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# Study of the influence of electrode material in the application of electrochemical advanced oxidation processes to removal of pharmaceutical pollutants from water

Flamur Sopaj

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Flamur Sopaj. Study of the influence of electrode material in the application of electrochemical advanced oxidation processes to removal of pharmaceutical pollutants from water. Agricultural sciences. Université Paris-Est, 2013. English. NNT : 2013PEST1183 . tel-00985537

**HAL Id: tel-00985537**

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Joint PhD degree in Environmental Science & Technology

UNIVERSITÉ —  
— PARIS-EST

Docteur de l'Université Paris-Est  
Spécialité : Science et Technique de l'Environnement



Doktor i Shkencave të Kimisë i Universitetit të Prishtinës

Thèse de doctorat d'université – PhD thesis

Flamur SOPAJ

**Study of the influence of electrode material in the application of  
electrochemical advanced oxidation processes to removal of pharmaceutical  
pollutants from water**

**Etude de l'influence du matériel d'électrode dans l'application des procédés  
électrochimiques d'oxydation avancée au traitement des polluants  
pharmaceutiques**

To be defended December 6<sup>th</sup>, 2013

In front of the PhD committee:

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## Remerciements

La présente thèse a été conduite au sein du laboratoire « Géomatériaux et Environnement » (LGE) de l'Ecole doctorale "Sciences, Ingénierie et Environnement" (SIE) de l'Université Paris-Est, sous la direction de Monsieur le Professeur Mehmet A. OTURAN qui a bien voulu m'accueillir dans son laboratoire, encadrer mes travaux, les accompagner de ses précieux conseils et me faire bénéficier de sa grande expérience scientifique. Je lui adresse mes plus vifs remerciements.

J'adresse ma reconnaissance infinie à Monsieur le Professeur Fetah PODVORICA, codirecteur de cette thèse, qui m'en a proposé le sujet, a permis sa réalisation par l'obtention d'une bourse du gouvernement français et m'a toujours fait profiter de ses compétences scientifiques.

Je ne saurais oublier Madame Nihal OTURAN, à qui je dois la concrétisation de mes recherches. Son aide m'a été inestimable au sein du laboratoire et je lui en suis très reconnaissant.

Je tiens à remercier Monsieur le Professeur Jean PINSON, Professeur émérite à de l'Université Paris 7, de l'honneur qu'il m'a témoigné en acceptant d'être rapporteur de cette thèse.

Je remercie les autres membres du jury, Messieurs les Professeurs, Ramë VATAJ et Avni BERISHA d'avoir bien accepté de juger ce travail.

Je voudrais une fois encore présenter de très sincères remerciements à Monsieur et Madame OTURAN pour leur chaleureuse hospitalité au début de mes études en France et leur soutien constant. Je n'oublierai jamais leur générosité et leur attention à mon égard.

À Madame Frédérique DUVERSIN va ma reconnaissance pour l'aide qu'elle m'a accordée à mon arrivée en France.

Je remercie tout particulièrement l'Ambassade de France au Kosovo pour la bourse d'études doctoral qui m'a été octroyée par le gouvernement français qui a permis la réalisation de mes travaux de thèse.

Durant ces trois années, mes collègues des laboratoires des universités de Paris-Est et de Prishtina ont contribué quotidiennement à l'excellent environnement scientifique et amical dans lequel se sont déroulées mes recherches. Qu'ils en soient vivement remerciés !

Enfin je souhaite témoigner à ma famille ma profonde gratitude pour son inconditionnel soutien et dédie cette thèse à mes parents Hajriz et Zelfie SOPAJ qui, tout au long de mes études et de ma vie, m'ont encouragé, entouré de leur affection et sans lesquels je n'aurais pu atteindre mes objectifs.

## ABSTRACT

Permanent production and use of organic chemicals for many purposes has resulted in their introduction and accumulation in the environment. Depending on their physicochemical properties they can be transported by different ways from the source to very remote regions of the planet. Many organic chemicals are used in agriculture as pesticides for cultures protection or nutrient. Residues of these chemicals can always be found in fields, and under the effect of precipitations they leach and pass in streams and rivers. Pharmaceuticals and personal health care products and other house holding chemicals are continuously introduced in the environment through municipal wastewaters. These substances exhibit, in most of the cases, perturbation effects towards the living organisms, moreover the effect of many of them is not known yet. Despite their concentration in water is low, the exposure of organisms for long periods can lead to negative consequences, but these effects cannot be measured instantly.

In order to reduce or avoid the pollution of water with chemicals many water treatment methods has been developed like adsorption of pollutants on adsorbents, membrane filtration, microbiological treatment, chemical oxidation with oxidizing agents and advanced oxidation processes.

Most of the methods used in waste water treatment plants (WWTP) do not completely destroy the organic contaminants or they only separate the contaminants from water. Then they have to be deposited somewhere else remaining always a potential source of contamination. Advanced oxidation processes and in particular electrochemical advanced oxidation processes are methods developed later and are proven as more effective as they can completely oxidize the organic matter in water.

The subject of this thesis is the use of electro-Fenton, an electrochemical advanced oxidation process for efficient destruction of organic pollutants in aqueous medium. In this method, organic pollutants are eliminated by hydroxyl radicals (high oxidation power species) which are produced in situ through the Fenton's reagent ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) itself generated in the solution electrochemically and continuously. In this process, the electrode material is of fundamental importance in order to have an efficient process, so we have studied at large extent the influence of both cathode and anode material in this work.

Firstly a systematic study on the oxidation capacity of the process of amoxicillin (AMX) as model pollutant with several anodes materials: BDD, Pt, DSA,  $\text{PbO}_2$  Carbon felt, Graphite and Carbon fibre was realised. In all cases a stainless steel electrode was used as cathode. The degradation of AMX was followed by HPLC analysis whereas the mineralization efficiency of the process was measured by total organic carbon analyser (TOC). This revealed that BDD was the most efficient anode for AMX oxidation and DSA was the weakest one. Carbon felt showed a characteristic behaviour; it was very efficient on AMX oxidation but it could not transform AMX to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

Afterwards four anodes were tested for their influence on electro-Fenton process efficiency namely Pt, BDD, DSA and Carbon felt, the cathode was always carbon felt. Sulfamethazine (SMT) was used as model pollutant. Apparent rate constants have given only moderate values

of mineralization for currents lower than 100 mA. Here again the BDD anode was distinguished for its excellent mineralization capacity owing to the additional hydroxyl radicals and other oxidizing species introduced in the system. When electro-Fenton applied good degradation and mineralization results were obtained even with the DSA anode. Carboxylic acids and inorganic ions released during electrolysis were also analysed. Complete removal of carboxylic acids could be reached with BDD anode, whereas they could still be measured at the end of treatment in the Pt/Carbon felt and particularly in DSA/Carbon felt cell. Inorganic ions were almost quantitatively released in the BDD/Carbon felt and Pt/Carbon felt systems but their concentrations in the solution were much lower for DSA/Carbon felt system.

Finally the cell composed of Carbon sponge cathode of five different porosities, and carbon felt, stainless steel and platinum anode was studied for their effect on the electro-Fenton process efficiency for oxidation of SMT. Kinetic analysis and TOC measurements demonstrated that carbon sponge of porosity 45 ppi (pore per linear inch) was the most efficient cathode compared to others to be used in electro-Fenton process. Then SMT oxidation experiments were brought about in the electrolytic cell constituted of the best anode estimated BDD and carbon sponge 45 ppi cathode, where the mineralization degree was remarkable.

As conclusion, the results obtained in this study showed clearly that the cathode material has a great effect on the efficiency of electro-Fenton process, and this process constitute an efficient method for treatment of organic pollutants in aqueous medium.

**Key words:** electro-Fenton, anode, cathode, oxidation, hydroxyl radicals, degradation, mineralization, amoxicillin, sulfamethazine, water treatment.

## RESUME

La production ainsi que l'utilisation massive des produits chimiques pour divers usages, a résulté à leur introduction et accumulation dans l'environnement. Ces produits peuvent se transporter par différentes façons de leur source à des régions très lointaines de la planète, ce qui dépend de leur propriété physico-chimiques. Une quantité et variété importante de composés organiques sont utilisées dans l'agriculture comme pesticides, afin de protéger les cultures et augmenter les rendements. Les résidus de ces produits peuvent toujours se trouver dans les champs, puis sous l'effet des précipitations ils passent par lixiviation dans les fleuves et d'autres system aqueux. Les produits pharmaceutiques et les produits de soins personnels sont introduits dans l'environnement de façon continue par les eaux usés municipales. Ces substances manifestent, dans la plus part des cas, des effets perturbants sur les organismes vivants. Malgré leur concentration faible dans les eaux naturelles, le contact permanent des organismes aquatiques peut avoir des conséquences négatives telles que la modification du comportement sexuel observé chez les poissons d'eaux douce.

Dans le but de réduire ou éliminer la pollution chimique des eaux des nombreuses méthodes ont vu le jour, telles que: l'adsorption des polluants sur des adsorbants, la filtration membranaire, le traitement microbiologique, l'oxydation chimique et les procédés d'oxydation avancée.

La plus part des méthodes utilisées dans les stations d'épuration des eaux ne détruisent pas efficacement les contaminants organiques. L'utilisation des méthodes physiques permet de les séparer de l'eau, ce qui nécessite des opérations supplémentaires pour leur élimination. Au contraire, les procédés d'oxydation avancée et en particulier les procédés électrochimiques d'oxydation avancée (méthodes développées récemment) se montrent plus efficace dans l'élimination des polluants toxiques et non-biodégradables, car ces procédés sont capables à conduire jusqu'à minéralisation totale de la matière organique.

Le sujet de cette thèse repose donc sur l'application du procédé électro-Fenton qui est un procédé électrochimique d'oxydation avancée pour la destruction des contaminants organiques dans l'eau. Cette méthode fait appel aux radicaux hydroxyles (espèces très oxydantes et extrêmement réactives) pour l'élimination des polluants récalcitrants, qui sont produit in situ à travers le réactif du Fenton ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ). Ce réactif est généré in situ électrochimiquement. . Dans ce procédé la nature du matériau de l'électrode a une importance cruciale. Ainsi nous avons étudié dans ce travail l'influence du matériel de l'anode et de la cathode sur l'efficacité du procédé électro-Fenton.

Dans un premier temps nous avons étudié de manière systématique le pouvoir d'oxydation d'anode comme de différents matériaux d'anodes tels que : BDD, Pt, DSA,  $\text{PbO}_2$ , Feutre de carbone, Graphite et Fibre de carbone dans l'oxydation de l'antibiotique amoxicilline (AMX). Dans tous les cas une électrode d'acier inox a été utilisée comme cathode. La dégradation de AMX a été suivie par l'analyse CLHP alors que la minéralisation de ses solutions par l'analyseur du carbone organique totale (COT). Il s'est avéré que l'anode BDD a été l'anode la plus puissante pour l'oxydation de l'AMX tandis que l'anode DSA a présenté les performances les plus faibles. D'autre part, le feutre de carbone a présenté un comportement

caractéristique; il était très efficace sur l'oxydation de l'AMX mais ces performances en minéralisation étaient médiocres.

Dans l'étape suivante, quatre anodes (Pt, BDD, DSA and Feutre de carbone) ont été testées pour élucider leur influence sur l'efficacité du procédé électro-Fenton, en utilisant toujours une cathode de feutre de carbone. L'antibiotique sulfaméthazine (SMT) a été choisi comme polluant modèle. Ici encore l'anode BDD a été distingué pour son excellent pouvoir de minéralisation due à sa capacité de générer une quantité de radicaux hydroxyles très importante et d'autres oxydants. Le taux minéralisation a été important aussi pour l'anode DSA. Nous avons aussi effectué l'analyse des acides carboxyliques et des ions inorganiques libérés durant l'électrolyse. Une destruction totale des acides carboxyliques a été atteinte avec l'anode BDD. Par contre, dans le cas des anodes Pt et DSA on a observé une concentration résiduelle de ces acides même en fin du traitement. Quant aux ions inorganiques, ils ont été quasiment quantitativement libérés dans les cellules BDD/Feutre de carbone et Pt/Feutre de carbone, ce qui n'était pas le cas de la cellule DSA/Feutre de carbone.

Enfin, nous avons étudié l'efficacité de l'oxydation du procédé électro-Fenton dans l'élimination de SMT en utilisant l'éponge de carbone de différentes porosités. L'analyse cinétique et les mesures de COT ont montré que la porosité de 45 ppi (pore per linear inch) donne de meilleurs résultats en termes de cinétique de dégradation et de l'efficacité de minéralisation.

En conclusion, les résultats obtenus dans ce travail ont clairement montré que la nature du matériel d'anode et de cathode a une grande influence sur le procédé électro-Fenton, et que ce procédé constitue une méthode très efficace pour le traitement des polluants organiques en milieux aqueux.

**Mots clés:** électro-Fenton, anode, cathode, oxydation, radicaux hydroxyles, dégradation, minéralisation, amoxicilline, sulfaméthazine, traitement des eaux.

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## RESUME ETENDU

La présence des produits chimiques dans l'environnement est très évidente et ne cesse pas à croître de jour au jour. A l'origine de cette pollution il y a l'activité anthropique. Les besoins humanitaires pour les produits alimentaires, de construction, immobilière, de transport et beaucoup d'autres, étant en croissance permanente ont engendré de nouvelles sources de pollution et l'intensification de ceux existant. Beaucoup de ces substances sont dangereuses. Une bonne partie de ces substances dangereuses sont directement introduites dans les milieux aquatiques. Parmi les sources de pollution chimique des eaux on peut citer la décharge directe d'effluents industriels et d'autres déchets chimiques dans des différents sites environnementales, l'utilisation des produits chimiques tels que pesticides dans l'agriculture, l'utilisation des médicaments dans la médecine humaine et vétérinaire etc. L'abondance des produits chimiques qui s'échappe de ces sources a mené à la contamination des eaux superficielles et sous terraines avec de nombreux polluants inorganiques et organiques.

Il y a plusieurs polluants organiques persistants (POP) de différentes classes des produits chimiques répandus dans l'environnement tels que les hydrocarbures aromatiques chlorés, les polychlorobiphényles (PCB), les dioxines, les furanes et les pesticides organochlorés (DDT, lindane, aldrine...) ou triazines etc. Des polluants organiques persistants fréquemment trouvés dans l'eau sont des phénols et des chlorophénols. Ces substances sont généralement peu solubles dans l'eau et par conséquent ils se dispersent dans la matière solide et notamment dans la matière organique du sol. Les POPs sont plus ou moins volatiles et proviennent dans l'atmosphère des sols, des eaux et de la végétation, et ensuite sont transportés par des courants, pouvant être ainsi amenés à des très longues distances avant précipitations sous forme de dépôt sec ou humide (pluie, neige). Ainsi les POPs ont été détectés même en Arctique et aux très hautes montagnes, aux différents pays où les températures basses ont favorisé la condensation des nuages. Les précipitations atmosphériques jouent ainsi un rôle très important dans le transfert des POPs plusieurs travaux ont montré leur présence dans la neige des hautes et des basses montagnes.

