. 5a the targeted compound in the working solution was oxidised with efficiencies of 40.4%, 78.5% and 85.4% after applying the ultrasonic, electrocatalytic and sono-electrocatalytic treatments respectively within 2 h. This fact indicates a significant modification of MB structure especially in the case of electrocatalytic and sono-electrocatalytic treatments and its possible decomposition to less toxic compounds. A proof of MB mineralisation and its oxidation to CO₂ can be obtained using TOC data. The TOC removal efficiency during degradation experiments is shown in Fig. 5b. Ultrasonic treatment provided a poor reduction of TOC which reached only 3.6% after 2 h and 11.4% after three hours of sonication. Electrocatalytic treatment showed more promising results in terms of TOC with decreases of 26 and 38.6% of after 2 and 3 h of electrolysis respectively. By using the combined sono-electrocatalytic treatment an efficiency of 38.4% TOC decrease was obtained in only 2 h compared with a similar result after 3 h of electrocatalytic treatment.

3.3. Energy consumption estimation required for the oxidation processes

Table 2 compares the EC (kWh/m³) required for the complete decolourisation of the working solution by electrocatalytic, sonochemical and sono-electrochemical methods. According to Table 2 sonication at 850 kHz (0.186 W/cm³ power) provided twice the efficiency of MB decolourisation in terms of time compared with sonication at 380 kHz (0.054 W/cm³ power) and electrolysis ($i = 20$ mA) and reached 100% in 1.5 h (850 kHz) versus 3 h (380 kHz). However, electrocatalytic treatment showed greater decolourisation efficiency in terms of EC and was 19 and 33 times more energy effective comparing to sonication at 380 and 850 kHz respectively. Sono-electrocatalytic treatment with ultrasonic irradiation at 850 kHz provided a complete decolourisation of working solution within 45 min while using the coupled electrolysis and sonication at 380 kHz allowed the complete color removal in 1 h. When the EC required for reaching the same effect of decolourisation is taken into account however a combination of 380 kHz with the electrolysis process was 2.5 times more energy effective and required less energy than electrolysis at 850 kHz. This suggests that a careful optimisation of the treatment process is required depending on whether the requirement is for fast degradation or cost efficiency.

Table 2

Energy consumption (kWh/m³) required for complete degradation of 0.025 mM MB in 0.1 M Na₂SO₄ using sonoelectrocatalytic, electrocatalytic and sonochemical treatments with a fixed input current of 20 mA and ultrasonic irradiation at 850 (power setting of 4) and 380 kHz (power setting of 80%).

The type of degradation	EC (kWh/m ³) required for 100% decolourisation of MB	Time (h) required for 100% decolourisation
Electrocatalytic	$i = 20$ mA	8.46
Sonochemical	380 kHz	162
	850 kHz	279
Sono-electrochemical:	20 mA + 380 kHz	56.43
	20 mA + 850 kHz	141.36

4. Conclusion

Sono-electrocatalytic decomposition of MB dye was conducted using Ti/Ta₂O₅-SnO₂ electrodes which have never been reported for the sono-electrochemical degradation of organic compounds. In order to ultrasonically assist electrocatalytic MB degradation, ultrasonic frequency optimisation experiments were carried out at frequencies of 20, 40, 380, 850, 1000 and 1176 kHz. The most effective frequency for dye decolourisation proved to be 850 kHz. It was shown that complete decolourisation of dye solution is achieved within 45 min using sono-electrocatalytic treatment comparing with 90 and 180 min required for the same degree of color removal separate sonication and electrocatalytic oxidation respectively. The COD reduction observed in 2 h of sono-electrocatalytic decomposition was 85.4% and was twice that of sonication. The TOC removal efficiency of 38.4% achieved after 2 h of joint sonolysis and electrolysis increased by a factor of 1.5 comparing to electrooxidation and by a factor of 10.5 comparing to sonication. The EC required for complete decolourisation of dye solution was estimated.

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Publication III

Shestakova, M., Graves, J., Sitarz, M. and Sillanpää, M.

Optimization of Ti/Ta₂O₅-SnO₂ electrodes and reaction parameters for electrocatalytic oxidation of methylene blue

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Optimization of Ti/Ta₂O₅–SnO₂ electrodes and reaction parameters for electrocatalytic oxidation of methylene blue

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Abstract Among existing water treatment methods for organic-containing wastewaters, advanced oxidation process, particularly electrocatalytic oxidation, is a technique allowing to reach high degradation and mineralization efficiencies. Electrodes tested for use in electrocatalytic oxidation processes contain either expensive or platinum/group metals such as Pt-, Ru-, Ir-, Pd-, or boron-doped diamond and Sb and Pb compounds which are toxic for the environment. Thereby, there is a need for environmentally friendly and less expensive electrodes. The objectives of this research were to optimize annealing temperature of Ti/Ta₂O₅–SnO₂ electrodes, establish the working media for organic compound oxidation processes

as well as check degradation, mineralization and current efficiencies for methylene blue dye oxidation. Decolorisation efficiency of 95 % was achieved in 2 h at pH = 6.5. Neutral media showed also higher efficiency towards COD decrease which was equal to 85 % after 2 h of electrolysis. The lowest energy consumption of 7.7 kWh m^{−3} required for 100 % decolorisation was observed for the electrodes annealed at 550 °C at pH = 2. The highest current efficiency of 10.1 % attributed to 80 % of COD reduction was obtained for the electrode annealed at 550 °C at pH = 6.5. The optimization data allow further extrapolating of electrocatalytic oxidation process on Ti/Ta₂O₅–SnO₂ electrodes to pilot scale.

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Graphical Abstract

Keywords Electrocatalysis · Electrolysis · Ti/Ta₂O₅-SnO₂ electrodes · Methylene blue

1 Introduction

Water, energy, food, and climate securities are the main global challenges nowadays where water is the core of the water-food-energy-climate nexus [1]. Spent industrial and domestic water cannot be directly released back to the environment or returned to a technological cycle since it is contaminated with mechanical impurities, organic, and inorganic pollutants.

Traditional treatment methods of wastewater containing organic compounds are biological treatment, chemical oxidation, coagulation, and adsorption. However, these methods are inefficient towards persistent organic compounds such as insecticides, pesticides, and pharmaceuticals [2]. In addition, a significant group of pollutants such as dyes which are widely used in textile, tannery, pulp and paper and pharmaceutical industries were found resistant to microorganism attack and cannot be efficiently treated by biological methods [3]. Despite the ease of implementation, all traditional wastewater treatment methods have the main disadvantage of the secondary waste formation. Spent adsorbents, coagulation, sedimentation, and sewage sludge should be regenerated or disposed which requires additional costs and working areas.

