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Advanced electrochemical degradation of nonsteroidal anti-inflammatory drugs - emergent pollutants from water, using dimensionally stable anodes

PhD Thesis – Abstract
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Chapter 1. Electrochemical methods applied to removal/degradation of organic pollutants from wastewaters. Mechanism of organics oxidation at DSA

The first part of this chapter shows the application of electrochemical methods to removal/degradation of organic pollutants from wastewaters.

Electrochemical processes for treatment wastewaters containing organic pollutants, such as electrocoagulation, electro-Fenton or electrochemical oxidation are taken into consideration. The operating conditions and control parameters of the process, as well as the type of wastewater and the obtained results are presented for each process [1-8].

The *electrochemical oxidation* of organic pollutants is presented more detailed, discussing the mechanism depending on the type of electrode material that governs the electrooxidation process and underlies the classification of this process [9-11]. It is highlighted the *indirect oxidation* with *surface mediators* that occurs at anodes activated with an oxides layer, world-wide known as dimensionally stable anodes (DSA) and their application to treatment of wastewaters from tannery, almond industry, an olive mill, petroleum exploration wastewaters or the removal/degradation of organic pollutants from high salinity wastewater [12-16].

Both for electro-Fenton process and electrochemical oxidation, a greater importance was given to the identification of degradation products: aromatic intermediates, short-chain carboxylic acids and inorganic ions.

The second part of this chapter shows the *mechanism of electrooxidation of organics* at DSA based on a generalized scheme for the electrochemical conversion/ combustion of organics at DSA, which has been proposed by Comninellis [17].

As part of this development, the conversion/combustion occurs with simultaneous oxygen evolution. The first step is represented by H_2O discharge at the anode to produce adsorbed hydroxyl radicals. The next steps occur depending on the nature of electrode material. The selective oxidation takes place at the "active" anodes (anodes that participate to oxidation) via the higher oxide (e.g. IrO_2 anode). At the "non-active" anodes (anodes that do not participate at the oxidation) the complete oxidation of organic substances to CO_2 occurs due to the formation of hydroxyl radicals (for example anodes of SnO_2, PbO_2).

An explanation for this type of catalytic phenomena is given by Trasatti [18], who has suggested that the reactions occurring at DSA are the result of the mechanism of chemical interaction between oxygen and active positions on the surface of the electrode.

Chapter 2. Non-steroidal anti-inflammatory drugs

This chapter deals with information about pollutants studied in the present doctoral research and the application of electrochemical processes to the removal/degradation of non-steroidal anti-inflammatory drugs (NSAIDs) from water.

Pharmaceutical active compounds are organic compounds with complex structures, and most of them are biorefractory and as a result they are not completely removed at municipal wastewater treatment plants. Thus, the effluents of the wastewaters treatment plants are one of the main sources by which the pharmaceuticals reach the aquatic environment.

The presence of pharmaceuticals in the aquatic environment even in very low concentration, in the order of ng-µg/L, is undesirable because their continuous penetration into this medium constitutes a long-term potential risk to aquatic organisms.

An important group of pharmaceutically active compounds is the anti-inflammatory drugs (NSAID) prescribed for pain relief. Among the NSAIDs are diclofenac, naproxen and piroxicam.

For these compounds, aspects related to their ecotoxicology or ecotoxicity were presented [19-21]. Thus, DCF induces oxidative stress on common carp (*Cyprinus carpio*), with the highest incidence of oxidative damage in the liver and gills. Based on the chronic EC_{50} results obtained for *Hydra attenuata* and interpreting the toxicity data using the EU Directive 93/67/EEC, NPX was classified as toxic. Inhibition of growth by PXC compared to control cultures in the 10th day of experiments was 13, 25 and 73.5%, respectively, on cyanobacteria *Synechococcus elongatus*, *Microcystis aeruginosa* and *Cylindrospermopsis raciborskii*, respectively and 44, 63 and 58%, respectively, on eukaryotic algae *Desmodesmus communis, Haematococcus pluvialis* and *Cryptomonas ovata*, respectively.