Les pesticides sont une classe des produits chimiques utilisés largement dans l'agriculture. Par conséquent elles se trouvent dans les champs des plantes cultivées où elles sont directement appliquées, ainsi que dans les rivières et les fleuves, les lacs, les sédiments et dans les eaux souterraines. Elles y arrivent par lixiviation sous l'effet des précipitations.

Une autre classe de polluants organiques omniprésente dans les eaux et les sols sont les produits pharmaceutiques dont la présence a été souvent signalée. Leurs sources sont les effluents de l'industrie pharmaceutique, et des hôpitaux, les déchets municipaux, et les fermes (médecine vétérinaire), etc.

Les composés organiques synthétiques produites pour différentes utilisations ainsi que leurs produits secondaires qui les accompagnent, les composés résiduels formés durant les processus de combustion, etc. ne sont pas des constituants naturels de l'environnement. Donc, ils sont suspectés de causer un impact négatif sur l'environnement. Ils peuvent entrer dans la chaîne alimentaire, en particulier les POPs, passant ainsi d'un niveau trophique à un autre. Il a été prouvé que les POPs sont impliqués dans la perturbation de l'endocrine chez les poissons et chez l'Homme. Mis à part des effets sur la reproduction, de nombreuses POPs sont suspectés d'être carcinogènes. Des études sur la toxicité des pesticides ont révélées que plusieurs d'eux étaient cancérigènes pour animaux, ceux qui suscitent de l'inquiétude pour les humains. Ils sont aussi toxiques pour les microorganismes photo trophiques, les poissons et les crustacés, la microflore, les abeilles, les oiseaux et d'autres organismes non ciblés.

Les médicaments comme une large classe des produits chimiques ont été détectés aux concentrations non très élevées mais ils sont introduits continuellement dans les eaux naturelles. Certains travaux ont été consacrés à leur influence sur la vie aquatique. Les médicaments sont des substances bioactives destinées à combattre les microorganismes pathogènes ; cependant ils peuvent avoir des effets négatifs non prévus. La concentration des produits pharmaceutiques dans les eaux superficielles est généralement inférieure à celle qui conduirait à une toxicité aiguë des organismes aquatiques. Néanmoins, des effets métaboliques, reproductives et d'autres perturbations sur les organismes aquatiques sont possibles dans le cas d'un contact chronique.

Afin de faire face au problème de la pollution de l'eau et sa protection, beaucoup d'efforts ont été faits. Il s'agit des réglementations administratives pour les composés toxiques et/ou persistants et le développement de méthodes de traitement des eaux usées avant qu'elles soient livrées dans le réseau de l'eau naturelle. Malgré l'amélioration considérable de la qualité de l'eau après traitement dans les stations de traitement des eaux usées, il s'est avéré que certains polluants chimiques peuvent s'y échapper comme par exemple les produits pharmaceutiques. Face à la difficulté des stations de traitement conventionnelles, la communauté scientifique a fait d'efforts considérables afin de développer des technologies plus

efficaces. Parmi les procédés développés dans ce contexte, les procédés d'oxydation avancée (POA) et en particulier les procédés électrochimiques d'oxydation avancée (PEOA) sont avérés d'être très efficaces dans l'élimination des polluants organiques; ils sont capables de minéraliser quasi-totalement la matière organique présente dans l'eau.

Ainsi le but des travaux effectués dans le cadre de cette thèse est de rechercher des conditions améliorant la performance d'un procédé électrochimique d'oxydation avancée, le procédé électro-Fenton (EF). Ce procédé, comme dans tous les POA, fait appel aux radicaux hydroxyles ( $\cdot\text{OH}$ ) créés in situ dans la solution sous traitement. Ces radicaux sont produits par le réactif de Fenton ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) qui est généré électrochimiquement :  $\text{H}_2\text{O}_2$  est formé par la réduction bi électronique de l' $\text{O}_2$  de l'air (comprimé). L'ion ferreux est régénéré à partir d'une quantité catalytique d'un sel soluble de fer ferrique par réduction mono-électronique. Les radicaux formés par la réaction entre ces deux réactifs (réactif de Fenton) sont des espèces chimiques très oxydantes ( $E^\circ = 2.80 \text{ V/ESH}$ ) et permettent une élimination efficace des polluants organiques de l'eau par leur transformation totale ou en  $\text{CO}_2$  et  $\text{H}_2\text{O}$ .

L'efficacité du procédé électro-Fenton dépend fortement des paramètres expérimentaux dont la nature du matériel d'électrode qui exerce un effet crucial sur la cinétique d'oxydation/minéralisation de la matière organique. Dans ce travail nous avons étudié le comportement de différents matériaux d'anode et de cathode lors d'application du procédé électro-Fenton à la destruction de deux composés pharmaceutiques fréquemment présents dans les eaux polluées, la sulfaméthazine [SMT] et l'amoxicilline [AMX] qui ont été choisies comme polluants modèle.

Ce mémoire de thèse est constitué de cinq chapitres: l'introduction, suivie par une discussion générale sur les méthodes courantes de traitement des eaux polluées et les procédés d'oxydation avancée et les procédés électrochimiques d'oxydation avancée (PEOA). Le deuxième chapitre décrit le matériel et les techniques analytiques utilisés lors de la réalisation de cette thèse. Dans le troisième chapitre, sont présentés les résultats obtenus sur l'efficacité d'abattement d'AMX avec différentes anodes telles que platine (Pt), diamant dopé au bore (BDD), anode dimensionnellement stable (DSA), dioxyde de plomb ( $\text{PbO}_2$ ), graphite, feutre (FC) de carbone et fibre de carbone (Fib C). Dans le quatrième et le cinquième chapitre l'effet de différents matériaux d'anode et de cathode sur l'efficacité du procédé électro-Fenton a été recherché en prenant la sulfaméthazine comme polluant modèle.

## **LES METHODES DE TRAITEMENT DES EAUX**

On peut regrouper les technologies de traitements de l'eau en deux groupes: les méthodes non destructives et les méthodes destructives. Les méthodes non destructives permettent de séparer les polluants de l'eau sans changer leur nature chimique, c'est-à-dire les polluants sont transférés d'une phase à une autre tout en conservant leurs propriétés physico-chimiques. Parmi ces méthodes on peut citer: l'Adsorption, l'extraction, la séparation membranaire, la distillation etc. Malgré leur efficacité plus ou moins élevée, ces méthodes n'offrent pas une solution définitive car les polluants ainsi séparés doivent être soit enfouis (une nouvelle pollution), soit traités par une méthode thermique (incinération) ou chimique (oxydation avancée).

Les méthodes destructives, contrairement à celles non destructives, transforment la matière organique chimiquement. Pour cela des oxydants chimiques comme le chlore ou l'ozone sont utilisés. Le traitement microbiologique est aussi souvent utilisé dans les stations d'épuration des eaux. Dans la technologie microbiologique ce sont les bactéries qui oxydent la matière organique en se servant d'elle comme source d'alimentation. La matière organique est transformée en  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  et en biomasse qui précipite au fond du réacteur. Le traitement biologique nécessite de long temps et souvent la minéralisation reste partielle, notamment lorsqu'il s'agit des molécules réfractaires à la biodégradation (POPs) ou toxiques aux bactéries. L'incinération thermique est effective pour le traitement des solutions concentrées (concentrateur de l'osmose inversée ou nano-filtration), mais c'est une méthode très coûteuse et peut émettre des composés toxiques tels que des dioxines.

### **Les procédés d'oxydation avancée (POAs)**

Les POAs et plus récemment les PEOA sont des méthodes chimiques destructives caractérisées par la génération des radicaux hydroxyles, une espèce chimique extrêmement réactive et très fortement oxydante. Ils peuvent oxyder les molécules organiques jusqu'à la minéralisation totale ou quasi-totale grâce à leur potentiel d'oxydation très élevé (2.80 V/ESH). Les POAs utilisent des réactifs chimiques tels que  $\text{TiO}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  seul ou combiné à l'irradiation UV afin de produire les  $\cdot\text{OH}$ . Par contre les PEOAs génèrent ces radicaux soit directement par l'oxydation de l'eau à la surface d'une anode appropriée, soit indirectement

dans la solution à partir du réactif de fenton généré électrochimiquement. Un schéma des POAs est é ci-dessous (Figure 1).

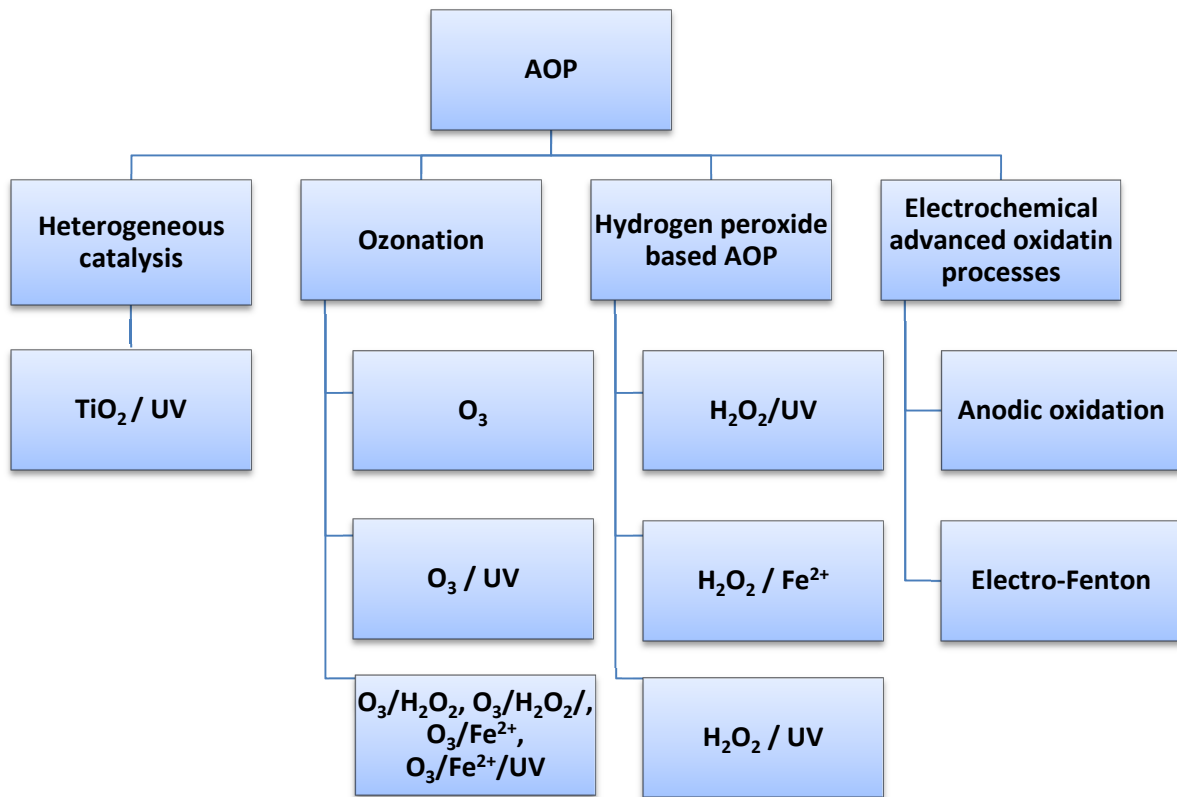


Fig. 1. Schéma des procédés d'oxydation avancé (POA).

## Les procédés d'électrochimiques d'oxydation avancée (PEOAs)

### Oxydation Anodique

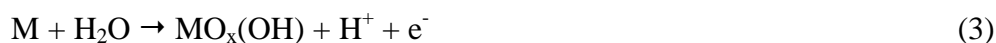
La dégradation des polluants organiques se fait dans une cellule électrochimique munie de deux électrodes (anode et cathode) et un électrolyte de support pour assurer la conductivité électrique. L'application d'un courant électrique entre les deux électrodes à travers la solution l'évolution de l'oxygène est d'une importance particulière. Le mécanisme de la réaction d'oxydation de l'eau sur anode conduisant à l'évolution d'oxygène moléculaire dépend de la nature du matériel de l'anode utilisé. Cela implique une surtension du dégagement d'O<sub>2</sub> qui est différente d'une anode à l'autre. Les anodes présentant une surtension élevée, comme le diamant dopé au bore (DDB), permettent la génération des radicaux hydroxyles comme espèces intermédiaires. Dans ce cas les radicaux formés sont physisorbés à la surface de

l'anode, sont quasi-libres (mobiles) et donc très réactives. Une fois générés (Eq. 1) ces radicaux réagissent avec la matière organique et l'oxyde jusqu'à sa transformation en CO<sub>2</sub> et H<sub>2</sub>O (Eq. 2):



M représente la nature de l'anode. La génération d'autres espèces oxydantes est aussi possible sur les anodes de haute surtension dégagement d'oxygène, telles que : O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> et S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, HOCl originaire de l'oxydation de l'électrolyte support. Ces espèces oxydantes participent à l'oxydation par le biais de l'oxydation méditée (en solution).

Quant aux anodes possédant une faible surtension de dégagement d'O<sub>2</sub>, elles présentent généralement un faible pouvoir d'oxydation. Les anodes DSA (RuO<sub>2</sub>-IrO<sub>2</sub> dans ce travail) et Pt font partie de ce type d'anodes. La structure électronique d'iridium permet les états d'oxydation plus élevé lorsqu'il est soumis au potentiel très positif (Eqs. 3 – 5):



Ensuite, l'oxyde de métal formé peut oxyder les molécules organiques, mais celle-ci est une réaction beaucoup plus lente que celle avec le M(·OH). La réaction (5) devient dominante aux potentiels très positif, ce qui amène à la perte de l'énergie.