Advanced oxidation processes (AOP) and particularly electrocatalytic oxidation are promising techniques allowing a complete mineralization of resistant organic pollutants to simple molecules like CO₂ and H₂O without generation of secondary wastes. Electrocatalytic oxidation of organic pollutants by direct electrolysis occurs by means of interaction of adsorbed hydroxyl radicals on the electrode surface (*M*) with an organic pollutant (*R*) [4, 5]:

Moreover, along with high mineralization efficiencies achieved by anodic oxidation, electrocatalytic methods are easy to implement and automate. The most commonly used electrodes for electrocatalytic oxidation of organic compounds are BDD, Pt, Sb-doped RuO₂/TiO₂, Ti/IrO₂-SnO₂-Sb₂O₅, Ti-Pt/β-PbO₂, Ti/Sb-SnO₂, Ti/PbO₂, Ti/(IrO₂ + Ta₂O₅), Ti/SnO₂-Sb₂O₅, Ti/SnO₂-Sb₂O₅-PtO_x, Ti/SnO₂-Sb₂O₅-RuO₂, Ti/RuO₂-IrO₂ [6–15]. As it can be seen, all of them contain either expensive compounds like diamond, Pt, Ru, Ir, or potentially environmentally toxic compounds such as Pb and Sb. Therefore, there is a search for less expensive, less toxic electrodes with a high electrocatalytic oxidation efficiency. Over the last few years, phosphotungstic acid/neutral red intercalated montmorillonite composite (PTA/NR-MMT) film electrodes assembled on a graphite electrode, magnetite/reduced graphene oxide

(Fe₃O₄/RGO) composite electrodes, Ni-doped nanoporous carbon electrodes, lithium-doped Ta₂O₅ film-coated electrodes, etc. were found active towards oxidation of *N*-acetylcysteine, methyl jasmonate, propargyl alcohol, ascorbic acid and glucose [16–20]. However, the above-mentioned electrodes have been only electrochemically and physically characterized and so far, there is no information on electrolysis experiments, degradation efficiencies, COD and TOC decrease of organic pollutants using these types of electrodes. Moreover, carbon-containing electrodes are expected to be suitable for detection of organic compounds rather than for their oxidation in wastewaters due to low potential for carbon corrosion [21] which is shown in the following reactions:

Recently, novel Ti/Ta₂O₅–SnO₂ electrodes were found potentially active towards electrocatalytic oxidation of organic compounds and particularly methylene blue (MB) dye [22]. However, the best process conditions for electrode preparation and electrocatalytic oxidation of MB still have to be determined. In this paper, we report for the first time on the optimization of the annealing temperature of Ti/Ta₂O₅–SnO₂ electrodes and determine the best media conditions for electrolysis processes in terms of energy and mineralization efficiency.

2 Experimental

2.1 Electrode preparation

Ti/Ta₂O₅–SnO₂ electrodes with the nominal composition of Ta(*x*)–Sn (100–*x*) where *x* = 7.5 at.% were prepared by a thermal decomposition and drop casting technique of the precursor solution onto a titanium substrate [23]. The detailed preparation method is described elsewhere [22]. The total concentration of metals ions was equal to 0.04 M. The total number of active Ta₂O₅–SnO₂ layers forming the ultrathin film deposited on the titanium substrate was eight. Three different annealing temperatures of 450, 550, and 650 °C were used for the electrode preparation. After 10-h final air-annealing, without additional air circulation in muffle furnace, the electrodes were cooled down and washed for 10 min in an ultrasonic bath and finally dried at 105 °C. Electrodes were weighed after etching and at the final stage of preparation. Ta₂O₅–SnO₂ material deposition was equal to 1.1 mg cm^{−2} ± 3 %.

All chemicals used for electrodes and working solution preparation were of analytical grade and used without

further purification. Tantalum (V) chloride (99.99 % trace metal basis, Sigma-Aldrich), tin (II) chloride dehydrate (≥99.99 % trace metals basis, Sigma-Aldrich), and absolute ethanol (Baker Analyzed VLSI grade, J.T. Baker) were used for the precursor solution preparation. Titanium substrate pretreatment was conducted in 10 wt% NaOH (≥98 % anhydrous, Sigma-Aldrich) and 18 wt% boiled hydrochloric acid (pro analysis, Fluka).

2.2 Physicochemical and electrochemical characterization of the electrodes

All electrodes were physically and electrochemically characterized. Microstructure of the produced materials was examined by means of scanning electron microscope (SEM) (Hitachi S-4800, Japan) with an attachment for chemical analysis of specimen in microareas with energy dispersive x-ray spectroscopy (Ametek, S4800, USA). X-ray diffraction (XRD) measurements at small incident angle (GID) were performed using the Empyrean (Panalytical) diffractometer with Cu anode and the focusing mirror. The range of measurement was from 20° to 80° of the angle 2 θ, with constant omega angle = 1. The measurement step was 0.02°, with measurement time of 2.4 s per step.

The electrochemical characterization of the electrodes was conducted with an Autolab PGSTAT12 Galvanostat/Potentiostat using cyclic voltammetry (CV) measurements in a conventional three electrode cell (200 ml). The potentiostat was computer-controlled by GPES EcoChimie software. The prepared Ti/Ta₂O₅–SnO₂ electrodes, with a surface area of 2.2 cm² controlled with Teflon ribbon, were used as working electrodes. Gold disk electrode of 2 mM diameter (Metrohm-Autolab) was used as a working electrode for comparison experiment. A coiled platinum wire served as a counter electrode and saturated calomel electrode (SCE) was used as a reference electrode. All CV measurements were performed versus this reference electrode between 0.15 and 2 V potential limits at a scan rate of 50 mV s^{−1}. Electrode conditioning, at potentials of 0.2 V for 15 s and 1.2 V for 5 s, was applied before each measurement as a pretreatment step. CV measurements were conducted in supporting electrolyte solution of 0.1 M Na₂SO₄ (anhydrous ACS reagent, Sigma-Aldrich), aqueous solution of 0.1 M Na₂SO₄ and 0.1 mM MB (Certistain, Merck) at room temperature in acidic (pH = 2), basic (pH = 12) and neutral (pH = 6.5) media. pH was adjusted by H₂SO₄ and NaOH. An aqueous solution of 0.5 mM potassium hexacyanoferrate (II) trihydrate (99 % trace metal basis, Riedel-de-Haën) and 0.1 M Na₂SO₄ was used for CV measurements to estimate the active surface. The supporting electrolyte solution and aqueous solution of Na₂SO₄ and MB are hereafter referred to as the blank and working solution, respectively. Ultrapure water (18.2 MΩ

Fig. 1 X-Ray diffractograms for Ti/Ta₂O₅-SnO₂ electrodes annealed at 450, 550, and 650 °C

cm) was used for the solution preparation and deoxygenated by bubbling nitrogen before every CV measurement. Hielscher UP-50H ultrasonic probe (Sonotrode MS3, 50 W maximum output power) with 80 % amplitude was used for conducting CV measurements in the ultrasonic field.

2.3 Electrolysis and degradation efficiency control

Electrochemical oxidation experiments were carried out in a jacketed reactor placed on a magnetic stirrer. The stirring rate was 1000 rpm. A constant temperature of 25 ± 2 °C was maintained by water circulation through a jacketed cooler. 30 ml samples of working solution were used for degradation experiments. The Ti/Ta₂O₅-SnO₂ electrodes with a surface area of 2.2 cm² were used as anodes and Ti plate of the same surface area served as the cathode. The distance between electrodes was 1 cm. Electrolyses at a constant current of 20 mA (current density of 9 mA cm⁻²) were carried out using a GW Instek PSM-6003 power supply.