Also, the processes applied for the removal/degradation of these pollutants from the effluents containing them have been reviewed: adsorption, advanced oxidation processes, advanced electrochemical oxidation processes, biological treatment, combined processes based on hydrodynamic cavitation-heterogenous photocatalysis, sequential biological degradation-photocatalytic solar oxidation, ultrafiltration/reverse osmosis followed by electrochemical oxidation of the concentrate from reverse osmosis, electrooxidation combined with photocatalysis, ultrafiltration combined with pre-treatment with activated carbon and biological treatment coupled with hydrodynamic cavitation/H_2O_2 and UV treatment.

Chapter 3. Motivation, purpose and main objectives of the thesis

The research topic approaches the removal/degradation of biorefractory organic pollutants from wastewaters by electrodegradation at DSA, which are electrode materials containing a layer of conductive metallic oxides with electrocatalytic properties deposited on titanium support. The introduction of the catalytic reaction into electrochemical technology not only results in a notable increase in efficiency, but also increases the availability for the removal/degradation of biorefractory organic pollutants.

Therefore, electrodegradation can induce the biodegradability of biorefractory organic pollutants or provide their removal by mineralization and can therefore be integrated as a treatment step before or after the biological step as an advanced treatment step in conventional sewage treatment schemes.

The NSAIDs studied in this research are:

- diclofenac, Sodium {2-[(2,6-dichlorophenyl)amino]phenyl}acetate (DCF)
- naproxen, (2S)-2-(6-Methoxy-2-naphthyl)propanoic acid (NPX)
- piroxicam, 4-Hydroxy-2-methyl-N-(2-pyridinyl)-2H-1,2-benzothiazine-3-carboxamide 1,1-dioxide

The main purpose of the research is the application of electrochemical methods in environmental protection. The proposed objectives are: (i) applying electrooxidation at DSA for the treatment of effluents containing biorefractory organic pollutants and (ii) obtaining data for the development of experimental models that provide environmental friendly effluents.

Chapter 4. Materials and methods

This chapter highlights the materials and methods used for the execution of the experimental part:

- the preparation of electrode materials, DSA having noble metals (Ru) or non-noble metals (Sn, Sb) in the electrocatalytic film by thermal decomposition of the corresponding salts to the oxides within the electrocatalytic layer:
  - ✓ Ti/RuO_2-TiO_2 molar ratio Ru:Ti in precursors solution 30:70
  - ✓ $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ molar ratio Sn:Sb:Ru in precursors solution 94:3:3

- Characterization of electrode materials by:
  - ✓ *scanning electron microscopy (SEM)*
  - ✓ *X-ray diffraction (XRD)*
  - ✓ *cyclic voltammetry (CV)*

- electrodegradation experiments:
  - ✓ *electrodegradation at DSA*
  - ✓ *electrodegradation at boron doped diamond (BDD)*
  - ✓ *DCF electrodegradation at DSA assessment by CV*
  - ✓ *pharmaceutical effluents biodegradability improvement*
  - ✓ *application of electrodegradation at DSA to real wastewaters containing NSAIDs treatment*

- Working techniques:
  - ✓ *molecular spectrophotometry UV/Vis*
  - ✓ *gas chromatography coupled with mass spectrometry (GC-MS)*
  - ✓ *high-performance liquid chromatography (HPLC) with UV detection*

- the determination of indicators to assess the removal/degradation of NSAIDs and the biodegradability improvement:
  - ✓ *total organic carbon (TOC)*
  - ✓ *biochemical oxygen demand (BOD_5)*
  - ✓ *chemical oxygen demand (COD)*

Chapter 5. Advanced electrochemical degradation of non-steroidal anti-inflammatory drugs on dimensionally stable anodes

This chapter shows the results of the experiments carried out within the research regarding the removal/degradation of NSAIDs by electrodegradation at DSA.