### **Electro-Fenton**

C'est une méthode électrochimique indirecte pour l'abattement des polluants organiques en milieu aqueux. La base de la technologie électro-Fenton est la chimie du réactif du Fenton (H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>). Ce réactif fut utilisé pour la première fois par H.J.H. Fenton en 1894 pour oxyder l'acide tartrique. Mais cette réaction n'a été utilisée dans le traitement de l'eau qu'environ un siècle après sa première mise en application. Les radicaux hydroxyles (·OH) ainsi formé (Eq. 6) en milieu homogène s'attaquent la matière organique conduisant à sa minéralisation (Eq. 7):





L'utilisation du réactif de Fenton ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) est beaucoup moins efficace comparée à l'électro-Fenton, car la régénération du catalyseur  $\text{Fe}^{2+}$  est très lente. D'autre part, les acides carboxyliques formés lors d'oxydation de la matière organique forme des complexes avec l'ion ferrique contribuant donc à l'empêchement de son régénération en  $\text{Fe}^{2+}$ ; ce qui aboutit au ralentissement de la production des  $\cdot\text{OH}$  et donc de dégradation de polluants organiques. Le fer est aussi perdu par la précipitation sous forme d'hydroxyde ferrique (formation de boues de process). Contrairement du procédé Fenton, dans l'électro-Fenton  $\text{H}_2\text{O}_2$  est produit électrochimiquement à la cathode (Eq. 8):



L'oxygène est fourni à la solution par le bullage de l'air comprimé. Quant aux ions  $\text{Fe}^{2+}$  (catalyseur), ils sont ajoutés initialement à la solution en très petite quantité (catalytique) et ensuite sont régénérés électrochimiquement (Eq. 9):



Ainsi, le réactif de Fenton, et par conséquent les radicaux hydroxyles sont produits continuellement dans le système et attaquent les polluants organiques conduisant à leur oxydation jusqu'à la minéralisation. La génération efficace de  $\text{H}_2\text{O}_2$  et la régénération de  $\text{Fe}^{2+}$  évite les inconvénients du système Fenton tels qu'une cinétique de dégradation rapide, élimination des réactions parasites et empêchement de la formation de boues d'hydroxyde ferrique, ce qui fait l'électro-Fenton largement plus performant que le procédé de Fenton chimique. Ainsi le procédé électro-Fenton constitue une technologie remarquable pour la destruction des micropolluants organiques en milieu aqueux.

Le procédé électro-Fenton est influencé par des conditions expérimentales telle que : le pH, la concentration du catalyseur, la température, l'intensité du courant et le matériel de l'électrode. La valeur optimale du pH pour ce procédé est 2.8-3, la concentration du catalyseur 0.1-0.2 mM. La vitesse de la réaction de Fenton augment avec la température mais au-delà de 35-40 °C la réaction parasite de la décomposition de  $\text{H}_2\text{O}_2$  est accélérée. Le matériel de l'électrode est d'une importance fondamentale. Platine et diamant dopé au bore sont les anodes couramment utilisées ainsi que feutre de carbone, cathode à diffusion de l' $\text{O}_2$  etc comme

cathode. Dans ce travail une étude comparative de l'effet du matériel d'électrode (anode et cathode) sur l'efficacité du procédé électro-Fenton a été réalisée. Les résultats obtenus seront présentés ci-dessous.

*Tableau 1. Les constantes apparentes de l'oxydation d'AMX par les radicaux hydroxyles produits par l'oxydation anodique en fonction de l'intensité de courant appliquée et du matériel de l'anode utilisé.*

Anode	DDB	Pt	DSA	PbO <sub>2</sub>	Graph	F C	Fib C
I (mA)	k <sub>app</sub> (min <sup>-1</sup> )						
50	0.02	0.02	0.0006	0.02	0.01	0.05	0.02
100	0.03	0.03	0.003	0.03	0.01	0.08	0.02
300	0.06	0.04	0.003	0.05	0.02	0.2	0.03
500	0.11	0.03	0.008	0.04	0.02	0.09	0.02

### **L'influence du matériel de l'anode sur l'oxydation anodique de l'amoxicilline (AMX)**

Sept différentes anodes ont été étudiées afin de comparer leur pouvoir oxydant pour dégrader l'AMX. Pour cela nous avons effectué les expériences de dégradation (la transformation simple de la molécule en sous-produit de d'oxydation) et de minéralisation de la solution aqueuse d'AMX. La cinétique de dégradation oxydante d'AMX a été suivie par la chromatographie liquide à haute performance (HPLC), alors que sa minéralisation a été suivie par les mesures du carbone organique totale (COT) contenu dans la solution, avec un analyseur TOC.

Les constantes apparentes (k<sub>app</sub>) de la réaction de l'oxydation de l'AMX avec les radicaux hydroxyles obtenues par analyse cinétique des courbes d'oxydation avec différents courants appliqués sont présentées dans la Tableau 1. Les expériences ont été réalisées dans les conditions suivantes: [AMX] = 0.1 mM, [Na<sub>2</sub>SO<sub>4</sub>] = 50 mM, V = 250 ml. La cathode était en acier inoxydable de surface égale à celle de l'anode (24 cm<sup>2</sup>). Vu les valeurs des constantes apparentes on constate que la vitesse d'oxydation d'AMX augmente avec l'intensité du courant, mais leurs valeurs varient beaucoup d'une anode à l'autre. On observe que l'anode DSA est celle la moins efficace pour la dégradation d'AMX suivit par le graphite et les fibres

de carbone. Les valeurs des  $k_{app}$  pour Pt et  $PbO_2$  sont entre celles pour fibre de carbone, feutre de carbone et DDB, cette dernière étant la plus performante notamment pour les courants élevés. On peut observer un comportement caractéristique du feutre de carbone; il manifeste une capacité d'oxydation plus élevée que les autres anodes en carbone tel que le graphite et fibres de carbone. Cela peut être expliqué par sa surface spécifique qui est largement plus grande que les autres anodes, puisqu'il s'agit d'un matériau poreux trois dimensionnel. . Néanmoins les valeurs de  $k_{app}$  chutent rapidement pour le courant 500 mA à cause de sa combustion. Par contre dans le cas de DDB la valeur de  $k_{app}$  devient la plus importante pour l'intensité du courant de 500 mA.

Le tableau 2 résume l'efficacité de minéralisation d'une solution aqueuse de l'AMX pour les différentes anodes.

*Tableau 2. Taux de minéralisation de 250 ml d'AMX en fonction de l'intensité de courant et du matériel d'anode après le temps de traitement de 6 h.*

Anode	BDD	Pt	DSA	$PbO_2$	Graph	F C	Fib C
I (mA)	TOC removal (%)						
300	86.9	29.8	9.7	62.5	0	0	0
500	92.2	41.3	13.8	81.2	0	0	0
1000	96.3	47.4	22.0	90.6	0	0	0

Les taux de minéralisation les plus élevés sont atteintes avec l'anode DDB suivit par  $PbO_2$ , Pt et DSA. Le graphite qui présentait un pouvoir oxydant élevé, conduit aux taux de minéralisation faible au faibles courants (43 et 37.3% pour les courants 150 et 50 mA) et il devient incapable de minéraliser AMX pour des courants supérieur à 150 mA puisqu'il est endommagé aux courants élevés. Il faut noter que le graphite donne des résultats de minéralisation comparables à celui e platine et légèrement mieux que le DSA aux faibles courants. La fibre de carbone et le feutre de carbone sont endommagés (combustion) même aux faibles courants en donnant un couleur noir à la solution.

Contrairement ses bons résultats à l'oxydation, le feutre de carbone ne peut pas être utilisé pour la minéralisation car il s'oxyde même aux faibles courants sur les temps de traitement prolongés. En revanche, avec DDB des taux de minéralisation de 86.9, 92.2 et

96.3% ont été atteintes pour les courants de 300, 500 et 1000 mA. Une efficacité de minéralisation aussi élevée de DDB est due à la production intense des radicaux hydroxyles grâce à son surtension de dégagement d'O<sub>2</sub> très élevée. Les radicaux hydroxyles se forment aussi à la surface de Pt, PbO<sub>2</sub> et DSA mais en quantités beaucoup moins importantes. En plus ils sont chemisorbés, donc moins disponibles. La génération des autres espèces oxydantes : S<sub>2</sub>O<sub>4</sub><sup>2-</sup>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, joue aussi un rôle important dans le cas d'anode DDB.

### L'effet du matériel de l'anode sur le procédé électro-Fenton

Afin d'estimer l'effet du matériel de l'anode sur le procédé électro-Fenton des expériences de dégradation et de minéralisation de SMT ont été effectuées. Puis l'analyse des acides carboxyliques et des ions minérales provenant des hétéroatomes présents da la molécule de SMT a aussi été effectuée. Les conditions expérimentales étaient comme suivants: [SMT] = 0.2 mM, [Fe<sup>2+</sup>] = 0.2 mM, V = 300 ml, pH = 3. La surface des anodes été 2 x 24 cm<sup>2</sup>, alors que la cathode été toujours un feutre de carbone avec les dimensions 23 x 6 x 0.5 cm. Les échantillons de SMT électrolysé ont été analysés par HPLC. L'enlèvement du COT de la solution traitée a été suivi par mesures de COT. Les acides carboxyliques ont été analysés par la chromatographie de l'exclusion et les ions minéraux par la chromatographie ionique.

Les constantes apparentes de d'oxydation de SMT par les radicaux hydroxyles sont pour les différents systèmes électrolytiques son donné dans le Tableau 3.

*Tableau 3. Les constantes apparentes de dégradation de SMT lors de traitement électro-Fenton en fonction de l'intensité du courant appliqué et du matériel de l'anode.*

Cellule	Pt	DSA	DDB	F C
I (mA)	$k_{app} / \text{min}^{-1}$			
50	0.08	0.06	0.07	0.22
100	0.15	0.09	0.12	0.31
200	0.19	0.14	0.18	0.37
300	0.27	0.20	0.24	0.44
400	0.37	0.27	0.27	0.43
500	0.40	0.27	0.25	0.43

Tableau. 4. Les constantes apparentes de l'oxydation de SMT par radicaux hydroxyles produits par l'oxydation anodique, en fonction de l'intensité de courant et du matériel de l'anode.

Cellule	Pt	DSA	DDB	FC
I (mA)	$k_{app}$			
100	0.02	0.01	0.02	0.22
500	0.04	0.02	0.06	0.29

La vitesse de dégradation de SMT augmente avec le courant appliqué dans toutes les cellules électrolytiques. Lorsque le courant augmente la production de  $H_2O_2$  et la régénération de  $Fe^{2+}$  sont plus rapides et par conséquent la dégradation de SMT aussi. Cette amélioration de la dégradation est jusqu'à une valeur de l'intensité de courant optimale 400 mA, au-delà de cette valeur la vitesse de dégradation cesse de croître. Cette limite du courant est due aux réactions parasitiques telles que le dégagement de  $O_2$  sur anode et le dégagement de  $H_2$  sur cathode, qui s'accroissent aux courants élevés. Les constantes apparentes (Tableau 3) calculées à partir de courbes  $[SMT] = f(t)$  qui correspondent à une cinétique de pseudo-première ordre, montre une différence légère entre les anodes utilisées, mise à part le feutre de carbone. Dans le Tableau 4 sont montrés les  $k_{app}$  pour l'oxydation anodique, c'est-à-dire en absence du catalyseur  $Fe^{2+}$ . On peut remarquer clairement la grande différence entre électro-Fenton et l'oxydation anodique. La dégradation de SMT est nettement plus rapide avec électro-Fenton grâce aux radicaux hydroxyles générés par la réaction de Fenton (en plus ceux générés à la surface d'onde). Les  $k_{app}$  obtenues avec le feutre de carbone sont nettement plus grandes que celles obtenues avec les anodes Pt, DDB, et DSA. Dans le cas de DDB/Feutre de carbone la dégradation du SMT est légèrement plus lente que la cellule Pt/Feutre de carbone. Le DDB étant une anode à grand pouvoir d'oxydation, il génère des  $S_2O_8^{2-}$ , qui vont oxyder le  $Fe^{2+}$  en  $Fe^{3+}$  (Eq. 10) diminuant ainsi  $[Fe^{2+}]$  et par conséquent la vitesse de production des radicaux hydroxyles.



Finalement une dégradation similaire de SMT dans des différentes cellules (anodes) est due au fait que la dégradation de SMT par les radicaux hydroxyles provenant de la réaction électro-Fenton est dominante par rapport à la contribution de l'oxydation anodique.

Les  $k_{app}$  pour le feutre de carbone sont remarquables, elles sont beaucoup plus grandes que les trois autres anodes, grâce à sa large surface trois dimensionnelle.

Les expériences de minéralisation ont été effectuées aux mêmes conditions que celles de la dégradation. Les pourcentages d'abattement du COT sont présentés dans le Tableau 5.

*Tableau 5. L'abattement du COT en fonction de l'intensité du courant et du matériel d'anode lors de minéralisation d'une solution de SMT par procédé électro-Fenton.*

Cellule	Pt	DSA	BDD	C F
I (mA)	% d'abattement de COT à 2h / 6h			I (mA) %COT (2h/6h)
100	35.5/69.6	25.5/62.2	57.2/91.9	50 33.6/68.2
300	55.9/83.9	34.1/71.1	76.4/96.8	100 44.4/70.2
500	71.5/90.3	41.9/76.1	84.7/97.9	
700	61.4/81.7	14.8/75.2	88.2/97.2	
1000	54.7/75.8	26.3/46.1	90.1/98.5	

*Tableau 6. L'abattement du COT en fonction de l'intensité du courant appliqué et du matériel de l'électrode (oxydation anodique).*

Cellule	Pt	DSA	DDB	F C
I (mA)	% d'abattement de COT à 2h/6h			
100	12.5/15.8	5.2/8.3	48.7/88.1	0/0
500	25.7/36.8	9.6/10.8	69.4/94.6	0/0
1000	24.0/41.4	9.8/9.8	80.9/97.4	0/0

Les résultats sur la minéralisation mettent en évidence un comportement très différent comparé aux résultats de dégradation. Si l'efficacité de dégradation était similaire pour Pt, DDB et DSA, une différence évidente apparaît dans le cas de minéralisation. La minéralisation de SMT augmente avec le courant jusqu'à une valeur limite qui n'est pas la même pour toutes les anodes. Dans les configurations Pt/Feutre de carbone et DSA/Feutre de carbone cette limite est de 500 mA. On peut voir aussi que dans le cas de DSA/Feutre de carbone l'abattement du COT avec 300 et 500 mA est très proche l'un de l'autre, ce qui veut

dire qu'à partir de 300 mA les réactions parasites deviennent importantes. Pour 700 et 1000 mA la minéralisation est même plus faible que pour 500 mA dans les cellules Pt/Feutre de carbone et DSA/Feutre de carbone à cause de ralentissement de la production du réactif du Fenton sur cathode, mais aussi à cause de inhibition de l'oxydation anodique de SMT. Le meilleur abattement de COT est obtenu avec l'anode DDB, le taux d'abattement atteint quasiment 100% au bout de 6 h de traitement. Dans le système DDB/Feutre de carbone, il y a deux sources de radicaux hydroxyles: les  $\cdot\text{OH}$  qui se forment par la réaction de Fenton dans le sein de la solution et ceux qui se forment sur la surface de l'anode amenant à une efficacité de minéralisation remarquable. Il est important de noter que la limite du courant optimale pour le DDB n'est pas à 500 mA, comme le tableau 5 le montre la minéralisation peut être effectuée efficacement jusqu'à 1000 mA. Le DDB ayant une haute surtension de dégagement d' $\text{O}_2$  la formation des  $\cdot\text{OH}$  est favorisée. Dans le cas de Pt et particulièrement DSA les  $\cdot\text{OH}$  peuvent oxyder le métal à l'état d'oxydation plus élevé en formant un oxyde. L'oxyde se libère l' $\text{O}_2$  ou il réagit faiblement avec les molécules organiques au potentiel moins élevé. Néanmoins au-delà de 500 mA, l'augmentation de l'abattement du COT avec augmentation du courant devienne plus faible même avec DDB, ce qui met en évidence le fait que le dégagement d' $\text{O}_2$  constitue toujours un obstacle important.