The decolorisation of MB was monitored by UV-Vis spectrophotometer (Lambda 45, Perkin Elmer) by measuring the absorbance of light by MB at 664 nm in neutral and acidic media and at 591 nm in basic media. Chemical Oxygen Demand (COD) was determined by means of a Hach Lange DRB 200 system. The non-purgeable organic carbon (NPOC) content was measured with a TOC analyzer (TOC-Vcpn, Shimadzu, Japan).

The energy consumption (EC) per volume of treated working solution (kWh m⁻³) and current efficiency (CE, %) of electrolysis processes in different media were calculated according to the following equations [24]:

$$EC(\text{kWh m}^{-3}) = IVt/V_s \quad (5)$$

$$CE(\%) = ((\Delta\text{COD})FV_s/8It) \times 100 \quad (6)$$

where I is the average applied current (A), V is the average cell voltage (V), t is the electrolysis time (h in the case of EC) or time of the COD decay (s in the case of CE), V_s is the solution volume (dm³), ΔCOD is the COD reduction (g dm⁻³) at time t , F is the Faraday constant (96487 C mol⁻¹) and the constant 8 is the oxygen equivalent mass (q equiv⁻¹).

3 Results and discussion

3.1 XRD analyses and SEM (and EDX)

To identify the crystal structure of the prepared electrodes, XRD analysis was conducted. Figure 1 shows XRD patterns of the Ti/Ta₂O₅-SnO₂ electrodes annealed at 450, 550, and 650 °C. XRD pattern of the electrode annealed at 450 and 550 °C contained intense peaks of hexagonal Ti substrate appearing at $2\theta = 35.097, 38.269, 40.141, 52.898, 62.965, 70.444, 76.134$, and 77.348° associated to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), and (2 0 1) crystal

Fig. 2 SEM images of Ti/Ta₂O₅-SnO₂ electrodes with element mapping: **d–f** Ta mapping, **g–i** Sn mapping and for the electrodes annealed at **a** 550, **b** 650 and **c** 450 °C, respectively

orientations of titanium, while XRD patterns of the electrode annealed at 650 °C showed the only clear peak of hexagonal titanium at $2\theta = 40.141^\circ$. This could be explained by high crystallinity of Ta₂O₅-SnO₂ films formed at 650 °C. Tantalum was represented by orthorhombic β -Ta₂O₅ with peaks corresponding to the (0 0 1), (1 1 0), (2 0 0), (1 1 1), (2 0 1), (0 0 2), (3 1 0), (2 0 2), (3 1 2), and (4 0 2) planes and hexagonal δ -Ta₂O₅ with peaks corresponding to (0 0 3), (2 0 0), (2 0 3), (0 0 6), and (2 2 0). Tetragonal cassiterite SnO₂ was evidenced through the presence of (1 1 0), (1 0 1), (1 1 1), (2 1 1), (3 1 0), (3 0 1), (2 0 2), (3 2 1), (4 0 0), and (3 3 0) reflections. The presence of tetragonal rutile TiO₂ in the Ti/Ta₂O₅-SnO₂ electrodes structure is explained by the oxygen solubility in the metal lattice of the titanium substrate [25]. The main peaks of TiO₂ were corresponding to the (1 0 1), (2 0 0), (1 1 1), (2 1 0), (2 1 1), (2 2 0), (0 0 2), (3 1 0), (3 0 1), and (1 1 2) atomic planes. The low intensity of TiO₂, SnO₂, and Ta₂O₅ peaks in the XRD pattern of the electrode annealed at 450 °C can be attributed to a low crystallinity of the formed oxides and as a result to a low performance of this electrode towards MB oxidation (see below).

Figure 2 shows typical SEM images and EDX element mapping of the Ti/Ta₂O₅-SnO₂ electrodes annealed at 450,

550, and 650 °C. In general, the SEMs show that the surfaces are very similar in appearance although the electrode prepared at 550 °C does have more cavities and pin holes present which tends to suggest a potentially larger active surface area for electrolysis. The surface roughness and porosity can influence diffusion to the electrode surface and this is investigated in Sect. 3.2. From the EDX mapping, the Ta distribution (Fig. 2d–f) over Ti substrate is rather scattered with the resulting Ta₂O₅ particles size varying from a few nanometers (dots on the mapping images) to a few micrometers forming agglomerates (bright blue spots). Sn distribution over Ti substrate (Fig. 2g–i) is more or less homogeneous with a greater accumulation on the electrode annealed at 550 °C and the smaller content on the electrodes annealed at 450 and 650 °C.

3.2 Cyclic voltammetry

3.2.1 Characterization of electrodes

To estimate the relative electrode surface area after annealing, cyclic voltammograms were recorded from an electrolyte containing a simple redox couple, from electrodes

prepared at the three chosen annealing temperatures. Figure 3 shows typical cyclic voltammograms recorded for a Ti/Ta₂O₅-SnO₂ electrode annealed at 550 °C from an aqueous solution of 0.5 mM K₄Fe(CN)₆ and 0.1 M Na₂SO₄ using a range of potential scan rates. The couple has the characteristics of a quasi-reversible electron transfer on this electrode surface; well-formed oxidation and coupled reduction peaks are observed around 0.25 and 0.15 V, respectively. The peak separations are greater than 60 mV expected for a reversible process (98–129 mV with the scan rates shown). However, this observation may simply be due to the high intrinsic resistance of this type of electrode material [26]. The value of the diffusion coefficient estimated from the slope of the linear I_p anodic against the square root of the sweep rate plot is $9.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ which is in good agreement with the literature-reported values [27–30].

Peak currents were recorded from cyclic voltammograms run at slow scan rates. Table 1 shows the peak current densities and peak separations recorded at a sweep rate of 5 mV s^{-1} , for the oxidation of 0.5 mM K₄Fe(CN)₆ at three electrode annealing temperatures and for comparison an entry for a gold disk electrode is also included.

In general, the peak current densities observed at the Ti/Ta₂O₅-SnO₂ electrodes are of the same order of magnitude with the lowest value recorded for the highest firing temperature. However, the recorded currents are all higher than that recorded from the smooth gold electrode. This observation suggests that Ti/Ta₂O₅-SnO₂ electrodes prepared

using the thermal decomposition technique described in [22] and imaged in Fig. 2, lead to rough electrode surfaces with approximately twice the active working area available. It is unclear why the peak currents are reduced at the higher firing temperature of 650 °C. Other workers have observed similar effects with different oxide electrodes and have suggested that the formation of a poorly conducting oxide layer between the Ta₂O₅-SnO₂ coating and the metal substrate interferes with the electron transfer process [31]. It was found that electrical conductivity of Sn_{0.97}Ta_{0.03}O₂ thin films grown on TiO₂ substrates and annealed at 500–600 °C is approximately 1100 S m^{-1} [32]. Trasatti suggests that lower crystallinity may be important. However from the XRD data, see above, a reduced degree of crystallinity was only recorded at 450 °C and the electron transfer for the ferricyanide redox couple proceeds rapidly at this surface.