- ***Characterization of electrode materials for the removal/degradation of organic biorefractory pollutants from wastewater by electrochemical oxidation***

This section describes the characterization of electrode materials by electronic scanning microscopy (SEM), X-ray diffraction (XRD) and cyclic voltammetry (CV).

The SEM images of DSA with noble metal oxides and non-noble metal oxides film showed a relatively compact surface morphology. XRD spectra confirmed that TiO_2 and RuO_2 oxides are present in the electrocatalytic film containing noble metals. Also, in the electrocatalytic film containing non-noble metals, SnO_2 was identified, while the presence of oxides of Sb_2O_5, RuO_2 and TiO_2 could not be identified with certainty either of the reduced phase content or the overlapping of the spectral lines.

The cyclic voltammograms allowed the electrochemical characterization of the anode materials as regards the potential window and the capacitive component. Both anode compositions are characterized by a narrow anode potential window, i.e., oxygen evolution occurs at low values of overpotential, behaviour characteristic of active metal oxides. This feature is exhibited by $Ti/RuO_2/SnO_2\text{-}Sb_2O_5\text{-}RuO_2$, even if this anode composition involves non-active metal oxides that reveal an important exhibition of RuO_2.

Studies on electrodegradation of non-steroidal anti-inflammatory drugs The electrodegradation experiments presented in this section were focused on the electrodegradation of DCF, NPX and PXC at DSA. Spectrophotometric characterization and evaluation of the removal/degradation process with the elucidation of some aspects of the mechanism of electrodegradation of pollutants at DSA were carried out using UV/Vis molecular spectrophotometry.

Electrodegradation intermediates were identified by using the GC-SM technique, and the residual concentration of the pollutants was performed by HPLC with UV detection. Mineralization of pollutants was quantified by determining the TOC indicator.

The biodegradability of effluents treated by electrodegradation on DSA was evaluated by determining the ratio R (R = CBO5/CCO) and implicitly determining the BOD_5 and COD indicators. CV was used to assess DCF electrodegradation on DSA. Also, a comparison was made between DCF electrodegradation on DSA and BDD.

✓ ***DCF electrodegradation***

The degradation of DCF at $Ti/RuO_2\text{-}TiO_2$ and $Ti/RuO_2/SnO_2\text{-}Sb_2O5\text{-}RuO_2$ was studied for concentrations of 50, 100 and 200 mg/L DCF in 0.1 M Na_2SO_4 support electrolyte, current density of 100, 200 and 300 A/m^2, electrolysis time of 30, 60 and 120 min and pH of 5.8.

The formation of DCF degradation products as well as their subsequent degradation, was revealed in the UV spectra of solutions resulting from degradation at $Ti/RuO_2\text{-}TiO_2$ and $Ti/RuO_2/SnO_2\text{-}Sb_2O_5\text{-}RuO_2$ by the shift of the A_{277} maximum and in some cases the increase of its value compared to the initial value followed by its decrease with the increase of the current density and electrolysis time. Analysis of UV spectra and TOC values of electrolyzed solutions proved the effectiveness of DSA in the advanced degradation of DCF.

Along with the degradation of DCF, a mineralization process occurred. At $Ti/RuO_2/ SnO_2\text{-}Sb_2O_5\text{-}RuO_2$ DCF mineralization occurred in a smaller extent contrary to $Ti/RuO_2\text{-}TiO_2$, where the results for TOC removal are close regardless of the initial concentration of DCF. For $Ti/RuO_2/SnO_2\text{-}Sb_2O_5\text{-}RuO_2$, the formation of degradation products to the detriment of mineralization prevailed, as indicated the GC-SM analysis [22].

Comparing TOC removal at DSA and boron doped diamond (BDD), it is easy to see that from the point of view of mineralization BDD had better performance. Thus, at 200 mg/L DCF and 75 A/m^2 at BDD, a TOC removal of 89.20% [23] was obtained compared to 44.17% at $Ti/RuO_2\text{-}TiO_2$ and 39.73% at $Ti/RuO_2/SnO_2\text{-}Sb_2O5\text{-}RuO_2$. The major drawback of the BDD is that during the experiments this anode suffered from the DDB layer detachment from the electrode support, although the applied current densities were not high (at most 75 A/m^2). In this respect, the resistance in the working environment, the DSA proved a good behaviour.