En comparant la minéralisation électro-Fenton avec oxydation anodique il est facile de conclure électro-Fenton est une procédure largement plus efficace quand il s'agit des systèmes Pt/Feutre de carbone et DSA/Feutre de carbone. Dans le cas du système DDB/Feutre de carbone la différence est moins importante, cela probablement à cause de l'exclusion d'une quantité du catalyseur du système électro-Fenton déjà mentionné.

L'analyse des acides carboxyliques montre aussi la supériorité de DDB sur Pt et DSA. Durant l'électrolyse les acides carboxyliques identifiés étaient les acides: oxalique, glyoxylique, pyruvique et formique. A la fin de l'électrolyse tous les acides carboxyliques sont détruits. Dans la cellule Pt/Feutre de carbone les acides carboxyliques identifiés étaient: les acides oxalique, glyoxylique, formique, fumarique, maléique et acétique. A la fin de traitement il reste encore de l'acide oxalique et formique dans la solution. Quant à la cellule DSA/Feutre de carbone, les acides carboxyliques identifiés étaient: oxalique, glyoxylique, formique, maléique, malonique, oxamique et tartronique. A la fin du traitement, il reste toujours des acides oxalique, formique, glyoxylique et oxamique en quantité résiduelle.

Puisque la SMT contient les atomes N et S dans sa structure, leur libération dans la solution sous forme d'ions inorganiques  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  et  $\text{SO}_4^{2-}$  est attendue. Dans le cas de l'anode Pt, l'analyse par chromatographie ionique montre que 90.2% de l'azote contenu dans la molécule initiale est libéré en forme de  $\text{NO}_3^-$  (majoritairement) et  $\text{NH}_4^+$ , alors que  $\text{SO}_4^{2-}$  est complètement libéré dans les premiers 30 min du traitement. La concentration des ions  $\text{NO}_3^-$  et  $\text{NH}_4^+$  est plus basse avec l'anode DSA, 62% de l'azote est libérée sous forme de nitrate et ammonium. Une partie de l'azote est probablement perdue sous forme de produits gazeux. En revanche 96.7% de l'azote initial est libéré quand BDD est utilisé comme anode, la somme des ions de nitrate et d'ammonium libérée, est quasiment égale à la totalité de l'azote présent dans la molécule. Quant à  $\text{SO}_4^{2-}$  il est quantitativement libéré dans la solution.

### **Influence du matériel de la cathode sur l'efficacité du procédé électro-Fenton**

Afin d'étudier l'effet du matériau de cathode sur le procédé électro-Fenton, nous avons effectué des expériences de dégradation de SMT dans une cellule d'électrolyse de 250 ml. Les cathodes testées sont : éponge de carbone de différentes porosités, feutre de carbone et acier inoxydable de dimensions 6 x 3.5 cm. L'anode est toujours le platine. Le pH de la solution a été ajusté à 3, la solution a été constamment agitée et barbotée par l'air comprimé tout au long de l'électrolyse. Les échantillons prélevés aux intervalles réguliers de temps ont été analysés par HPLC et TOC.

La production de  $\text{H}_2\text{O}_2$  constitue un paramètre d'efficacité d'une cathode pour le procédé électro-Fenton. Pour cela le dosage de  $\text{H}_2\text{O}_2$  est effectué pour les cathodes : éponge de carbone 45 ppi, éponge de carbone 80 ppi, feutre de carbone et acier inoxydable en prenant le platine comme anode. Les courants appliqués ont été : 50, 100, 200, 300, 400, 500 mA. La solution à électrolyser contenait de l'eau pure avec 50 mM de l'électrolyte de support au pH 3 sous le barbotage permanent de l'air comprimé.

Pour les courants de 50-200 mA, la concentration maximale est atteinte au bout de 40 minutes dans la cellule Pt/ éponge de carbone 45 ppi. Cette concentration a été 3.5 mM pour 100 mA, ce qui représente la valeur la plus élevée des courants appliqués. La concentration de  $\text{H}_2\text{O}_2$  augmente avec le courant jusqu'à 100 mA puis elle devient de plus en plus faible avec l'augmentation du courant appliqué. Aux courants de 300, 400 et 500 mA la concentration de  $\text{H}_2\text{O}_2$  arrive à son niveau maximale très rapidement (au bout de 10 minutes).



Le même comportement est observé pour les autres cathodes aussi la valeur maximale de la production de  $H_2O_2$  est obtenue avec 100 mA et se détériore au-delà de cette limite. La concentration maximale avec éponge de carbone de 80 ppi est 2.5 mM, quant à feutre de carbone le maximum de la concentration de  $H_2O_2$  est 1.2 mM. La cellule Pt/acier inoxydable produit une concentration maximale de  $H_2O_2$  de seulement 0.04 mM avec des courants de 50 et 100 mA. Les résultats obtenus pour le dosage de  $H_2O_2$  sont bien cohérent avec les résultats obtenus pour l'oxydation et la minéralisation de SMT. Les cathodes pouvant produire une concentration élevée de  $H_2O_2$  permettent aussi un abattement efficace de SMT. Il est aussi à noter que même si l'accumulation de  $H_2O_2$  est maximum au 100 mA la vitesse de dégradation de SMT augmente avec le courant jusqu'à 300 mA. Cela s'explique avec le fait qu'en présence de SMT et l'ion ferreux, le  $H_2O_2$  formé est immédiatement consommé par la réaction de Fenton sans avoir le temps de se détruire par les réactions parasites.

Tableau 7 montre les valeurs de  $k_{app}$  de la réaction d'oxydation de SMT par les  $\cdot OH$  pour les cathodes étudiées. Ces valeurs sont calculées toujours à partir des droites semi-logarithmiques  $\ln(C_0/C_t) = f(t)$ . Les valeurs de  $k_{app}$  révèlent que la dégradation de SMT est la plus rapides avec l'éponge de carbone, en particulier avec l'éponge de carbone de porosité 45 ppi. On peut voir aussi que les plus basses valeurs des  $k_{app}$  pour l'éponge de carbone sont nettement plus élevées de celle obtenues avec le feutre de carbone et notamment celles obtenues avec acier inoxydable.

*Tableau 7. Constantes apparentes de dégradation de SMT abstru avec différentes cathodes.*

Cell.	EC 30 ppi	EC 45 ppi	EC 60 ppi	EC 80 ppi	EC 100 ppi	F C	Ac Inox
I (mA)	$k_{app} / \text{min}^{-1}$						
50	0.11	0.19	0.19	0.19	0.19	0.06	0.03
100	0.22	0.34	0.28	0.28	0.29	0.07	0.04
200	0.36	0.49	0.43	0.42	0.38	0.14	0.06
300	0.41	0.60	0.50	0.43	0.39	0.16	0.07
400	0.43	0.61	0.48	0.41	0.37	0.11	0.07
500	0.37	0.57	0.38	0.33	0.31	0.09	0.06

On peut expliquer les grandes valeurs des  $k_{app}$  pour l'éponge de carbone avec sa large surface grâce à sa porosité qui permet une production plus intense du réactif du Fenton. Le feutre de carbone est aussi une cathode trois dimensionnelle et très poreuse, et donc avec grande surface mais sa capacité de dégrader le SMT est beaucoup plus faible que celle d'éponge de carbone. Le feutre de carbone est un matériau très souple et beaucoup plus dense que l'éponge de carbone, ce qui défavorise la circulation de la solution dans le sein de la cathode, donc le transport de masse de l' $O_2$  et  $Fe^{2+}$  est entravé. Tandis que l'éponge de carbone est moins dense et très rigide permettant un transport de masse plus favorable. De même façon, on peut expliquer les différences entre les éponges de carbone de différente porosité. Quant à l'acier inoxydable il a une surface spécifique comparativement très petite, donc la production du réactif du Fenton y est très faible.

Les pourcentages de l'abattement du COT de la solution SMT sont présentés dans le tableau 8.

*Tableau 8. Les pourcentages de l'abattement de COT en fonction de courant et de matériau de cathode.*

Cell.	EC 30 ppi	EC 45 ppi	EC 60 ppi	EC80 ppi	EC 100 ppi	FC	Ac Inox
I (mA)	% d'abattement de COT à 8 h						
50	46.5	63.4	62.1	54.8	54.1	43.4	20.9
100	67.7	76.6	74.3	69.7	69.7	49.7	29.9
300	80.2	91.1	91.2	83.9	82.6	55.6	37.2
500	79.5	90.1	83.6	83.3	80.7	56.6	41.2

L'abattement du COT suit le même ordre que l'oxydation. La cathode la plus performante est l'éponge de carbone 45 ppi dont l'abattement de COT est 91,1% avec le courant de 300 mA. Cette valeur est la limite du courant optimale. Les autres porosités de l'éponge de carbone présentent aussi de très bonnes efficacités de minéralisation. Tandis que le feutre de carbone est moins efficace. L'acier inoxydable est nettement la cathode la moins efficace pour l'abattement du COT.

Finalement après avoir identifié l'éponge de carbone come la meilleure cathode pour le procédé électro-Fenton, nous avons réalisé des expériences avec cette cathode en utilisant le DDB comme la meilleure anode déjà constaté. Les expériences ont été effectuées dans les

mêmes conditions que celles réalisées pour mesurer l'efficacité des cathodes. Les constantes apparentes et les pourcentages d'abattement du COT sont donnés dans le tableau 9.

*Tableau 9. Valeurs des constantes apparentes ( $k_{app}$ ) et les pourcentages d'abattement de COT obtenus avec la cellule DBB/Eponge de carbone 45 ppi.*

<b>I (mA)</b>	<b><math>k_{app}/\text{min}^{-1}</math></b>	<b>Enlevement %COT t à 6 h</b>
<b>50</b>	<b>0.12</b>	<b>77.7</b>
<b>100</b>	<b>0.21</b>	<b>82.6</b>
<b>200</b>	<b>0.35</b>	<b>-----</b>
<b>300</b>	<b>0.38</b>	<b>95</b>
<b>400</b>	<b>0.36</b>	<b>-----</b>
<b>500</b>	<b>0.35</b>	<b>98</b>

La vitesse de dégradation de SMT augmente avec le courant jusqu'à 300 mA, grâce à l'accélération de la réaction du Fenton, puis elle diminue, indiquant la limite du courant optimale. En comparant les  $k_{app}$  obtenus avec DDB/Eponge de carbone 45 ppi on peut conclure qu'elles sont plus faibles que celles obtenues avec le système Pt/Eponge de carbone 45 ppi et nettement plus élevées que les  $k_{app}$  obtenues avec les cellules Pt/Acier inoxydable et Pt/Feutre de carbone. Contrairement la minéralisation est beaucoup plus efficace avec la cellule DDB/éponge de carbone, ce qui s'explique par les radicaux hydroxyles supplémentaires provenant de la surface de l'anode DDB par oxydation de l'eau.

## PËRMBLEDHJE

Prezenca e substancave kimike në ambient është shumë e evidente dhe ka një rritje të pandërprerë si rezultat i aktiviteteve antropogjene. Nevojat e njerëzve për produkte ushqimore, të banimit, të transportit e të tjera, duke qenë gjithmonë në rritje kanë dërguar në formimin e burimeve të reja të ndotjes si dhe në intensifikimin e emitimit të kemikaljeve nga ato ekzistuese. Shumë nga këto substanca janë të rrezikshme dhe një numër i madh i tyre futen direkt në mjediset ujore. Nga burimet kimike të ndotjes mund të përmendim: shkarkimin direkt të mbetjeve kimike industriale dhe të llojeve të tjera në hapësirat e ambientit, përdorimin e produkteve kimike të tilla si pesticidet në agrikulturë, përdorimin e medikamenteve në mjekësi dhe veterinarit etj. Si pasojë e sasive të mëdha të këtyre substancave që rrjedhin nga këto burime të ndotjes ka ardhur deri te kontaminimi me substanca kimike inorganike dhe organike të ujërave sipërfaqësor dhe nëntokësor.

Ekzistojnë një numër i madh i ndotësve organik rezistent (NOR) që rrjedhin nga disa klasa komponimesh kimike të shpërndarë në ambient, të tillë si: hidrokarburet aromatike të kloruara, poliklorobifenilet (PCB), dioksinat, furanet dhe pesticidet e kloruara (DDT, lindani, aldrini,...) apo triazinat etj. Si ndotës organik rezistent që shpesh gjenden në ujëra janë fenolet dhe fenolet e kloruara. Këto substanca janë përgjithësisht pak të tretshme në ujë dhe si pasojë shpërndahen në materien e ngurtë e veçanërisht në materien organike të dheut. NOR-të janë pak a shumë të avullueshëm dhe nga toka, uji dhe bimët mund të kalojnë në atmosferë prej nga barten me rrymat e ajrit deri në distanca shumë të largëta dhe pastaj bien në tokë nën veprimin e reshjeve atmosferike. Kështu që NOR-të janë gjetur madje edhe në Antarktik dhe në male të larta, në vende të ndryshme ku temperaturat e ulta kanë favorizuar kondensimin e mjegullave. Kështu reshjet atmosferike luajnë një rol shumë të rëndësishëm në transportin e NOR-ve, gjë që është vërtetuar nga shumë hulumtime shkencore të cilat tregojnë për prezencën e tyre në borën e maleve të larta dhe të ulta.

Pesticidet janë një klasë e komponimeve kimike që përdoren gjerësisht në agrikulturë dhe si pasojë gjenden gjithandej në fushat me kultura bimore ku janë përdorur për trajtimin e bimëve, në lumenj, liqene, sedimente dhe ujëra nëntokësor ku arrijnë si pasojë e shpërlarjes nën veprimin e të reshurave.

Një klasë tjetër e ndotësve organik të zakonshëm në ujëra dhe tokë paraqesin produktet farmaceutike, prania e të cilave është raportuar shpesh. Burim i tyre janë mbetjet e industrisë farmaceutike, spitalet, ujërat e zeza si dhe fermat e shtazëve, etj.