3.2.2 MB oxidation

Figure 4a shows the CV results of prepared Ti/Ta₂O₅-SnO₂ electrodes recorded from a working solution of 0.1 mM MB and 0.1 M Na₂SO₄. All voltammograms, with the exception of electrode annealed at 450 °C, contained an anodic current peak with a maximum at potential of 1.1 V absent on CVs in the blank solution and attributed to oxidation of MB [22]. Anodic current of $60 \mu\text{A cm}^{-2}$ at potential of 1.1 V is 3 and 8 times higher for the electrode annealed at 550 °C than for electrodes annealed at 650 and 450 °C, respectively. The higher capacitance current observed from the electrode annealed at 550 °C also confirms a greater microroughness. Therefore, at an annealing temperature of 550 °C, the tantalum/tin oxide coating shows some promise as a non-precious metal electrode for the electrocatalytic oxidation of MB. Further investigations at different pH were carried out to determine the optimum conditions for MB oxidation.

To investigate the electrochemical behavior of prepared Ti/Ta₂O₅-SnO₂ electrodes in different media, CVs were run in the working solutions of 0.1 M Na₂SO₄ and MB at pH 2, 6.5 and 12. Figure 4b represents the CV results in 0.1 M Na₂SO₄ and 0.1 mM MB aqueous solution at the pH 2, 6.5, and 12. Voltammograms recorded at pH 6.5 and at pH = 2 showed anodic current peaks of 60 and $30 \mu\text{A cm}^{-2}$ respectively attributed to the MB oxidation. However, when pH was changed to the value of 12, no anodic

Fig. 3 CVs Ti/Ta₂O₅-SnO₂ electrode annealed at 550 °C in 0.5 mM K₄Fe(CN)₆·3H₂O and 0.1 M Na₂SO₄ at different scan rates ν

Table 1 Peak currents for the oxidation of 0.5 mM K₄Fe(CN)₆ in 0.1 M Na₂SO₄ for Ti/Ta₂O₅-SnO₂ electrodes and a Au electrode recorded at a scan rate of 5 mV s^{-1}

Electrode	Annealing temperature (°C)	Peak Current Density ($\mu\text{A cm}^{-2}$)
Ti/Ta ₂ O ₅ -SnO ₂	450	41.2
	550	35.4
	650	32.8
Au disk electrode	–	22.1

Fig. 4 CV of Ti/Ta₂O₅-SnO₂ electrodes prepared at different temperatures (Fig. 4a) and run in different media (Fig. 4b) in working solution of 0.1 mM MB and 0.1 M Na₂SO₄ (Fig. 4b) adjusted to of pH = 2 and pH = 12 (Inset Fig. 4b) with H₂SO₄ or NaOH respectively for Ti/Ta₂O₅-SnO₂ electrode annealed at 550 °C. $\nu = 50 \text{ mV s}^{-1}$

current of MB oxidation was observed (Inset Fig. 4b). The absence of MB oxidation peak is explained by a significant shift of the OER onset potential to more negative values from about 1.8–1.4 V and masks the MB oxidation peak. Running an electrolysis process in alkali is therefore more favorable for oxygen formation rather than MB oxidation.

To ensure an efficient electrolysis process, the concentration of the electroactive species near the surface of the electrode should be maintained and not depleted. Typically, this is achieved on an industrial scale by efficient agitation of the electrolyte using a number of techniques for example rapid stirring, pumping or using turbulence promoters [33]. Ultrasound can also be used to improve mass transport. The advantages of applying ultrasonic irradiation are twofold: first, it can increase the movement of electroactive species to the electrode surface and second through the process of cavitation hydroxyl radicals can be generated and thereby increase the rate of oxidation of MB.

Figure 5 records the first and sixth cyclic voltammograms from an electrochemical cell without agitation (a),

Fig. 5 Different CV scans made in the working solution of 0.1 mM MB and 0.1 M Na₂SO₄ in acidic media (pH = 2) without external exposure (a), under the influence of ultrasonic field (b) and with magnetic stirrer (c). $\nu = 50 \text{ mV s}^{-1}$

using a magnetic stirrer (b) and with a 30 kHz ultrasonic field applied (c). The cyclic voltammogram without agitation shows the characteristic depletion of the electroactive species and gradually decreases with time whereas stirred and ultrasonically irradiated cells show no change in the current response. The MB is replenished as fast as it is consumed at the electrode surface. Applying ultrasound to any laboratory cell will therefore ensure good electrolyte movement and through cavitation generate radicals which have the potential to accelerate the oxidation of MB.

3.3 Electrolysis (degradation experiments)

To prove electrocatalytic activity of Ti/Ta₂O₅-SnO₂ electrodes towards MB oxidation and show the effect of

Fig. 6 Color (a) and COD (b) removal efficiency after 8 h of electrolysis of 0.1 M Na₂SO₄ and 0.1 mM MB working solution. Inset Fig. 6a: NPOC removal efficiency (mineralization)

different media on MB degradation rates, a series of electrolysis experiments were conducted with 0.1 mM MB and 0.1 M Na₂SO₄ solution using magnetic stirring. Preparative electrolysis tests in an ultrasonic field are reported in [34]. According to Fig. 6a 95 and 85 % decolorisation efficiency was achieved in two hours of electrolysis at pH of 6.5 and 2, respectively. Degradation rate of MB in basic media was considerably slower and reached only 78 % after 2 h of electrochemical oxidation that coincides with the preliminary prediction obtained by CV measurements (Fig. 4b) and was attributed to a low oxygen evolution overvoltage [35, 36]. Efficiency of Ti/Ta₂O₅-SnO₂ electrodes in regard of MB oxidation was confirmed by the data on COD and NPOC removal

(Fig. 6b, inset Fig. 6a). The fastest COD removal efficiency was obtained at a pH of 6.5 and after 2 h of electrolysis was equal to 85 %. It increased slowly to 90 % and was stable during 8 h of electrochemical oxidation. Lower COD removal values were achieved after 2 h of electrolysis at pH of 2 (70 %) and 12 (26 %). However, COD removal efficiency increased to 85–99 % for all media after 8 h of electrolysis. Mineralization data obtained during electrolysis showed that MB was mostly oxidized to CO₂. Overall NPOC reduction (Inset Fig. 6a) of 71, 74, and 76 % was reached after 8 h of electrolysis for the electrodes annealed at 550 °C at pH of 12, 6.5, and 2, respectively.

Table 2 shows the data on EC required for the complete decolorisation and 80 % COD decrease of 0.1 mM MB and 0.1 M Na₂SO₄ solution and CE obtained at 80 % COD reduction in different media of working solution. Electrolyses in acidic media were the most energy effective for conducting decolorisation experiments and required 7.7 kWh m⁻³ of energy to achieve 100 % color removal. Basic and original media of working solution needed 24.4 and 21.5 kWh m⁻³ respectively to obtain 100 % decolorisation. The EC data are comparable to those required for decolorisation of other organic dyes [37–39]. The original media of working solution were the most energy effective towards COD reduction and basic media were the least effective. The energy required for 80 % COD decrease at pH = 6.5 was equal to 9.3 kWh m⁻³ versus 33.9 kWh m⁻³ consumed at pH = 12. The highest CE of 10.1 % was observed for the lowest EC of 9.3 kWh m⁻³ required for 80 % COD removal at pH = 6.5 that is a typical behavior for many mixed metal oxide electrodes [40–42]. The lowest CE of 1 % was obtained for 80 % COD decrease in basic conditions which was attributed to oxygen evolution being the favored reaction.