There was no detachment of the electrocatalytic film from the support. In addition, although DSA were not as effective in mineralization, they induced the biodegradability of DCF-containing effluents and were cheaper. These findings recommend the DSA as potential candidates for the removal/degradation of DCF.

The degradation of DCF by electrooxidation at Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 was assessed by using the CV technique and the BDD electrode, for which a DCF detection methodology was developed [24], but this is not a part of this thesis. The anodic current peaks recorded at +0.7 V and +1 V vs. SCE respectively are directly proportional to the concentration of DCF and intermediates. However, for + 1V vs. SCE was not possible the intermediates identification. However, for + 1V vs. SCE, it was not possible to identify intermediates. The total disappearance of the peak current in cyclic voltammograms at the higher potential value (+ 1V/SCE) could be assigned to an advanced degradation process, but not to the DCF mineralization [25].

Based on peak current abatement efficiency at 0.7 V/SCE and +1 V/SCE, it was found that DCF degradation at the concentration of 100 and 200 mg/L was more efficient at $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 for any applied current density of 100, 200 and 300 A/m^2 and 120 min of electrolysis. These results, corroborated with those obtained for TOC removal indicating that Ti/RuO_2-TiO_2 was more efficient for DCF mineralization, A_{277} evolution and GC-MS analysis results, showed that at $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 the formation of degradation products prevailed in the detriment of their mineralization.

✓ *NPX electrodegradation*

The NPX electrodegradation in aqueous solutions at the concentration of 10, 50, 100 and 200 mg/L at Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 was studied. The supporting electrolyte was 0.1 M Na_2SO_4 was used, the electrolysis time was 60, 120 and 180 minutes, and the applied current density was 100, 200 and 300 A/m^2.

The evaluation of NPX electrodegradation on the two anode compositions as well as the elucidation of some aspects of its mechanism was carried out by corroborating the results of UV/Vis spectra analysis with those of COT and GC-SM analysis.

The evolution of absorbances showed the dynamics of the process and the yielding in the first stage of intermediates having molar absorption coefficients higher than NPX. An intermediate containing the methoxy group, 2-Methoxy-6-vinylnaphthalene was identified by GC-SM according to previously reported results in the literature.

Analysis of the UV/Vis spectra versus electrolysis time, current density and concentration showed significant changes in the evolution of the absorptions attributed to the methoxy, carboxyl and aromatic ring of naphthalene. For both anode compositions under the same working conditions, the electrodegradation of the methoxy and carboxylic groups occurred to a greater extent at a lower concentration of NPX, while at higher concentrations the naphthalene ring was degraded more strongly. Consequently, the concentration gradient proved to be a key factor that determined the opening of the naphthalene ring.

✓ *PXC electrodegradation*

Electrochemical degradation of PXC was performed on Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2. The Ti/RuO_2-TiO_2 anode composition proved to be more effective in PXC mineralization than $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2, for any PXC concentration and applied current density. Thus, the best value for COT removal was 42.07% for 50 mg/L PXC, 300 A/m^2 and 180 min of electrolysis [26]. Analysis of UV spectra suggested that the structure of the benzene ring was poorly affected, while the pyridine ring and the substituents attached to the aromatic ring were degraded to a greater extent.

- ✓ ***Kinetic studies and aspects of the mechanism of the mineralization process. Energy consumption. Limiting current density. Mass transfer coefficient. Specific energy consumption***

The mass transfer coefficient (k_d) and limiting current density (j_{lim}) for ADS were calculated and one can notice that as the applied current density increased, k_d increase regardless of the pollutant concentration for both anode compositions.

This finding showed that the mineralization of the pollutants was favoured by a higher applied current density. At the same current density applied for both anode k_d increased as the concentration of the pollutant increased, suggesting that mineralization occurred more rapidly at higher concentrations, in agreement with the results of UV spectra analysis.