Komponimet organike sintetike që prodhohen për qëllime të caktuara ashtu si dhe produktet sekondare që i shoqërojnë ato, mesproduktet e formuara gjatë proceseve të djegies etj, nuk janë përbërës natyror të mjedisit kështu që pritet të kenë një efekt negativ mbi të. Ato mund të futen në zingjirin ushqimor, në veçanti NOR-të, duke kaluar nga një nivel trofik në tjetrin. Në fakt është vërtetuar që NOR-të janë të implikuara në çrregullimet e gjëndrrave endokrine te peshqit dhe te njeriu. Pastaj, pos efekteve të tyre mbi procesin e reprodukimit shumë NOR dyshohen të jenë kancerogjene. Disa studime mbi toksicitetin e pesticideve kanë zbuluar që shumë prej tyre janë kancerogjene për kafshët, gjë që është shqetësuese edhe për njerëzit. Ato janë poashtu toksike edhe për mikroorganizmat fototrofik: peshqit, mikroflora, bletët, zogjët dhe organizma të tjerë që nuk janë cak i tyre.

Medikamentet si klasë shumë e gjerë e komponimeve kimike janë gjetur në ujëra në përqëndrime jo shumë të larta por ato futen në ujëra në mënyrë permanente, kështu që një numër i konsiderueshëm punimesh u është kushtuar atyre. Medikamentet janë substanca bioaktive të destinuara për t'i luftuar mikroorganizmat patogjen, megjithatë ato mund të kenë efekte negative të papritura. Përqëndrimi i substancave farmaceutike në ujëra sipërfaqësor zakonisht është nën përqëndrimin i cili do të shkaktonte helmimin akut të organizmave ujorë. Megjithatë efektet metabolike, të riprodhimit e të tjera, janë të mundshëm mbi organizmat ujorë në rast të ekspozimit kronik të tyre.

Me qëllim të përballimit të problemit të ndotjes së ujit si dhe mbrojtjes së tij, janë bërë shumë përpjekje, duke përfshirë rregullime administrative për komponimet toksike dhe/ose rezistente dhe zhvillimin e metodave të trajtimit të ujërave hedhurinë para se ato të hidhen në rrjetin e ujërave natyror. Por përkundër përmirësimit të konsiderueshëm të kualitetit të ujit pas trajtimit në stacione të trajtimit të ujërave hedhurinë, është vërejtur që disa ndotës kimik si për shembull produktet farmaceutike, mund të kalojnë pa pësuar transformim ose si pjesërisht transformuara. Duke parë këto vështirësi apo të meta të trajtimit klasik, komuniteti shkencor ka bërë përpjekje të konsiderueshme me qëllim të zhvillimit të teknologjive më efikase. Mes metodave të zhvilluara në këtë kontekst, metodat e oksidimit të avancuar të (MOA) dhe veçanërisht metodat elektrokimike të oksidimit të avancuar (MEOA) janë shumë efikase në

eliminimin e ndotësve organik; ato mund të mineralizojnë pothuajse plotësisht materiet organike që gjenden në ujë.

Kështu që punimet e realizuara në këtë temë të doktoratës kanë për qëllim gjetjen e kushteve optimale të veprimit të një metode elektrokimike të oksidimit të avancuar, metodës elektro-Fenton (EF). Kjo metodë, ashtu si edhe të gjitha MOA-të e tjera, bazohet në reaktivitetin e lartë të radikaleve hidroksile ( $\cdot\text{OH}$ ) të formuara in situ në tretësirën që trajtohet. Këto radikale përfitohen nga reaktivi i Fentonit ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) i cili prodhohet elektrokimikisht:  $\text{H}_2\text{O}_2$  formohet në katodë nga reduktimi elektrokimik i  $\text{O}_2$  që futet në tretësirë përmes ajrit të komprimuar. Joni ferror rigjenerohet në katodë nga joni ferrik i shtuar në sasi katalitike në formë të një kripe të tretshme të hekurit hekurit. Radikalet e formuara nga reaksioni i këtyre dy reagjentëve (reagjenti i Fentonit) janë specie kimike me veti shumë oksiduese ( $E^\circ = 2.80 \text{ V/ESH}$ ) dhe mundësojnë eliminimin efikas të ndotësve organik nga uji duke i transformuar ata në  $\text{CO}_2$  dhe  $\text{H}_2\text{O}$ .

Efikasiteti i procesit elektro-Fenton varet shumë nga parametrat eksperimental si: natyra e materialit të elektrodës që ka rëndësi themelore në kinetikën e oksidimit/mineralizimit të materieve organike. Në këtë hulumtim kemi studiuar sjelljen e materialeve të ndryshme të anodës dhe katodës gjatë aplikimit të metodës elektro-Fenton në shkatërrimin e dy komponimeve farmaceutike që gjenden shpesh në ujërat e ndotura, Sulfametazina (SMT) dhe amoksicilina (AMX), të cilët janë zgjedhur si ndotës model.

Kjo temë e doktoratës përbëhet nga pesë kapituj: hyrja, që pasohet nga një diskutim i përgjithshëm mbi metodat që aplikohen në trajtimin e ujrave të ndotura, proceset e oksidimit të avancuar (POA) dhe proceset elektrokimike të oksidimit të avancuar (PEOA). Në kapitullin e dytë përshkruhen materiali dhe teknikat analitike të përdorura gjatë këtij hulumtimi. Kapitulli i tretë përshkruan rezultatet e fituara mbi efikasitetin e shkatërrimit të AMX me anë të anodave të ndryshme si platina (Pt), diamanti i dopuar me bor (boron doped diamon (BDD)), anoda dimenzionalisht stabile (dimensionaly stable anode (DSA)), dioksidi i plumbit ( $\text{PbO}_2$ ), grafiti, karboni shpuzor (carbon felt (KF)), dhe fibrat e karbonit (FK). Në kapitullin e katërt dhe të pestë është studiuar efekti i materialeve të ndryshme të anodës dhe katodës në procesin elektro-Fenton, duke pasur si model sulfametazinën.

## **METODAT E TRAJTIMIT TË UJËRAVE**

Teknologjitë e trajtimit të ujërave mund të ndahen në dy grupe: metodat destruktive dhe jo destruktive. Metodatat jo destruktive mundësojnë ndarjen e ndotësve nga uji pa ndryshuar natyrën e tyre kimike, dmth. ndotësit vetëm transferohen nga një fazë në fazën tjetër. Në kuadër të këtyre metodave mund të përmendim: adsorbimin, ekstraktimin, ndarjen membranore, distilimin etj. Përkundër efikasitetit pak a shumë të madh, këto metoda nuk ofrojnë zgjidhjen përfundimtare pasi që ndotësit e ndarë në këtë mënyrë duhet të vendosen diku tjetër (rindotje), ose duhet të trajtohen me ndonjë metodë termike (djegie) apo kimike (oksidim i avancuar).

Metodat destruktive, ndryshe nga ato jo destruktive, e transformojnë kimikisht materien organike. Për këtë qëllim përdoren oksidant kimik si klori apo ozoni. Trajtimi mikrobiologjik gjithashtu përdoret shpesh për pastrimin e ujërave ku agjent shkatërrues i materieve organike janë bakteriet të cilat e përdorin atë si lëndë ushqese. Materia organike transformohet në CO<sub>2</sub>, H<sub>2</sub>O dhe biomasë e cila fundërrrohet në fund të reaktorit. Trajtimi biologjik kërkon shumë kohë si dhe shpeshherë mineralizimi është vetëm i pjesshëm, e sidomos kur bëhet fjalë për molekula refraktare ndaj biodegradimi (NOR) apo toksike ndaj bakterieve që përdoren për trajtim. Djegia është metodë efektive për trajtimin e tretësirave të përqëndruara (pas trajtimit membranor), por është e kushtueshme dhe mund të lirojë komponime toksike të tilla si dioksinat.

### **Proceset e oksidimit të avancuar (POA-të)**

POA dhe më vonë PEOA janë metoda kimike destruktive që karakterizohen nga përfitimi i radikaleve hidroksile, të cilat janë specie kimike me reaktivitet ekstrem dhe mjete të fuqishme oksiduese. Ato mund t'i oksidojnë molekulat organike deri në mineralizimin e tyre të plotë ose kuazi të plotë duke iu falënderuar potencialit të tyre të oksidimit shumë të lartë (2.80 V/ESH). Në POA përdoren reaktiv kimik si: TiO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> të vetëm apo të kombinuar me rrezatim UV më qëllim të prodhimit të <sup>•</sup>OH. Për dallim nga POA, në PEOA radikalet hidroksile përfitohen qoftë në mënyrë direkte nga oksidimi i ujit në sipërfaqen e një anode të caktuar, ose në mënyrë indirekte në tretësirë nga reaktivi i Fentonit i prodhuar elektrokimikisht. Një skemë e POA është dhënë në vazhdim (fig. 1)

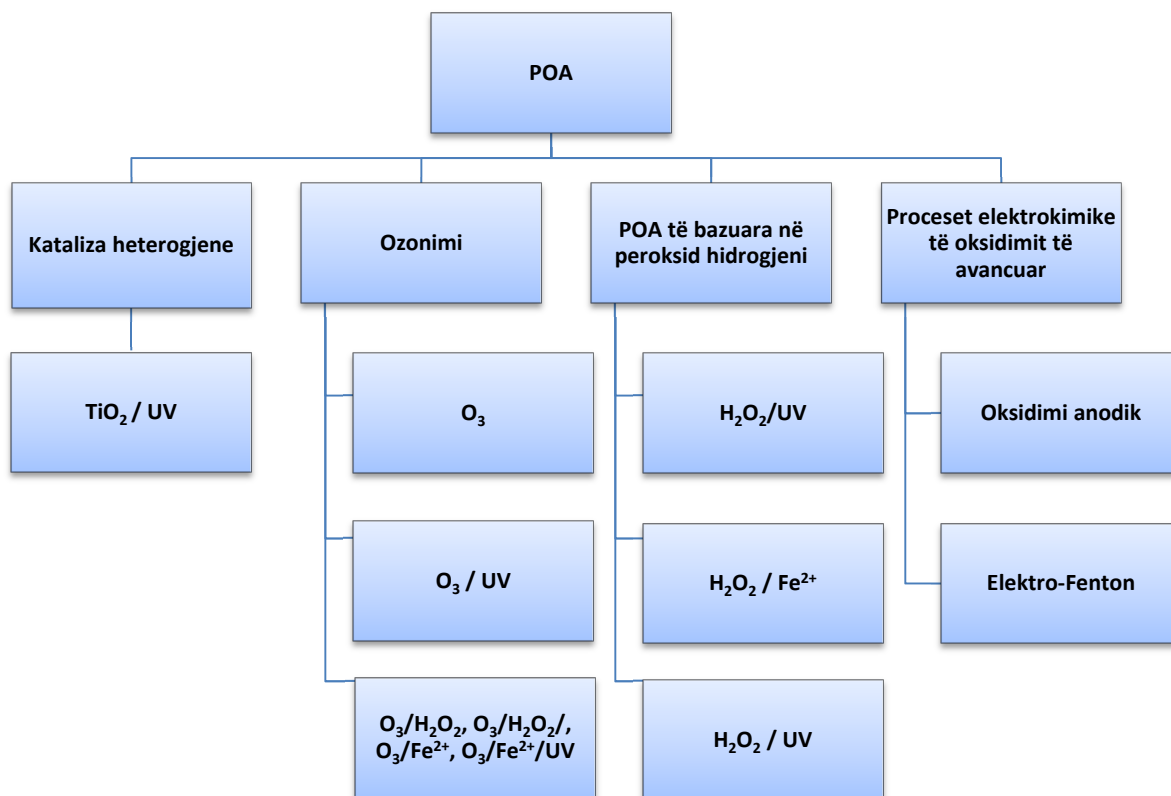


Fig. 1. Skema e proceseve të oksidimit të avancuar (POA)

## Proceset elektrokimike të oksidimit të avancuar

### Oksidimi anodik

Degradimi i ndotësve organik bëhet në një celulë elektrokimike të pajisur me dy elektroda (anodë dhe katodë) dhe një elektrolit bartës për të përmirësuar përqeshmërinë elektrike. Gjatë kalimit të rrymës elektrike nëpër tretësirë, lirimi i oksigjenit në anodë ka një rëndësi të veçantë. Mekanizmi i reaksionit të oksidimit të ujit në anodë që qon në lirim të oksigjenit molekular varet nga natyra e materialit të anodës të përdorur. Kjo implikon një mbipotencial të lirit të oksigjenit që ndryshon nga një anodë te tjetra. Anodat që kanë një mbipotencial të lartë, si psh diamanti i dopuar me bor (BDD), mundësojnë gjenerimin e radikaleve hidroksile si specie intermediare. Në këtë rast radikale të formuara janë të adsorbuar fizikisht në sipërfaqe të anodës potujse të lira e kështu shumë reaktive. Këto radikale reagojnë menjëherë sapo janë formuar me molekulat organike duke i transformuar ato në CO<sub>2</sub> dhe H<sub>2</sub>O (Ek. 2):





M paraqet natyrën e anodës. Gjithashtu është i mundshëm formimi i specieve të tjera oksiduese në anodat me mbipotencial të lartë të oksigjenit si: O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> et S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, HOCl që vinë nga oksidimi i elektrolitit bartës. Këto specie marrin pjesë gjithashtu në oksidim (oksidimi indirekt).

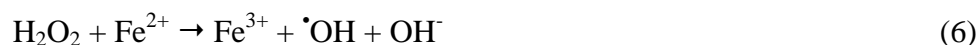
Ndërsa anodat që kanë mbipotencial të ulët të lirim të oksigjenit kanë aftësi të ulët oksiduese. Në këtë grup bëjnë pjesë anodat DSA (RuO<sub>2</sub>-IrO<sub>2</sub> në këtë punim) dhe Pt. Struktura elektronike e iridiumit lejon gjendje të oksidimit më të larta kur ai i nënshtrohet potencialit të lartë pozitiv (Ek 3-5):



Pastaj oksidi i metalit i formuar mund t'i oksidoj molekulat organike, por ky është një reaksion shumë më i ngadalshëm se ai me M(·OH). Në potenciale të larta reaksioni (5) bëhet dominant dhe qon në humbje të energjisë.