4 Conclusion

The annealing temperature of Ti/Ta₂O₅-SnO₂ electrodes and working media for electrocatalytic oxidation of MB was investigated. The electrodes were characterized by XRD, SEM, and EDX analysis. Cyclic voltammetry suggested the electrode surface area of Ti/Ta₂O₅-SnO₂

Table 2 EC (kWh m⁻³) and CE (%) obtained at complete decolorisation and 80 % COD reduction of 0.1 mM MB in 0.1 M Na₂SO₄ solution at pH of 6.5, 2, and 12 for the electrodes annealed at 550 °C and at pH of 6.5 for the electrode annealed at 650 °C

Electrode annealing temperature and electrolysis media	EC (kWh m ⁻³) at 100 % decolorisation	EC (kWh m ⁻³) at 80 % COD reduction	CE (%) at 80 % COD reduction
550 °C, pH = 2	7.7	12.9	5.2
550 °C, pH = 6.5	21.5	9.3	10.1
550 °C, pH = 12	24.4	33.9	1

electrodes annealed at 550 °C was high in comparison with an electroplated Pt electrode. An annealing temperature of 550 °C showed the best electrocatalytic activity for oxidation of MB. The original media of the 0.1 M Na₂SO₄ and 0.1 mM MB solutions were found optimal for conducting degradation experiments since it gave high anodic currents of OER and provided decolorisation, COD and TOC removal efficiencies analogous to that in acidic media. Moreover, these media were the most energy effective towards COD decrease providing the lowest value of EC and highest value of CE. Acidic conditions were found energy effective for achieving complete color removal. Decrease of Ti/Ta₂O₅-SnO₂ electrodes efficiency toward MB decolorisation and COD removal during the electrocatalytic oxidation at pH = 12 was observed due to a low OER overvoltage and current leakage for water oxidation. Ultrasonic field showed the improved electrodes performance towards MB oxidation due to enhancement of MB mass transport to the electrode surface which was supported by the data on diffusion-controlled process.

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Publication IV

Shestakova, M., Vinatoru, M., Mason, T.J., Iakovleva, E. and Sillanpää, M.
Sonoelectrochemical degradation of formic acid using Ti/Ta₂O₅-SnO₂ electrodes

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Sonoelectrochemical degradation of formic acid using Ti/Ta₂O₅-SnO₂ electrodes

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Abstract

Advanced oxidation processes (AOPs) are modern methods using highly reactive hydroxyl radicals for the oxidation of persistent organic (sometimes inorganic) compounds in aqueous phase. Among AOPs, sonoelectrochemical degradation is a technique employing electrochemistry and ultrasound as the main source of energy without the need for additional chemicals for the process. The annual production of formic acid (FA) is around 800,000 tonnes and is a constituent in wastewaters from tannery, chemical, pharmaceutical, dyeing industries etc. Thus far sonoelectrochemical methods have never been applied to FA decomposition. The aim of this paper is to investigate the sonoelectrochemical decomposition of FA, optimize the sonochemical and electrochemical parameters involved in FA degradation and compare the results with other existing AOPs. Sonoelectrochemical degradation of FA was found to be either comparable or better than other AOPs in terms of time and degradation efficiency. The highest 97% mineralization of FA was obtained using 1176 kHz ultrasonic irradiation combined with 20 mA electrolysis in 120 minutes. The fastest FA degradation kinetics with a rate constant of 0.0374 min⁻¹ were generated at 381 kHz at 20 mA at an ultrasonic power of 0.02 W/cm³.

Keywords: Sonoelectrochemical degradation, formic acid, Ti/Ta₂O₅-SnO₂ electrodes, electrolysis, ultrasound, advanced oxidation process.

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Shestakova).

1 Introduction

In recent years AOPs have been developed to increase the efficiency of the wastewater treatment [1]. A basic principle of AOPs is the generation of the powerful oxidizing agents, hydroxyl radicals, which can mineralize refractory organic compounds and pathogens [2]. Mineralization is defined as the destruction of harmful compounds, which is generally a much better option than simply transferring them from one phase to another which occurs in conventional water treatment processes such as adsorption, coagulation and filtration. Mostly AOPs are used for water and wastewater treatment however they also find applications in soil remediation and air cleaning [3]. The sonoelectrochemical decomposition of organic compounds, recently reviewed, is a relatively new AOP, which has the advantage of not requiring additional chemicals in the treatment and use of electricity as a main component [4]. Although sometimes required in laboratory experiments the addition of salts to maintain electrolytic ambient is not required in real system because of the high conductivity of industrial

wastewaters. The method is based on the synergetic effect of sonochemical and electrochemical degradation, which generate highly oxidizing species such as hydroxyl radicals. In direct electrochemical process, the formation of hydroxyl radicals takes place through the reaction 1 [5].

where M is the surface of electrode.

The mechanism of subsequent oxidation of organic compounds depends on the anode nature, which are divided on “active” and “non-active” [6]. In the case of “active” electrodes, on which $\cdot OH$ radicals are strongly adsorbed, oxidation of organics (R) to oxidation products is occurred through the intermediate step of higher oxide formation (reactions 2 and 3) [5]

In a case of “non-active” electrodes, $\cdot OH$ radicals do not interact with anodic material and directly mineralize organic compounds (4) [6] [7] [5]:

One of the main disadvantages of electrochemical method is the polarization and passivation of electrodes due to poor mass transfer. Polarization can be caused also by gas accumulation near to the electrode surface and as a result depletion of pollutant in the electrode’s boundary layer [8]. Passivation can be caused by the deposition of reaction products on the surface of electrodes, which results in diminishing of the process efficiency.

Ultrasound combined with the above electrochemical degradation process eliminates electrode contamination because of the continuous mechanical cleaning effect produced by the formation and collapse acoustic cavitation bubbles near to the electrode surface [9]. Some of the first uses of ultrasound in electrochemistry were for the removal of any passivation layer from electrode surfaces, for the homogenization of electrolytes and for the improvement of structural properties in films deposited during electroplating [10] [11] [12]. The first studies relating to the use of sonoelectrochemical methods in pollutant degradation date back to the turn of the 21st century [4] where ultrasound assisted the electrochemical degradation of diuron herbicide, Procion Blue dye and N,N-dimethyl-p-nitrosoaniline [13] [14] [15]. Over the last few years, ultrasonically assisted electrochemical methods were tested for the degradation of a range of different compounds such as pesticides, dyes, pharmaceuticals etc. [16] [12] [17] [18] [19].

Ultrasonic irradiation of water leads to formation of hydrogen atoms and hydroxyl radicals according to reaction 5 [20]:

The free radicals produced in a sonoelectrochemical process can be consumed either by reaction with organic pollutant leading to its decomposition or by recombination reactions.