The j_{lim} values were lower than those for current densities applied practically for both anode compositions, which proved that the process was controlled by diffusion, a finding that was consistent with UV spectra analysis.

No major differences were found for the specific energy consumptions between the two anode compositions, but the values were slightly higher at $Ti/RuO_2/SnO_2\text{-}Sb_2O_5\text{-}RuO_2$. It could be concluded that economically, $Ti/RuO_2\text{-}TiO_2$ was better for degradation of the studied pollutants.

- ✓ ***Applications of electrodegradation on ADS for real waters***

Experiments carried out to improve the biodegradability of an effluent containing DCF characterized by low biodegradability were performed by using the following DSA-based methods: electrochemical, photo-electrochemical and a combination of photocatalytic and electrochemical techniques. All applied methods were effective and led to an increase of the R ratio from 0.05 to 0.30 - 0.62, which provided effluents that could be effectively biodegradated in municipal wastewater treatment plants [27].

The removal efficiency of DCF from an effluent of a wastewater treatment plant at a current density of 300 A/m^2 and 120 minute of electrolysis time at $Ti/RuO_2/SnO_2\text{-}Sb_2O_5\text{-}RuO_2$ was lower than that obtained in the same conditions on synthetic solutions, reflecting the influence of the matrix to which DCF belongs [28].

Degradation experiments of a mixture of organic pollutants belonging to NSAIDs: DCF, IBP and NPX dosed in a municipal wastewater treatment plant effluent (tens of μg/L) were carried out by electrodegradation $Ti/RuO_2\text{-}TiO_2$ and $Ti/RuO_2/SnO_2\text{-}Sb_2O_5\text{-}RuO_2$. Removal efficiencies greater than 99% were obtained for any of the pollutants for either of the two anode compositions used.

Chapter 6. Conclusions

The research theme deals with the removal/degradation of biorefractory organic pollutants of the type of pharmaceutical active compounds belonging to the non-steroidal anti-inflammatory drugs from wastewater by electrodegradation at dimensionally stables anodes (ADS), that contain a layer of conductive metal oxides having electrocatalytic properties deposited on titanium support.

The anode compositions studied in this thesis were:

✓ $Ti/RuO_2\text{-}TiO_2$	molar ratio Ru:Ti in precursors solution 30:70
✓ $Ti/RuO_2/SnO_2\text{-}Sb_2O_5\text{-}RuO_2$	molar ratio Sn:Sb:Ru in precursors solution 94:3:3

DSA were prepared by thermal decomposition of the corresponding salts to the oxides within the electrocatalytic layer. Characterization of electrocatalytic films from a morphological and structural point of view was accomplished by scanning electron microscopy (SEM), X-ray diffraction (XRD) and electrochemical properties by cyclic voltammetry (CV).

The organic pollutants taken into consideration were biorefractory organic compounds, namely pharmaceuticals active compounds of the non-steroidal anti-inflammatory drugs: diclofenac (DCF), naproxen (NPX) and piroxicam (PXC). The removal/degradation of these pollutants was carried out both from synthetic and real water solutions, either individually or in combination, and optimal operating parameters were established to operate pollutants electrodegradation at DSA.

Characterization of the resulting effluents was carried out by ultraviolet-visible (UV/Vis) spectrophotometry, total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5). Qualitative determination of degradation products was carried out by gas chromatography coupled with mass spectrometry (GC-MS) and determination of residual concentrations of anti-inflammatory agents by high-performance liquid chromatography (HPLC) with UV detection.

The SEM images of DSA with noble metal oxides and non-noble metal oxides film showed a relatively compact surface morphology. XRD spectra confirmed that TiO_2 and RuO_2 oxides are present in the electrocatalytic film containing noble metals. Also, in the electrocatalytic film containing non-noble metals, SnO_2 was identified, while the presence of oxides of Sb_2O_5, RuO_2 and TiO_2 could not be identified with certainty either of the reduced phase content or the overlapping of the spectral lines.