### **Elektro-Fentoni**

Është një metodë elektrokimike indirekte për shkatërrimin e ndotësve organik në mjedis ujor. Baza e teknologjisë elektro-Fenton është reaktivi i Fentonit (H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>). Ky reaktiv është përdorur për herë të parë ng H.J.H. Fenton në vitin 1894 për oksidimin e acidit tartarik. Por ky reaksion është përdorur për trajtimin e ujërave vetem pas afër një shekulli nga përdorimi i tij i parë. Radikalet hidroksile (·OH) të formuara kështu (Ek. 6) në mjedis homogjen sulmojnë materien organike deri në mineralizimin e saj (Ek. 7):



Përdorimi i reaktivit të Fentonit (H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>) është shumë më pak efektiv në krahasim me atë elektro-Fenton, sepse rigjenerimi i katalizatorit Fe<sup>2+</sup> është shumë i ngadalshëm. Në anën tjetër acidet karboksilike të krijuara gjatë oksidimit të molekulave organike formojnë

komplekse me jonin  $\text{Fe}^{3+}$  gjë që pengon regjenerimin e tij në  $\text{Fe}^{2+}$  dhe shkakton ngadalsimin e prodhimit të  $\cdot\text{OH}$  pra dhe atë të degradimit të ndotësve organik. Një sasi e joneve të hekurit humbet gjithashtu si pasojë e precipitimit në formë të hidroksidit ferrik (formimi i fundërrinave gjatë procesit). Ndryshe nga procesi Fenton, në rastin elektro-Fenton  $\text{H}_2\text{O}_2$  përfitohet elektrokimikisht në katodë (Ek. 8):



Oksigjeni futet në tretësirë duke gurgulluar ajër të komprimuar nëpër të. Ndërsa jonet  $\text{Fe}^{2+}$  (katalizatori) shtohen në fillim në tretësirë në sasi shumë të vogla (katalitike) dhe pastaj rigjenerohen elektrokimikisht (Ek. 9):



Në këtë mënyrë reaktivi i Fentonit dhe rrjedhimisht radikalet hidroksile gjenerohen pa ndërprerje në sistem dhe degradojnë materien organike deri në mineralizimin e saj. Përfitimi efikas i  $\text{H}_2\text{O}_2$  dhe rigjenerimi i  $\text{Fe}^{2+}$  eviton të metat e sistemeit Fenton, pra kemi një kinetikë të shpejtë të degradimit, eliminimin e reaksioneve parazite dhe pengimin e formimit të fundërrinës së hidroksidit ferrik, gjë që e bënë procesin elektro-Fenton shumë më efikas se procesi kimik Fenton. Prandaj metoda elektro-Fenton përbën një teknologji të dalluar për shkatërrimin e mikrondotësve organik në mjedis ujor.

Procesi elektro-Fenton varet nga kushtet eksperimentale si: pH, përqëndrimi i katalizatorit, temperatura, intensiteti i rrymës dhe materiali i elektrodave. Vlera optimale e pH është 2.8-3 dhe përqëndrimi i katalizatorit 0.1-0.2 mM. Shpejtësia e reaksionit Fenton rritet me rritjen e temperaturës, por përtej 35-40°C përshpejtohet reaksioni i zbërthimit të  $\text{H}_2\text{O}_2$  gjë që e ngadalson procesin. Materiali i elektrodës ka një rëndësi fundamentale. Platina dhe diamanti i dopuar me bor janë anoda që përdoren shpesh ndërsa karboni sfungjeror, katoda me difuzion oksigjeni etj si katoda. Në këtë punim është realizuar një studim krahasues i efektit të materialit të elektrodës (anodës dhe katodës) ndaj efikasitetit të procesit elektro-Fenon. Rezultatet e fituara do të prezantohen këtu poshtë.

### **Efekti i materialit të anodës në oksidimin anodik të amoksicilinës (AMX)**

Shtatë anoda të ndryshme janë studiuar me qëllim të krahasimit të aftësisë së tyre oksiduese ndaj degradimit të AMX. Për të realizuar këtë studim janë bërë eksperimente të degradimit (transformimi i thjeshtë i molekulës në nënprodukte të oksidimit) dhe

mineralizimit të tretësirave ujore të AMX. Kinetika e degradimit oksidativ të AMX është përcjellur me anë të kromatografisë së lëngët me performancë të lartë (high performance liquid chromatography (HPLC)), ndërsa mineralizimi është bërë me matje të karbonit organik total (KOT) në tretësirë me anë të një analizuesi të karbonit organik total (total organic carbon analyser (TOC)).

Në tabelën 1 janë dhënë konstantet e dukshme ( $k_d$ ), të fituara nga analiza e lakoreve kinetike të oksidimit në intensitete të ndryshme të rrymës, të reaksionit të oksidimit të AMX me radikale hidroksile. Eksperimentet janë bërë në këto kushte:  $[AMX] = 0.1 \text{ mM}$ ,  $[Na_2SO_4] = 50 \text{ mM}$ ,  $V = 250 \text{ ml}$ , si katodë është përdorur çeliku i paoksidueshëm (stainless steel) me sipërfaqe të njëjtë si të anodës ( $24 \text{ cm}^2$ ). Duke u bazuar në vlerat e konstanteve të dukshme të shpejtësisë së reaksionit, konstatohet që shpejtësia e oksidimit të AMX rritet me rritjen e intensitetit të rrymës, por vlerat e tyre ndryshojnë shumë nga një anodë te tjetra. Shohim se DSA, është anoda më së paku efikase për degradimin e AMX, e pasuar nga ajo e grafitit dhe fibrave të karbonit. Vlerat e  $k_d$  për Pt dhe  $PbO_2$  janë mes atyre të gjetura për fibrat e karbonit, karbonit shpuzor dhe BDD, ku kjo e fundit është më efikasja e veçanërisht në intensitete të larta të rrymës. Karbon felt shihet se ka një sjellje më karakteristike; kjo anodë ka kapacitet më të lartë oksidues se anodat tjera të karbonit si grafiti dhe fibrat e karbonit. Kjo mund të spjegohet me sipërfaqen e saj specifike që është shumë më e madhe se e anodave tjera, meqë ajo është një material poroz tre dimensional. Megjithatë verat e  $k_d$  zvogëlohen shumë për intensitet të rrymës 500 mA për shkak të djegies së saj si anodë. Përkundrazi në rastin e BDD vlera e  $k_d$  rittet më së shumti në 500 mA.

*Tabela 1. Konstantet e dukshme të shpejtësisë së degradimit të SMT gjatë trajtimit me procesin elektro-Fenton, si funksion i intensitetit të rrymës së aplikuar dhe materialit të anodës.*

Anoda	BDD	Pt	DSA	$PbO_2$	Grafiti	KF	FK
I (mA)	$k_d / \text{min}^{-1}$						
50	0.02	0.02	0.0006	0.02	0.01	0.05	0.02
100	0.03	0.03	0.003	0.03	0.01	0.08	0.02
300	0.06	0.04	0.003	0.05	0.02	0.2	0.03
500	0.11	0.03	0.008	0.04	0.02	0.09	0.02

Në tabelën 2 janë përmbledhur rezultatet e fituar për efikasitetin e mineralizimit të një tretësire të AMX me anoda të ndryshme.

*Tabela 2. Përqindja e mineralizimit të 250 ml tretësirë të AMX si funksion i intensitetit të rrymës dhe materialit të anodës pas 6 orë trajtimi.*

Anoda	BDD	Pt	DSA	PbO <sub>2</sub>	Grafiti	K F	FK
I (mA)	Eliminimi i KOT pas (%) 6h						
300	86.9	29.8	9.7	62.5	0	0	0
500	92.2	41.3	13.8	81.2	0	0	0
1000	96.3	47.4	22.0	90.6	0	0	0

Përçindjet më të larta të mineralizimit janë arritur duke përdorur anodën BDD pastaj atë të PbO<sub>2</sub>, të Pt dhe të DSA. Anoda e grafitit që kishte aftësi relativisht të mirë oksidimi ndaj AMX deri në 500 mA, e mineralizon atë deri në 43% dhe 37% për rrymat 150 përkatësisht 50 mA, dhe dështon plotësisht në rryma mbi 150 mA për shkak të diegjes së saj në potencial më pozitiv. Vlenë të theksohet se grafiti si anodë në rryma të ulëta jep rezultate të mineralizimit të krahasueshme me platinën dhe pak më të mira se DSA edhe kur në këto elektroda aplikohen intensitete rryme më të larta. Fibrat e karbonit dhe karbon felt dëmtohen (oksidohen) madje edhe në rryma të ulëta, duke i dhënë ngjyrë të zezë tretësirës.

Përkundër rezultateve të mira të oksidimit të fituara me karbon felt, kjo anodë nuk mund të përdoret për mineralizim të ndotësve organik sepse oksidohet madje edhe në rryma të ulëta për kohë të gjatë të elektrolizës. Përkundrazi, në rastin e BDD janë arritur përçindje të mineralizimit 86.9, 92.2, dhe 96.3 % për rrymat 300, 500, 1000 mA. Një shkallë aq e lartë e mineralizimit e arritur me këtë anodë, është rrjedhojë e formimit intenziv të radikaleve hidroksile për shkak të mbipotencialit të lartë të lirimit të O<sub>2</sub> mbi të. Radikalet hidroksile formohen gjithashtu edhe në Pt, PbO<sub>2</sub> dhe DSA por në përqëndrim shumë të vogël. Poashtu një rol të rëndësishëm në shkatërrimin e AMX luajnë edhe oksidantët tjerë si S<sub>2</sub>O<sub>4</sub><sup>2-</sup>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> që formohen në anodë.

### **Efekti i materialit të anodës në procesin elektro-Fenton**

Për të parë efektin e materialit të anodës në procesin elektro-Fenton ngjajshëm si më lart, janë realizuar eksperimente të degradimit dhe mineralizimit të ndotësit model SMT.

Pastaj është bërë analiza e acideve karboksilike dhe joneve minerale që formohen gjatë oksidimit nga heteroatomet që gjenden në strukturën e sulfametazinës. Kushtet eksperimentale kanë qenë: [SMT] = 0.2 mM, [Fe<sup>2+</sup>] = 0.2 mM, V = 300 ml, pH = 3, sipërfaqja e anodës ka qenë 2 x 24 cm<sup>2</sup>, ndërsa si katodë gjithmonë është përdorur karbon felt (KF) me dimensione 23 x 6 x 0.5 cm. Mostrat e tretësirës së SMT që iu kanë nënshtruar elektrolizës janë analizuar me HPLC. Eliminimi i karbonit total (TOC) nga tretësira e elektrolizuar është përcjellur me anë të matjeve me analizues TOC. Analiza e acideve karboksilike është bërë me kromatografi të përjashtimit të joneve dhe jonet minerale me kromatografi jonike.

Konstantet e dukshme të shpejtësisë së oksidimit të SMT me radikalet hidroksile në sisteme të ndryshme elektrolitike janë dhënë në tabelën 3.

*Tabela 3. Konstantet e dukshme të shpejtësisë së degradimit të SMT gjatë trajtimit me procesin elektro-Fenton, si funksion i intensitetit të rrymës së aplikuar dhe materialit të anodës.*

Cel.	Pt	DSA	BDD	KF
I (mA)	$k_d / \text{min}^{-1}$			
50	0.08	0.06	0.07	0.22
100	0.15	0.09	0.12	0.31
200	0.19	0.14	0.18	0.37
300	0.27	0.20	0.24	0.44
400	0.37	0.27	0.27	0.43
500	0.40	0.27	0.25	0.43

*Tabela 4. Konstantet e dukshme të shpejtësisë së degradimit të SMT me radikalet hidroksile të formuara me oksidim anodik, si funksion i intensitetit të rrymës së aplikuar dhe materialit të anodës.*

Cel.	Pt	DSA	BDD	K F
I (mA)	$k_d / \text{min}^{-1}$			
100	0.02	0.01	0.02	0.22
500	0.04	0.02	0.06	0.29

Nga vlera e  $k_d$  në tabelë shihet qartë se shpejtësia e degradimit të SMT rritet me intensitetin e rrymës në të gjitha celulat elektrolitike. Me rritjen e intensitetit të rrymës shpejtësia e prodhimit të  $H_2O_2$  dhe rigjenerimit të  $Fe^{2+}$  është më e madhe dhe si pasojë shpejtësia e degradimit të SMT rritet. Një rritje e tillë e shpejtësisë së degradimit ndodhë deri në një intensitet optimal të rrymës 300-400 mA mbi të cilin intensitet shpejtësia e degradimit nuk rritet më. Ky limit i intensitetit të rrymës mbi të cilin nuk ka përsheptim të reaksionit të degradimit, paraqitet si rezultat i reaksioneve parazite të cilat intensifikohen në rryma të (potenciale) larta. Këto reaksione janë lirimi i  $O_2$  në anodë dhe lirimi i  $H_2$  në katodë. Konstantet e dukshme kinetike (tabela 3) të llogaritura nga lakoret  $[SMT] = f(t)$ , tregojnë një ndryshim të vogël më mes anodave të përdorura, me përjashtim të karbon felt. Në tabelën 4 janë paraqitur  $k_d$ -të për oksidimin anodik, domethënë në mungesë të katalizatorit  $Fe^{2+}$ . Vërehet qartë ndryshimi i madh në mes procesit elektro-Fenton dhe atij të oksidimit anodik. Shpejtësia e degradimit është shumë më e madhe në rastin elektro-Fenton duke iu falenderuar radikaleve hidroksile të formuara nga reaksioni i Fentonit (pos atyre të formuara në anodë).  $k_d$ -të e fituara me karbon felt janë ndjeshëm më të mëdha se ato të fituara me anodat Pt, DDB, et DSA. Në rastin e sistemit elektrolitik BDD/Karbon felt shpejtësia e degradimit të SMT është pak më e vogël se në rastin Pt/Karbon felt. BDD duke qenë një anodë me fuqi të madhe oksiduese, i oksidon jonet  $SO_4^{2-}$  në  $S_2O_8^{2-}$ , pastaj joni peroksodisulfat oksidon jonin ferror (Ek. 10), pra eliminon një sasi të katalizatorit duke zvogëluar kështu shpejtësinë e prodhimit të radikaleve hidroksile.



Së fundi fakti që shpejtësia e degradimit të SMT ndryshon shumë pak mes celulave të ndryshme, shpjegohet duke pasur parasysh se sasia e molekulave të SMT që oksidohen nga radikalet hidroksile që vijnë nga reaksioni elektro-Fenton është dominante ndaj atyre që oksidohen si kontribut i oksidimit anodik.

Konstantet e dukshme të shpejtësisë së degradimit janë shumë të mëdha në celulën Karbon felt/Karbon felt, si dhe janë më të mëdha se në të gjitha celulat tjera elektrolitike.

Eksperimentet e mineralizimit janë bërë në të njëjtat kushte si ato të degradimit dhe përqindjet e eliminimit të karbonit organik total janë prezantuar në tabelën 5.