A search of the literature reveals that there have been no studies reported of the sonoelectrochemical degradation of FA. However, it is widely used chemical with an annual production of about 800,000 tons [21]. The major consumers of FA are agriculture where it is used for silage preservation and as animal feed additive [22]; the textile and leather industries in dyeing and tanning; rubber production and in the chemical and pharmaceutical industries where it is used as an intermediate in a range of production processes [23]. Wastewaters from any of the above-mentioned industries contain FA as a pollutant [23]. It is resistant to many of the degradation processes of other organic compounds [24] [25] [26] [27] [28].

The aim of this work is to study sonoelectrochemical decomposition of FA using recently developed Ti/Ta₂O₅-SnO₂ electrodes, which were found to be effective in the oxidation of organic compounds [29]. In this work, we report for the first time a synergetic effect of electrochemical and sonochemical parameters in the sonoelectrochemical decomposition of FA. The results are compared with those from other existing AOPs used for FA degradation.

2. Experimental

2.1 Electrodes and working solution preparation

Ti/Ta₂O₅-SnO₂ electrodes containing 7.5 at.% of Ta were prepared by thermal decomposition and drop-casting of a precursor solution on Ti substrate [30]. The detailed information on the electrodes preparation method and pretreatment procedure is described elsewhere [29] [31]. Pretreatment of Ti substrates was conducted in 10 wt.% NaOH ($\geq 98\%$ anhydrous, Sigma-Aldrich) and 18 wt.% boiled hydrochloric acid (pro analysis, Fluka). Precursor solution was prepared using absolute ethanol (Baker Analyzed VLSI grade, J.T. Baker), TaCl₅ (99.99% trace metal basis, Sigma-Aldrich) and SnCl₂•2H₂O ($\geq 99.99\%$ trace metals basis, Sigma-Aldrich).

A stock solutions of 250 mg/l FA (~ 5.4 mmol/l, reagent grade $\geq 95\%$, Sigma-Aldrich) and 3 g/l NaCl (BDH Analab[®], reagent grade 99.5%) was used as a working solution in electrochemical, ultrasonic and sonoelectrochemical experiments. All chemicals were of analytical grade and used without further purification. Ultrapure water (18.2 M Ω ·cm, Millipore) was used at all stages of preparation process including working solutions.

2.2 Electrochemical, ultrasonic and sonoelectrochemical experiments and degradation efficiency control

The experimental set-up for the sonoelectrochemical degradation of FA is shown on Fig. 1. The electrochemical section consisted of electrodes connected to a programmable power supply (GW Instek, PSP-405). Ti/Ta₂O₅-SnO₂ electrodes of 2.2 cm² surface area served as an anode in electrochemical experiments and Ti plate of the same surface area was a cathode. Electrolyses were conducted at a constant current of 10, 20 or 30 mA. The distance between electrodes was 1 cm. The sonochemical part included an ultrasonic power multi-frequency

generator (Meinhardt, Ultraschalltechnik, 250 W of maximum output power) driving an ultrasonic transducer (type E/805/TM, 75 mm diameter) fitted into a jacketed glass reactor, two different transducers were employed.

Fig.1. Experimental set-up

Ultrasonic experiments were carried out indirectly at operating frequencies of 381 (0.007 and 0.02 W/cm³), 863 (0.0067 W/cm³), 992 (0.003 W/cm³) and 1176 (0.003 W/cm³) kHz by placing a pyrex glass beaker with 40 ml of working solution in the glass reactor. The temperature of the working solution during degradation experiments was kept constant at 20±2°C by means of water circulating through the jacketed reactor. The actual ultrasonic power entering the system during ultrasonic experiments was measured by calorimetry [32] [33] [34]. The combined sonoelectrochemical degradation process was carried out by the simultaneous application of electrolysis and sonication.

The non-purgeable organic carbon (NPOC) content was measured with a TOC analyzer (TOC-Vcpn, Shimadzu, Japan). Concentration of FA during degradation experiments was monitored using a Shimadzu LC-20 High Performance Liquid Chromatograph (HPLC) using RSpak KC-811 column (300 × 8.0 mm, Shodex) and UV-Vis detector SPD-20AV ($\lambda = 210$ nm). The mobile phase consisted of 0.1% phosphoric acid aqueous solution with flow rate 1 mL/min. Column was kept at 40°C.

The energy consumption (EC) consumed per volume of treated working solution (kWh/m³) during the electrolysis and sonication processes was calculated using CO/TECH plug in watt meter.

The rate constants for the sonoelectrochemical degradations were calculated and compared with those from the individual processes of electrolysis and sonication.

3. Results and discussions

3.1 Electrochemical and sonochemical degradation of FA

To estimate the effect of ultrasonic frequencies and applied current on FA removal efficiency ultrasonic irradiation of the working solution (Fig. 2a) at 381, 863, 992 and 1176 kHz frequencies and galvanostatic electrolysis at applied currents of 10, 20 and 30 mA (4.5, 9.1 and 13.6 mA/cm² respectively) were conducted. Figure 2 shows the dependence of FA removal efficiency during sonication and electrolysis. Kinetic data derived from the plots of the logarithm of FA concentration versus time for the degradation experiments were best fitted to the first-order model represented by:

$$\ln C(t) = \ln C_0 - kt$$

where C_0 is the initial concentration of pollutant, C is the concentration of pollutant at time t and k is the first-order rate constant which was estimated from the slope by plotting. The data on the obtained kinetic rate constants for all degradation processes and actual powers obtained at ultrasonic irradiation of working solution are listed in Table 1.

Table 1. Variation of degradation rates constants and energy consumption with the applied current at electrolyses processes

The type of degradation experiment	Working parameters		The first-order kinetic rate constant, k , min ⁻¹	Energy consumption required for 90% pollutant degradation, EC, kWh/m ³	Time required for 90% pollutant degradation, h
	Ultrasonic frequency, kHz (actual power W/cm ³)	Applied current, I, mA			
Sonication	381 (0.02)	-	0.0002	-	-
	381 (0.007)	-	0.0002	-	-
	863 (0.0067)	-	0.0001	-	-
	992 (0.003)	-	0.00004	-	-
	1176 (0.003)	-	0.00005	-	-
Electrolysis		10	0.0079	-	-
		20	0.0185	675	2
		30	0.0207	700	2

As can be seen on Fig. 2a sonication alone (1176, 992, 862, 381) had no significant effect on FA decomposition. The maximum compound removal were about 3 % after 2 h of sonication at 381 kHz (0.007 W/cm³). A slightly lower removal efficiency of 2.5% was obtained for the same 381 kHz frequency and higher power of 0.02 W/cm³. Even though the difference in removal efficiencies is insignificant, the same effect was observed for FA degradation using ultrasonic frequencies of 22.7 kHz (rated output power 240W) [35]. The same research reported the degradation efficiency of 250 mg/l FA using 22.7 kHz horn to be equal 14% and 6% in direct sonication using 20 kHz ultrasonic bath [35]. Study on 1.5 h irradiation (590 kHz) of 1000 mg/l FA solution showed the maximum removal efficiency of FA equal to about 3% without stirring under direct sonication. In the case of stirring at 200 rpm applied the removal was increased more than twice up to 6% [36]. The low degradation efficiencies obtained

in this work is probably attributed to the low powers used, indirect sonication and absence of stirring in the reactor, which causes a non-sufficient compound distribution in the reactor. In a case of indirect sonication only around 37% of energy is transmitted across water/pyrex glass interface (based on acoustic impedance data) and about 63% is lost due to reflection. The first-order kinetic rate constants for sonication processes at 863, 992 and 1176 kHz were lower than those obtained at 381 kHz and were in the range from 0.00004 to 0.0001 min⁻¹ (Table 1). The mechanism of sonochemical degradation of FA is complicated with formation of different intermediates such as CO₂, H₂O, H₂C₂O₄, CO [37]. However, the main degradation occurs through FA decarboxylation shown in reaction 5 – 7 [37].