CV allowed the electrochemical characterization of DSA in the presence of pollutants, establishing the potential window for each anode composition and consequently the value of oxygen evolution potential. The results obtained by analysing cyclic voltammograms showed that the presence of pollutants did not significantly influence their shape, showing polarization/depolarization effects depending on the anode composition and the type of pollutant. These results showed that the oxidation of pollutants for degradation/mineralization could only occur in the potential/current range corresponding to oxygen evolution.

Electrodegradation of the pollutants was performed at the following current densities: 100, 200 and 300 A/m^2 and at electrolysis time of 30, 60, 120 and 180 min. Experiments were conducted with solutions of pollutants at concentrations of 10, 50, 100 and 200 mg/L. The working pH was as follows: 5.8 for DCF, 7.5 for NPX and 7 for PXC. For each pollutant a set of values for the working parameters was chosen: concentration, current density and electrolysis time.

The yielding of pollutants degradation products as well as their subsequent degradation was highlighted in the UV spectra of solutions resulting from degradation on Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2.

In the case of DCF electrodegradation, UV spectra analysis was performed by the study of the maximum absorbance at 277 nm (A_{277}) evolution depending on the anode composition, current density, electrolysis time and initial concentration of DCF. Analysis of UV spectra and TOC values revealed advanced degradation of DCF by yielding of degradation products, their subsequent degradation, aromatic rings opening and DCF mineralization.

As the GC-MS analysis showed, the cleavage of the chemical bond NH-aromatic ring substituted with CH_2-COO^- group occurred at both anode compositions. For $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2, the formation of degradation products predominated in detriment of their mineralization.

In terms of DCF mineralization, the best results were obtained for both anode compositions at 300 A/m^2 and 120 min of electrolysis, TOC removal being 44.17% for Ti/RuO_2-TiO_2 and 39.73 % For $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2. These results are consistent with the predictions resulting from the analysis of the electrochemical behaviour of the anode materials by CV in the presence of DCF.

A very important aspect of this study is the evaluation of the degradation process of DCF by electrooxidation at Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 by CV technique by using boron doped diamond electrode. The evaluation of cyclic voltammograms evolution recorded after the application of electrodegradation at DSA, coupled with UV spectra analysis, allowed characterization of the degradation process of DCF according to the operating parameters. These results, correlated with those obtained for TOC removal revealed Ti/RuO_2-TiO_2 more efficient in DCF mineralization, A_{277} evolution and GC-MS analysis, showed that at $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ predominated the yielding of degradation products in detriment of their mineralization.

The study of NPX electrodegradation at Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ was conducted so as to track the influence of the initial concentration of NPX. The UV spectra analysis was performed so that by examining the absorbance relative variation at wavelengths at which the NPX UV spectrum exhibits peak absorbances: 231 nm, 264, 272, 318 and 331 nm. The analysis of UV spectra evolution versus the electrolysis time, the current density for each initial concentration, it was observed that the absorbances assigned to methoxy, carboxyl and naphthalene groups of the NPX showed significant changes. For both anode compositions, electrodegradation of methoxy and carboxyl groups occurred to a greater extent at lower NPX concentration, while the naphthalene ring was degraded more strongly at higher concentrations of NPX. Therefore, the concentration gradient has been found to be the main force driver for the opening of the aromatic ring.

Along with NPX degradation, its mineralization occurred. NPX concentration was the main parameter that improved the mineralization degree. The best results were obtained at 200 mg/L NPX when removal of TOC at 300 A/m^2 and 180 min of electrolysis was 72.73% at Ti/RuO_2-TiO_2 and 69.48% at $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$.

Examination of UV spectra in the case of PXC electrodegradation at Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ indicated a complex degradation process that is explained by oxidation and breakage of the chemical bond between pyridine and condensed rings as well as their oxidation. The appearance of new maxima in the spectra confirms the oxidation of the pollutant and the formation of some degradation products.