*Tabela 5. Eliminimi i KOT si funksion i intensitetit të rrymës dhe materialit të anodës gjatë mineralizimit të një tretësire të SMT me anë të procesit elektro-Fenton.*

Cel.	Pt	DSA	BDD	K F	
I (mA)	Eliminimi i KOT pas (%) 2h / 6h			I (mA)	%KOT (2h/6h)
100	35.5/69.6	25.5/62.2	57.2/91.9	50	33.6/68.2
300	55.9/83.9	34.1/71.1	76.4/96.8	100	44.4/70.2
500	71.5/90.3	41.9/76.1	84.7/97.9		
700	61.4/81.7	14.8/75.2	88.2/97.2		
1000	54.7/75.8	26.3/46.1	90.1/98.5		

*Tabela 6. Eliminimi i KOT si funksion i intensitetit të rrymës së aplikuar dhe materialit të anodës (oksidim anodik).*

Cel.	Pt	DSA	BDD	KF
I (mA)	Eliminimi i KOT (%) pas 2h/6h			
100	12.5/15.8	5.2/8.3	48.7/88.1	0/0
500	25.7/36.8	9.6/10.8	69.4/94.6	0/0
1000	24.0/41.4	9.8/9.8	80.9/97.4	0/0

Rezultatet nga eksperimentet e mineralizimit tregojnë një sjellje krejt të ndryshme nga njëra celulë elektrolitike në tjetrën, në krahasim me ato të degradimit. Këtu vërejmë një ndryshim shumë të qartë në efikasitetin e mineralizimit në mes anodave të ndryshme. Shkalla e mineralizimit të SMT rritet me intensitetin e rrymës deri në një limit të intensitetit optimal, që nuk është i njëjti për të gjitha anodat. Në sistemet Pt/Karbon felt dhe DSA/Karbon felt ky limit është 500 mA. Shihet gjithashtu që eliminimi i KOT në celulën DSA/Karbon shpuzor në 300 dhe 500 mA nuk ndryshon shumë, që do të thotë se reaksionet parazite (të përmendura më lartë) intensifikohen ndjeshëm duke filluar nga 300 mA. Në celulat Pt/Karbon felt dhe DSA/Karbon felt përqindja e mineralizimit për 700 dhe 1000 mA është madje edhe më e ulët se për 500 mA, kjo për shkak të ngadalsimit të gjenerimit të reagjentit të Fentonit në katodë, porë gjithashtu për shkak të inhibimit të oksidimit anodik të SMT. Përqindja më e lartë e mineralizimit është arritur me anodën BDD, në tabelën 5 shihet se mineralizimi arrin gati në 100% pas 6 orë trajtimi. Në sistemin BDD/Karbon felt ka dy burime të radikaleve hidroksile: ato që formohen nga reaksioni i Fentonit në tretësirë dhe ato që formohen në sipërfaqe të

anodës, gjë që mundëson një efikasitet të mineralizimit shumë të lartë. Gjithashtu limiti optimal i intensitetit të rrymës për anodën BDD nuk është 500 mA, siç shihet mineralizimi mund të bëhet me efikasitet deri në 1000 mA. BDD duke pasur mbipotencial të lartë të O<sub>2</sub> favorizon formimin e radikaleve hidroksile madje edhe në 1000 mA. Në rastin e anodave Pt dhe veçanërisht DSA radikalet hidroksile mund ta oksidojnë metalin në gjendje më të larta duke formuar okside. Oksidi pastaj liron oksigjenin ose reagon ngadal me molekulat organike në potenciale më të ulëta. Megjithatë përtej 500 mA, rritja e eliminimit të KOT me rritjen e rrymës bëhet më e vogël edhe në rastin e BDD, që do të thotë se lirimi i oksigjenit është gjithmonë një pengesë serioze.

Duke krahasuar mineralizimin me metodën elektro-Fenton dhe oksidimin anodik lehtë vërehet se elektro-Fenton është një proces shumë më efikas kur bëhet fjalë për sistemet Pt/Karbon felt dhe DSA/Karbon felt. Në rastin e sistemit BDD/Karbon felt diferenca është më pak e rëndësishme, kjo me sa duket për shkak të eliminimit nga sistemi elektro-Fenton i një sasive të katalizatorit tashmë të përmendur.

Edhe analiza e acideve karboksilike dëshmon superioritetin e BDD ndaj DSA. Acidet karboksilike të identifikuar gjatë elektrolizës në celulën BDD/Karbon felt ishin: acidi oksalik, glioksilik, piruvik dhe formik, dhe të gjitha këto acide u shkatërruan plotësisht në fund të elektrolizës. Në celulën Pt/Karbon felt acidet karboksilike të identifikuar ishin: acidi oksalik, glioksilik, formik, fumarik, maleik dhe acetik. Në fund të trajtimit mbetet ende një sasi e acideve oksalik dhe formik në tretësirë. Ndërsa në celulën DSA/Karbon felt acidet e identifikuar ishin: acidi oksalik, glioksilik, formik, maleik, malonik, oksamik dhe tartronik. Acidet që mbesin në përqëndrime të ulta pa u shkatërruar në fund të elektrolizës janë acidi oksalik, formik, glioksilik, dhe oksamik.

Me që SMT përmban heteroatomet N dhe S në strukturën e saj, pritet të gjenden në tretësirë jonet përkatëse inorganike NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> dhe SO<sub>4</sub><sup>2-</sup>. Në rastin e anodës Pt, analiza me kromatografi jonike tregon që 90.2% e azotit të përmbajtur në molekulën fillestare lirohet në formë të NO<sub>3</sub><sup>-</sup> (pjesa më e madhe) dhe NH<sub>4</sub><sup>+</sup>, ndërsa SO<sub>4</sub><sup>2-</sup> është liruar në 30 minutat e parë të elektrolizës. Përqëndrimi i joneve NO<sub>3</sub><sup>-</sup> dhe NH<sub>4</sub><sup>+</sup> i gjetur në tretësirën e elektrolizuar është shumë më i vogël - 62% e përqëndrimit fillestar - kur përdoret DSA si anodë, ndërsa joni sulfat lirohet plotësisht. Ndërsa pothuajse i gjithë azoti prezent në tretësirë në molekulën e SMT lirohet në formë të NO<sub>3</sub><sup>-</sup> dhe NH<sub>4</sub><sup>+</sup>, përkatësisht 96.7% e tij. Kurse sulfuri edhe në këtë



rast lirohet në sasi kuantitative si në rastet e mëparme. Një sasi e azotit me sa duket humbet në formë të produkteve të gazta.

### **Ndikimi i materialit të katodës në efikasitetin e procesit elektro-Fenton**

Njëjtë si më parë, eksperimente të degradimit dhe mineralizimit janë bërë për të studiuar efektin e materialit të katodës në procesin elektro-Fenton. Eksperimentet janë zhvilluar në një celulë me vëllim 250 ml, përqëndrimi [SMT] = 0.2 mM ndërsa ai i elektrolitit ndihmës [Na<sub>2</sub>SO<sub>4</sub>] = 50 mM dhe pH e tretësirës është rregulluar në 3. Katodat e testuara: Karbon shpuzor (KSH) me porozitet të ndryshëm, karbon felt (KF), dhe çelik i pa oksidueshëm (S steel) . 6 x 3.5 cm. Si anodë është përdorur gjithmonë platina. Nëpër tretësirë është gurgulluar ajër gjatë gjithë kohës së elektrolizës. Analiza e mostrave të marrura në intervale kohore të caktuara është bërë me anë të HPLC dhe TOC.

Prodhimi i H<sub>2</sub>O<sub>2</sub> përbën një parametër të efikasitetit të një katode në procesin elektro-Fenton. Për këtë arsye është bërë përcaktimi i H<sub>2</sub>O<sub>2</sub> gjatë elektrolizës me katodat: karbon shpuzor 45 ppi, karbon shpuzorë 80 ppi, karbon felt dhe çelik të paoksidueshëm duke lidhur Pt si anodë. Intensitetet e rrymës së aplikuar ishin: 50, 100, 200, 300, 400, 500 mA. Tretësira për elektrolizë përmbante ujë të distiluar me 50 mM elektrolit ndihmës në pH 3 nën gurgullim të përhershëm të ajrit.

Për rrymat 50-200 mA përqëndrimi maksimal i H<sub>2</sub>O<sub>2</sub> në celulën Pt/karbon shpuzor 45 ppi është arritur pas 40 minutave. Për I = 100 mA përqëndrimi maksimal ishte 3.5 mM dhe paraqet përqëndrimin më të lartë nga të gjitha intensitetet e aplikuara të rrymës. Përqëndrimi i H<sub>2</sub>O<sub>2</sub> rritet me rritjen e intensitetit deri në 100 mA, pastaj fillon të zvogëlohet për rryma më të mëdha. Për intensitetet të rrymës 300, 400 dhe 500 mA përqëndrimi i H<sub>2</sub>O<sub>2</sub> të përfituar në tretësirë arrin nivelin e tij maksimal shumë shpejtë (pas rreth 10 minutave).

Ngjajshëm sillen edhe katodat tjera, përqëndrimi maksimal i H<sub>2</sub>O<sub>2</sub> në tretësirë arrihet në intensitetin e rrymës I = 100 mA dhe në rryma më të larta ky përqëndrim është më i vogël. Përqëndrimi maksimal i H<sub>2</sub>O<sub>2</sub> me karbon shpuzor 80 ppi është 2.5 mM, kurse ai i fituar me karbon felt është 1.2 mM. Në celulën Pt/çelik i paoksidueshëm në rastin me të mirë (I = 50, 100 mA) përfitohen vetëm 0.04 mM H<sub>2</sub>O<sub>2</sub>. Këto rezultate të përcaktimit të H<sub>2</sub>O<sub>2</sub> janë koherente me rezultatet e eksperimenteve të degradimit dhe mineralizimit të SMT. Katodat që prodhojnë sasi më të mëdha H<sub>2</sub>O<sub>2</sub> bëjnë të mundur gjithashtu një shkatërrim më efikas të SMT. Një fakt për tu vërejtur është se edhe pse përqëndrimi maksimal i H<sub>2</sub>O<sub>2</sub> i arritur është në

100 mA, shpejtësia e degradimit të SMT rritet deri në 300 mA. Kjo ndodhë për shkak se në prezencë të SMT dhe  $\text{Fe}^{2+}$   $\text{H}_2\text{O}_2$  i formuar konsumohet menjëherë pa pasur kohë të zbërthehet në reaksionet parazitare.

Tabela 7 tregon vlerat e  $k_d$  të reaksionit të oksidimit të SMT me radikalet  $\cdot\text{OH}$  për katodat e studiuar. Si edhe më parë këto vlera janë llogaritur nga drejtëzat  $\ln(C_0/C_t) = f(t)$ . Konstantet kinetike tregojnë që degradimi i SMT është më i shpejtë kur merret karboni shpuzor si katodë, e veçanërisht katoda me porozitet 45 ppi (pore per linear inch). Shihet qartë se vlerat më të ulëta të  $k_d$  për karbonin shpuzor që janë ato për 100 ppi, janë shumë më të lartë se ato të fituara me karbon felt e sidomos se ato me çelik të paoksidueshëm.

*Tabela 7. Konstantet e dukshme të shpejtësisë së degradimit të SMT të fituara me katoda të ndryshme.*

Cel.	KSH 30 ppi	KSH 45 ppi	KSH 60 ppi	KSH 80 ppi	KSH 100 ppi	KF	S steel
I (mA)	$k_d / \text{min}^{-1}$						
50	0.11	0.19	0.19	0.19	0.19	0.06	0.03
100	0.22	0.34	0.28	0.28	0.29	0.07	0.04
200	0.36	0.49	0.43	0.42	0.38	0.14	0.06
300	0.41	0.60	0.50	0.43	0.39	0.16	0.07
400	0.43	0.61	0.48	0.41	0.37	0.11	0.07
500	0.37	0.57	0.38	0.33	0.31	0.09	0.06

Vlerat e mëdha të  $k_d$  për karbonin shpuzor mund të spjegohen me faktin që kjo anodë ka sipërfaqe të madhe duke iu falënderuar porozitetit të lartë, i cili mundëson prodhimin intenziv të reagjentit të Fentonit. Katoda karbon felt ka gjithashtu porozitet të lartë pra sipërfaqe të madhe, por aftësia e saj për ta shkatërruar SMT është shumë më e vogël se e karbonit shpuzor. Karbon felt është material shumë elastik dhe shumë më i dendur se karboni shpuzor, gjë që vështirëson qarkullimin e tretësirës në brendi të katodës, pra ptransporti i masës së  $\text{O}_2$  dhe  $\text{Fe}^{2+}$  është shumë më i ngadalshëm. Ndërsa karboni shpuzor është më pak i dendur dhe më rigjid, strukturë kjo e cila favorizon transportin e masës. Në të njëjtën mënyrë mund të shpjegohen edhe ndryshimet e  $k_d$  në mes katodave të karbonit shpuzor me porozitete të ndryshme. Ndërsa çeliku i paoksidueshëm ka një sipërfaqe specifike shumë të vogël, prej nga gjenerimi i reaktivit të Fentonit është shumë i dobët.

Përqindjet e eliminimit të KOT të tretësirës së SMT janë dhënë në tabelën 8.

*Tabela 8. Përqindjet e eliminimit të KOT në funksion të intnsitetit të rrymës dhe materialit të katodës.*

Cel.	KSH30 ppi	KSH 45 ppi	KSH 60 ppi	KSH 80 ppi	KSH 100 ppi	KF	S steel
I (mA)	Eliminimi i KOT (%) pas 8 h						
50	46.5	63.4	62.1	54.8	54.1	43.4	20.9
100	67.7	76.6	74.3	69.7	69.7	49.7	29.9
300	80.2	91.1	91.2	83.9	82.6	55.6	37.2
500	79.5	90.1	83.6	83.3	80.7	56.6	41.2

Eliminimi i KOT ndjek të njëjtin rend si oksidimi. Katoda më efikase është karboni shpuzor me porozitetet 45 ppi, me përqindje të eliminimit të KOT 91.1% në 300 mA. Kjo vlerë është optimumi mineralizimit në intensitetin optimal të rrymës. Katodat tjera të karbonit shpuzorë japin gjithashtu rezultate shumë të mira të mineralizimit, ndërsa karbon felt është më pak efikase. Qeliku i paoksidueshëm është treguar si katoda më jo efektive nga të gjitha të tjerat.

Dhe në fund pas identifikimit të katodës më të mirë për procesin elektro-Fenton, janë bërë eksperimente me këtë katodë duke përdorur si anodë BDD që tashmë është parë si anoda më e mirë. Eksperimentet janë realizuar në të njëjtat kushte si ato për matjen e efikasitetit të katodave. Konstantet kinetike të dukshme të shpejtësisë dhe përqindjet e eliminimit të KT janë dhënë në tabelën 9.