Fig. 2. Effect of ultrasonic frequencies (a) and current applied (b) on FA removal efficiency in sonochemical and electrochemical degradation experiments respectively. Inset Fig.2b: variation of the kinetic behavior with the applied current

Figure 2b shows FA removal at electrolysis process and its kinetic behavior (Inset Fig. 2b) from the electrolysis time with currents applied. As can be seen, the slowest kinetics for FA removal was at an applied current of 10 mA and showed a maximum removal efficiency of 64% after 2h of electrolysis. An increase of current from 10 to 20 mA, more than doubled the rate of FA degradation with rate constants increased from 0.0079 to 0.0185 min⁻¹ (Table 1) and degradation efficiency reached 92% after 2 h of electrolysis. A further rise of the current to 30 mA provided only small improvement in FA degradation rate (rate constant 0.0207 min⁻¹) and efficiency (92.8%). This can be explained by mass transfer limitations in the process and higher electrode polarization at higher currents [38]. The kinetic rate constant for electrolysis alone at an applied current of 20 mA was 92 times higher than sonication at 381 kHz (Fig. 3b). Taking into account relatively high mineralization efficiencies (which will be described below) and molecular structure of FA it can be assumed that degradation of the compound in electrolysis is following the mechanism of direct oxidation shown in reaction 4 and similar to that introduced on elsewhere for boron-doped diamond electrode [39]:

In contrast to sonication the use of electrolysis alone achieved a 90% reduction in FA in the same time period (Fig. 3a). For this reason it was considered that 20 mA was the best current to employ because 30 mA provided only a slight improvement in rate constant and a negligible increase in removal efficiency. To prove the suggestion sonoelectrochemical experiments were conducted at 381 kHz (0.02 W) at applied currents of 10, 20 and 30 mA.

3.2 Sonoelectrochemical degradation experiments.

3.2.1 Effect of applied current on sonoelectrochemical degradations of FA

Sonoelectrochemical experiments were performed on the degradation of FA applying currents of 10, 20 and 30 mA and irradiating solution with 381 kHz (0.02 W/cm^3). The degradation efficiencies in these processes and kinetic behaviour are shown in Fig. 3. The combined use of sonication (381 kHz, 0.02 W/cm^3) and electrolysis (20 mA) increased the kinetic rate constant over electrolysis alone by a factor of 2 from 0.0185 min^{-1} to 0.0374 min^{-1} and almost 200 fold comparing with sonication alone (Table 2). In addition to the improvement in rate constants, the time required for achieving the same degradation efficiency of 90% was reduced from 2 h in electrolysis to 1.1h in combined electrolysis (20 mA) and sonication. When combining 10 and 30 mA electrolyses with sonication at the same conditions, the increase of kinetic rate constants in sonoelectrochemical experiment comparing to electrochemical was insignificant, from 0.0079 to 0.0097 min^{-1} for 10 mA applied current and from 0.0207 to 0.0273 min^{-1} for 30 mA applied current. The maximum removal efficiencies of FA after 2h of sonoelectrooxidation slightly improved comparing to the single electrolysis process from 64 to 78%, 92 to 99% and 93 to 97% for 10, 20 and 30 mA applied current respectively. The lower degradation rates of FA at electrolysis (30 mA applied current) combined with sonication (381 kHz, 0.02 W/cm^3) comparing to the same sonoelectrochemical process at 20 mA applied current can be explained by higher corrosion of the electrodes. It can be speculated that higher currents combined with ultrasonic irradiation, enhances the corrosion rates of electrodes thus reducing their efficiency. Increased currents enhance the gas evolution such as oxygen and toxic chlorine gas (generated from the presence of Cl^- ions in the electrolyte solution), which can initiate the corrosion of electrodes. The known cleaning effect of ultrasound due to the formation of liquid microjets and shock waves during the cavitation bubbles collapse can assist the initiated corrosion of electrodes at higher currents. Moreover, it was reported that ultrasound can both promote and suppress the corrosion of metals and metal alloys [40] [41] [42]. In this regards, the careful optimization of working parameters should be done for both electrochemical, sonochemical and sonoelectrochemical processes.

Taking into account higher performance of 20 mA applied current in both electrochemical and sonochemical experiments, the further studies on the effect of ultrasonic frequencies on FA removal in sonoelectrochemical experiments were conducted at a constant applied current of 20 mA.

Fig. 3. Effect of applied current on sonoelectrochemical FA degradation (a) and kinetic of the degradation (b).

Table 2. Variation of degradation rates constants and energy consumption with the ultrasonic power and applied current at different processes

The type of degradation experiment	Working parameters		The first-order kinetic rate constant, k , min^{-1}	Energy consumption required for 90% pollutant degradation, EC, kWh/m^3	Time required for 90% pollutant degradation, h
	Ultrasonic frequency, kHz (actual power W/cm^3)	Applied current, I, mA			
Combined electrolysis and sonication	381 (0.007)	20	0.0304	1785	1.2
	381 (0.02)	20	0.0374	2434	1.1
	381 (0.02)	10	0.0097	-	-
	381 (0.02)	30	0.0273	3115	1.4
	863 (0.0067)	20	0.0234	4399	1.7
	992 (0.003)	20	0.0184	3675	2
	1176 (0.003)	20	0.0201	4346	1.9

3.2.2 Effect of ultrasonic frequency on the electrochemical decomposition of FA.

The effect of ultrasound on the sonoelectrochemical degradation of FA, were studied at different frequencies. The actual ultrasonic powers entering the system were measured by calorimetry using the same experimental set-up as in the sonoelectrochemical degradation experiments (see values in Table 1 or 2). The highest powers of 0.02 and 0.007 W/cm^3 were generated by the 381 kHz multi-frequency system, 0.0067 W/cm^3 at 863 kHz and the lowest (0.003 W/cm^3) were obtained at both 992 kHz and 1176 kHz.

Fig. 4. Effect of different ultrasonic frequencies and powers on FA degradation in sonoelectrochemical experiments.

An analysis of Figure 4 shows that the degradation efficiencies achieved after 2 h of sonoelectrochemical experiments at frequencies of 381 (0.007 W/cm³), 863 (0.0067 W/cm³) and 1176 kHz (0.003 W/cm³) were all approximately the same (96 – 97%). Sonication at higher actual power of 0.02 W/cm³ of 381 kHz frequency showed a slightly higher degradation of 99%. However at a frequency of 992 kHz (0.003 W/cm³) a slightly lower degradation of 91% was obtained. This is in accord with the use of these conditions for sonication alone which gave the lowest FA degradation of 0.8% after 2 hours compared to other sonication frequencies (Fig. 2a). When ultrasound was applied in conjunction with electrolysis it improved the degradation rate (Table 2). The highest rate corresponded to the highest power of 0.02 W/cm³ obtained at 381 kHz followed by the same frequency but lower actual power of 0.007 W/cm³. Comparing the same actual powers of 0.003 W/cm³ the higher kinetic rate constant of 0.0201 min⁻¹ was obtained for 1176 kHz versus 0.0184 min⁻¹ obtained at 992 kHz sonication.