Based on the relative absorbance variation at the wavelengths corresponding to the absorbance maxima at 206, 253, 288 and 357 nm, it can be assumed that the structure of the benzene ring is poorly affected, while the pyridine ring and the adjacent aromatic ring substituents are degraded to greater extent.

Ti/RuO_2-TiO_2 was more efficient in PXC mineralization than $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$, for any PXC concentration and applied current density, as shown by the TOC values.

The comparative results of mineralization processes of non-steroidal anti-inflammatory pollutants at DSA showed a similarity between DCF and NPX mineralization at DSA from the point of view of the influence of initial pollutant concentration. A higher degree of TOC removal was obtained with increasing the initial concentration of the pollutant, due to the concentration gradient at the surface of the anode.

However, the PXC behaviour was different, the increase of its initial concentration reduced the TOC removal, and therefore the mineralization efficiency. It was found that among all the pollutants studied, PXC was the most difficult to mineralize on the studied anode compositions. It was also found that Ti/RuO_2-TiO_2 showed a higher mineralization performance than $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ regardless of the pollutant concentration.

The results of the kinetic studies showed that for Ti/RuO_2-TiO_2 the rate of mineralization of the pollutants decreased in the DCF > NPX > PXC sequence for the concentration of 50 mg / L and NPX> DCF> PXC for the concentration of 200 mg/L. For $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$ the sequence was NPX > DCF and PXC for the concentration of 50 mg/L and NPX > DCF > PXC for the concentration of 200 mg/L. It was also found that the rate of mineralization was higher at Ti/RuO_2-TiO_2 than at $Ti/RuO_2/SnO_2-Sb_2O_5-RuO_2$. In addition, economically related to specific energy consumption, Ti/RuO_2-TiO_2 showed superiority for the degradation of studied pollutants.

In order to integrate this process in a treatment technological flow containing biological treatment, experiments were carried out to improve the biodegradability of a DCF-containing effluent characterized by low biodegradability by applying DSA-based methods: electrochemical, photo-electrochemical and a combination of photocatalytic and electrochemical techniques. All applied methods increased the biodegradability R ratio from 0.05 to values between 0.30 and 0.62, indicating a significant improvement in biodegradability following the application of all applied electrodegradation processes at DSA.

Degradation experiments of a mixture of organic pollutants belonging to non-steroidal anti-inflammatory drugs: diclofenac, ibuprofen and naproxen dosed in an effluent of a municipal wastewater treatment plant (tens of μg/L) were performed by electrodegradation at Ti/RuO_2-TiO_2 and $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2. Removal efficiencies greater than 99% were obtained for any of the pollutants for either of the two anode compositions used.

Following the research on the effectiveness of DSA for the degradation and mineralization of biorefractory organic pollutants from wastewaters, the utility of these anodes was demonstrated by an electrochemical process that could be integrated in a treatment technological flow either before the biological treatment step to improving biodegradability or after biological treatment in the finishing step that aims their mineralization.

Original contributions

The original contributions and the innovative character are as follows:

- extending the application of electrochemical oxidation at DSA for the degradation/ mineralization of biorefractory pollutants belonging to the non-steroidal anti-inflammatory drugs of emerging pollutants
- synthesis of a new anode composition of $Ti/RuO_2/SnO_2$-Sb_2O_5-RuO_2 by the presence of the RuO_2 intermediate layer along with its characterization
- use of a reliable and simple UV-spectrophotometry technique to provide quick and valuable information to elucidate aspects of the degradation mechanism of the emerging pollutants
- correlation of spectrophotometric, gas chromatography coupled with mass spectrometry, high-performance liquid chromatography and electrochemical techniques to assess the electrodegradation process of anti-inflammatory drugs at DSA and validation of the electrodegradation process by application to real wastewaters treatment containing nonsteroidal anti-inflammatory drugs
- assessing the versatility of the electrodegradation process at DSA over a large range of the concentration of non-biodegradable pollutants, from tens of μg/L to tens and hundreds of mg/L

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