3.2.3 Mineralization efficiency and energy consumption

Another method of assessing FA degradation is through NPOC (non-purgeable organic carbon) reduction. Results after 2h for both electrochemical (10, 20 and 30 mA) and sonoelectrochemical (10, 20 and 30 mA and 20 mA along with 381, 863, 992 and 1176 kHz) are shown in Figure 5. Using this method the highest mineralization efficiency of electrochemical degradation was 78% for applied current of 30 mA and the lowest value of 59% was obtained for 10 mA applied current. The best results were obtained in sonoelectrochemical processes (20

mA) at the highest frequency of 1176 kHz (97%) with both 381 kHz (0.02 W/cm³) and 863 kHz having similar mineralization efficiency of 94.7%. The FA degradation at 30 mA current and 381 kHz (0.02 W/cm³) sonication provided 92.2% compound complete oxidation. The slightly lower mineralization obtained at 30 mA and 381 kHz (0.02 W/cm³) than at the same frequency but 20 mA current was explained by higher corrosion rates at these conditions. Overall the NPOC reduction data in sonoelectrochemical degradation experiments with 20 mA constant current can be placed in series with increasing mineralization at 381 kHz (0.007 W/cm³) < 992 kHz < 381 kHz (0.02 W/cm³) < 863 kHz < 1176 kHz.

Figure 5. NPOC reduction after 2h of electrolysis and combined electrolysis and sonication.

The effect of ultrasonic frequency on energy efficiency was estimated using EC data of actual energy transferred in the system (Table 1 and 2) during degradation experiments, which are required for 90% of FA degradation. The most energy-efficient processes (675 and 700 kWh/m³ EC) yielding 90% FA degradation were achieved using electrolysis at 20 and 30 mA applied current (Table 1). Among sonoelectrochemical degradation

experiments the most energy-efficient process (1785 kWh/m^3) was with 20 mA applied current and 381 kHz at 0.007 W/cm^3 sonication followed by sonoelectrolysis at the same frequency of 381 kHz at 0.02 W/cm^3 with 20 mA current (2434 kWh/m^3). The most energy consuming processes with nearly the same EC of 4399 and 4346 kWh/m^3 were sonoelectrolysis at 20 mA current combined with 863 and 1176 kHz respectively. Even though the EC required for 90% FA degradation under sonoelectrochemical treatment at 20 mA and 381 kHz (0.007 W/cm^3) was 2.6 times higher than electrolysis alone at 20 mA applied current, the time required for achieving the same degradation efficiency was reduced about twice in sonoelectrochemical experiments. It was in the range between 1.1 and 1.4 h for 381 kHz at 20 and 30 mA.

3.3 Comparison of different AOPs for formic acid degradation

Table 3 summarizes published degradation efficiencies and kinetic rate constants obtained using different AOPs for the decomposition of FA together with our results involving the sonoelectrochemical procedure. From this data the best method for FA decomposition was photocatalytic degradation using Fe/TiO_2 catalyst. The method had the highest kinetic rate constant of 955 min^{-1} and provided 99% FA decomposition efficiency however the initial concentration of FA used in this method was very low 2.3 mg/l . The second and third highest kinetic constants of 0.0374 and 0.0185 min^{-1} were obtained in this study using sonoelectrochemical and electrochemical degradation methods respectively with a degradation efficiency of over 99% in the former. Wet air oxidation along with the use of catalyst showed high degradation efficiency of FA, however the time required for 99% pollutant decomposition was significantly longer at 8.3 h.

The main advantage of the sonoelectrochemical method over photocatalytic degradation is the elimination of a catalyst separation step from the treatment process. Even though additional chemicals were used in the model study, real industrial wastewaters usually do not require any addition of electrolytes because they normally have sufficient electric conductivity which can exceed 10 mS/cm [43].

Table 3. Comparison of studied methods with different AOPs methods in literature for FA degradation.

No.	Method	C_0 , mg/l	V, ml	k, min^{-1}	t_D , h	D, %	Chemicals	Reference
1	Sonochemical							
	20 kHz	500	7000	$2.94 \cdot 10^{-4}$	1.5	2.4	—	[35]
	30 kHz	500	7000	$3.45 \cdot 10^{-4}$	1.5	2.8	—	
	50 kHz	500	7000	$3.55 \cdot 10^{-4}$	1.5	3.6	—	
	22.7 kHz	250	50	—	2	14	—	
2	Sonochemical							
	590 kHz (200 rpm)	500	300	—	0.75	12	—	[36]
	590 kHz (200 rpm)	1000	300	—	0.75	6		
	590 (no stirring)	1000	300	—	0.75	2		
2	Sonochemical							
	40 kHz	300	200	n.a.	1	10	—	[44]
3	Photocatalytic	103	300	$6.29 \cdot 10^{-4}$	1	99.5	Catalyst (TiO_2)	[45]

4	Photocatalytic	2.3	100	955	0.75	99	Catalyst (Fe/TiO ₂)	[46]
5	Photo-Fenton	101	3000	n.a.	1	81	H ₂ O ₂ Fe ₂ (SO ₄) ₃	[47]
6	Wet air oxidation	4603	40	n.a.	8.3	99	Catalyst (PtSO106)	[48]
7	US + UV + H ₂ O ₂ (20 + 30 + 50 kHz)	100	7000	n.a.	1.5	55	Catalyst (TiO ₂)	[49]
8	Sonochemical (381 kHz)	250	40	2·10 ⁻⁴	2	2	NaCl	This work
9	Electrochemical	250	40	0.0185	2	92.7	NaCl	This work
10	Sonoelectrochemical	250	40	0.0374	2	99	NaCl	This work

C₀ – initial concentration of FA; V – reaction volume; k – rate constant; t_D – degradation time; n.a. – data not available; D – degradation efficiency.

Conclusions

This study is the first reported work conducted on the sonoelectrochemical decomposition of FA in water. In addition the Ti/Ta₂O₅-SnO₂ electrodes have never been used in electrochemical and electrochemically assisted FA degradation. The study revealed a synergetic effect of combined sonochemical and electrochemical decomposition of FA on mineralization efficiency. An applied current of 20 mA was found to be the most energy-efficient for the electrolysis process. The ultrasonic powers of 0.02, 0.007 W/cm³ at 381 kHz frequency provide higher kinetic rate constants for FA degradation, following a first order kinetic model. Applying ultrasonic frequencies of 381, 863 and 1176 kHz to the electrolysis increase the mineralization efficiency over 94%. The sonoelectrochemical degradation of FA described here was found to be one of the most effective among different AOPs in that it provides high kinetic rate constants and degradation efficiencies over 99%.

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