*Tabela 9. Vlerat e konstanteve kinetike të dukshme dhe përqindjet e eliminimit të KOT të fituara në celulën BDD/Karbon shpuzorë 45 ppi.*

I (mA)	$k_d/\text{min}^{-1}$	Eliminimi i %KOT pas 6 h
<b>50</b>	<b>0.12</b>	<b>77.7</b>
<b>100</b>	<b>0.21</b>	<b>82.6</b>
<b>200</b>	<b>0.35</b>	-----
<b>300</b>	<b>0.38</b>	<b>95</b>
<b>400</b>	<b>0.36</b>	-----
<b>500</b>	<b>0.35</b>	<b>98</b>

Shpejtësia e degradimit të SMT rritet me rrymën deri në 300 mA, falë përshpejtimit të reaksionit të Fentonit, pastaj ajo zvogëlohet, që tregon se është arritur niveli ptimal i

intensitetit të rrymës. Nëse i krahasojmë  $k_d$  e fituara me BDD/Karbon shpuzorë 45 ppi, mund të përfundojmë se ato janë pak më të vogla se ato të fituara me Pt/Karbon shpuzorë 45 ppi e shumë më të mëdha se  $k_d$  e fituara me Pt/Qelik i paksidueshëm dhe Pt/Karbon felt. Përkundrazi mineralizimi është shumë më efikas në celulën BDD/Karbon shpuzorë 45 ppi, gjë që shpjegohet me radikalet hidroksile shtesë që vijnë nga sipërfaqja e anodës BDD nga oksidimi i ujit.

## **CHAPTER 1**

# **INTRODUCTION TO METHODS FOR POLLUTED WATER TREATMENT**

## 1.1 INTRODUCTION

Nowadays the issue of the polluted water is becoming the more and more serious. There are many sources of pollutants in waters: the discharge of industrial effluents and other waste materials in different environmental sites, the usage of chemicals like pesticides, herbicides, insecticides, etc. in agriculture, sanitary activities, the usage of medicaments in human and veterinary medicine etc. The abundance of different chemicals escaping from these sources, has led to the contamination of surface and ground waters with many inorganic and organic pollutants. There are many persistent organic pollutants (POPs) coming from different classes of chemicals, present in the environment<sup>1,2,3,4,5,6,7,8,9,10,11,12</sup>. Among them are chlorinated aromatics including polychlorinated biphenyls (PCBs) dibenzo-p-dioxines (PCDD), furans, polybrominated diphenyl ethers (PBDEs) and different organochlorine pesticides such as DDT, aldrine, HCH (hexachlorocyclo hexane), etc.. Other frequently occurring POPs are phenols and chlorinated phenols. These substances are slightly water soluble so, in aquatic environment, they disperse strongly in solids especially in organic matter. POPs are moderately volatile at ambient temperature, thus they can volatilise from soils, water bodies and vegetation, being resistant in atmospheric conditions they can be transported by air currents to long distances before settling on the ground. So POPs have been found even at Antarctic<sup>13,14,15,16,17,18</sup> and high mountains<sup>19,20,21</sup> in different countries where low temperatures favoured the condensation of POP's vapours. Precipitations play an important role on the POPs settling too<sup>22,23</sup>, several papers have reported their presence in high and low mountain's snow<sup>24,25,26,27</sup>. Pesticides are a class of compounds widely used in agro-culture. They are found in fields where directly applied and also in rivers, lakes, sediments and ground waters where they reach by leaching under the action of precipitations<sup>28,29,30,31,32,33,34,35,36,37</sup>. Among organic pollutants, pharmaceuticals are ubiquitous contaminants of water and soils and their presence in these media have been often reported<sup>38,39,40,41</sup>. Their sources are pharmaceutical industry effluents, hospital effluents, municipal sewage and farms.

Synthetic organic compounds produced for certain purposes and their accompanying by products along with the species generated during combustion processes are not natural constituents of the environment, whereby, they are suspected to alter the normal course of events in the nature. They can enter the food chain<sup>42,43,44</sup> so passing from one trophic level of organisms to the other. There has been evidence for POPs to be implicated into endocrine disruption in humans and animals<sup>45,46,47</sup>. Apart from reproductive effects many organic pollutants are suspected as carcinogens<sup>48</sup>. Investigation on toxicity of pesticides have revealed

that many of them are carcinogenic towards animals thus raising concern for the humans<sup>49,50</sup>. They are also toxic to phototrophic microorganisms<sup>51,52</sup>, fishes and crustaceans<sup>53</sup> micro flora, bees, birds and other non-targeted organisms<sup>54</sup>.

Pharmaceuticals as wide class of chemicals are found at low concentration but permanently entering water systems. Some papers dealt with their influence on aquatic life<sup>55,56,57</sup>. Pharmaceuticals are bioactive substances intended for action against pathogenic microorganisms, but they can also have unintended effects<sup>58</sup>. The concentration of pharmaceuticals in surface waters is below the concentration for which acute toxicity on aquatic organisms has been proven to occur. However, the development of induced antibiotic resistance<sup>59,60</sup>, metabolic, reproductive and other perturbations on aquatic organisms are possible for chronic exposure<sup>57,61</sup>.

The permanent and increasing quantities of organics entering the environment and their ability to influence the biology of living organisms have raised much concern to humans. To face the pollution problem many efforts have been done in terms of making administrative regulation<sup>62,63,64,65</sup> of toxic compounds and also by developing methods for the treatment of waste waters before releasing them in the nature. Some classical methods which are currently in use in waste water treatment plants (WWTP) will be described briefly in the following sections along with emerging technologies. It has been reported that many organic pollutants can escape the treatment process in the classical WWTP<sup>66,67,68,69,70,71,72</sup> as many have been found in their effluents and areas where these effluents pass through. The difficulties to come across when polluted waters are treated by classical methods makes the scientific community to search for other more effective technologies, which have resulted with the development of many new methods for organic pollutants removal from waters. The efforts done have led to the development of AOPs as more effective methods for organic contaminants destruction. And most recently the electrochemical advanced oxidation processes (EAOPs) seems to be very promising technology for environmental applications.

This thesis is devoted to the relatively recently developed EAOPs for organic pollutants removal from contaminated water, namely "electro-Fenton process". This is a method based on the electrochemically monitored Fenton's reagent ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) which produces hydroxyl radicals that are capable of destroying any organic matter. The particularity of this technique consists in the efficient electrochemical generation of these

reagents ( $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ ). As it is an electrochemical method the role of electrode material is crucial, so this work was realised in order to estimate its effect.

This thesis is constituted of five chapters: the introduction where current water treatment technologies are discussed in general. A brief description of the principle of non-destructive methods will be given. AOPs and EAOPs will be treated more rigorously.

The second chapter describes the chemicals used during this study as well as the analytical methods applied to analyse samples from treated solutions.

In the third chapter a comparative study between several anodes on the degradation and mineralization of a model pollutant amoxicillin is realised.

The fourth and fifth chapters have been devoted to the effect of anode and cathode material on the electro-Fenton process efficiency. Sulfametazine, a pharmaceutical of antibiotic class, was used as model pollutant. The degradation and mineralization experiments were realized comparatively, and the formation and evolution of short-chain carboxylic acids and inorganic ions were investigated.

## **1.2. WATER TREATMENT METHODS**

The socio-economic development of the countries is closely related to the chemical industry and to the production of many chemicals which causes the problem of water pollution. So in this frame many efforts have been done during decades in order to find effective technologies for the removal of toxic substances from contaminated waters. The current water technologies can be divided in two general groups; non-destructive (or separative) and destructive ones. We will describe briefly the non-destructive methods for polluted water treatment, whereas the destructive methods will be discussed in more details, since the topic of this work is about a destructive method for the removal of toxic organic compounds from polluted waters.



### **1.2.1. NON-DESTRUCTIVE METHODS**

The non-destructive methods consist on the removal of toxic substances from the polluted water without changing the nature of compounds, that means that these species pass from one phase to another but their initial chemical and physical properties remain unchanged. These are separation techniques. Separated pollutants are in a concentrated phase and will be treated by another technique for final elimination. Some of these techniques are as follows.

#### **1.2.1.1. Adsorption**

Adsorption is a process of separation of a substance from the liquid phase on a solid one, called adsorbent. The adsorption is based on the specific interactions between the adsorbent material surface and the molecules to be adsorbed. This is a separation technique used very frequently in chemical industry and in pollutants removal from waters<sup>73,74,75,76</sup>. The adsorption capacity of the adsorbent depends on the specific surface of the solid material, the pollutant concentration in solution and the affinity to interact between adsorbent surface and pollutant molecules.

One of the most exploited adsorbents in industry and in water remediation particularly, is the active carbon<sup>77,78,79</sup> which can be obtained from many raw materials as for instance: the coco nuts, the wood, the bituminous oil etc. These materials are first carbonised and then activated. Activated carbon has very good textural (high porosity, large specific surface) and physicochemical (surface chemistry) properties that make it possible to explain its excellent adsorption ability<sup>80,81,82,83</sup>. Nonetheless, there are some difficulties accompanying water treatment with activated carbon related to the saturation of adsorbent and its elimination after use. Whereas it's thermal or chemical regeneration is very expensive.

#### **1.2.1.2. Extraction**

Extraction is a separation technique based on the solubility difference of a pollutant in two immiscible liquid phases as for instance water and an organic phase, or liquid-solid<sup>84,85,86</sup>. The solvents can then be regenerated by distillation or consecutive extraction. The concentrated products after treatment can be recycled or burned.

### **1.2.1.3. Membrane filtration**

Undesirable compounds can also be removed from the water by membrane processes<sup>87,88,89,90,91,92,93,94,95</sup>. A membrane is a mediator which controls the transport of chemical species between two liquid phases it separates. When a driving force is applied over the fluids in a given direction the membrane will behave differently towards the transport of different species through it, depending on membrane and species properties. The pollutants separation is based on their affinity for the membrane, their dimensions (pore size) and electrical charge of molecules and ions. Among membrane processes we can distinguish microfiltration<sup>96,97</sup>, ultrafiltration<sup>98,99</sup>, nano-filtration<sup>100,101,102</sup> and reverse osmosis<sup>100,103,104</sup> which differ in the ability to retain particles of different size. So, the choice of type of the membrane is related directly with the size of species to be retained on it.

Membrane filtration processes or physical separation and their efficacy depend on their porosity and permeability, its nature, and also on the size of the particles to be removed. There are several advantages attributed to membrane processes; the separations need small quantities of chemicals, automatable procedures, good selectivity and better water quality. But, some molecules, especially pesticides cannot be retained by all membranes<sup>105</sup> thus representing a disadvantage. The relatively high cost of the membrane treatment is another inconvenience. Certain membranes retain bacteria but not viruses (except nanofilters) which are smaller than their porosity.

### **1.2.1.4. Membrane distillation**

Membrane distillation is a separation technique employing a hydrophobic membrane which serves as a selective barrier for contaminants removal from water<sup>106,107,108,109</sup>. The driving force through the membrane is the pressure difference between the two sides of the membrane pores. The difference of partial vapour pressure is provided by the difference in the temperature. Volatile compounds evaporate, diffuse or convect across membrane pores and are condensed or removed on the opposite side of the system (pure water), whereas non-volatile compounds are rejected (pollutants). Unlike in membrane filtration, in membrane distillation process no mechanical force is needed. In comparison with common distillation lower temperatures and pressures are required to attain a significant flux of water through the membrane. Typical feed temperatures varies in the range 30°C -60°C, thus permitting the exploitation of waste or low-grade energy, as well as the use of alternative energy source such as solar or wind energy<sup>110</sup>.

### **1.2.2. DESTRUCTIVE METHODS**

These methods are called destructive methods because the organic pollutants are chemically transformed on other species than the initial compounds, generally the transformation proceeds until their conversion into carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). Commonly applied destructive methods include biological, thermal and chemical (AOPs) treatments.

#### **1.2.2.1. Biological methods**

In the biologic technology the acting agent are bacteria that consume organics in the solution which serve as their nutrition source. Then, through the metabolism the organic material is transformed into cellular biomass which settles on the bottom of the reactor. There are two types of biological treatment; aerobic treatment<sup>111,112,113,114</sup> which takes places in the presence of air and utilizes the bacteria (called aerobes) demanding molecular oxygen for the conversion of the organics into CO<sub>2</sub>, H<sub>2</sub>O and biomass, and anaerobic treatment<sup>115,116,117</sup> which is realised in the absence of air by bacteria (called anaerobes) which do not require the molecular oxygen to assimilate the organic impurities. The final products of organic destruction by anaerobic treatment are methane, carbon dioxide and biomass. This technology requires long residence time for microorganisms to degrade the pollutants particularly when pollutants show toxic activity<sup>118,119,120</sup>.

#### **1.2.2.2. Thermal method (incineration)**

Thermal treatment consists on the incineration of toxic wastes and it is a very effective method especially in case of small concentrated volumes. Nevertheless it is very expensive, needs storage and transport to incinerators, and presents considerable emission of hazardous compounds<sup>121</sup>.

### **1.2.3. ADVANCED OXIDATION PROCESSES (AOPs)**

Other technologies to be mentioned are oxidation methods such as wet oxidation (which uses air or oxygen as oxidation agent), treatment using oxidizing agents like potassium permanganate, chlorine, hydrogen peroxide, and the so called advanced oxidation processes (AOPs) and electrochemical advanced oxidation processes (EAOPs) that are based on the in

situ production and reaction of a highly oxidizing agent, the hydroxyl radical. We will not discuss here about all these techniques, except for the two last ones which have been proven to be very effective on organic pollutants degradation in waters and especially the later that is related to the indirect electrochemical oxidation technique for polluted water remediation, called electro-Fenton process, which is the subject of this thesis. So, the following section/subsections will be devoted to the description of advanced oxidation processes giving the principal of work of each technique.

### **1.2.3.1. THE REACTIVITY OF HYDROXYL RADICALS**

Non-destructive methods do not give a complete solution for pollutants elimination because the material charge separated (concentrate) from contaminated water must be treated by thermal or chemical techniques, or be deposited somewhere, thus representing another problem of pollution to deal with. Considering this fact, efforts have been done to find more effective methods to improve the overall treatment process of pollutants. In this frame the advanced oxidation processes (AOPs)<sup>122,123,124,125,126,127,128,129</sup> have emerged as effective and versatile techniques for environmental applications. There exist many advanced oxidation processes; all of them are based on the production and action of hydroxyl radicals, very oxidizing species that attack the most of organic compounds. Thus, they are distinguished only in the way of generation of hydroxyl radicals. These radicals are extremely unstable and react with organics<sup>130,131,132,133,134</sup> in solution transforming them in less harmful products, like oxygenated organic compounds and low molecular organic acids. They are characterised with high non-selectivity which is an advantage for an oxidant used in wastewater treatment and pollution problems, but their application becomes difficult in case of the treatment of waters containing inorganic scavenging material. The rate constants for degradation reactions of organics with hydroxyl radical range between  $10^7 \text{ mol}^{-1} \text{ s}^{-1}$  and  $10^{10} \text{ mol}^{-1} \text{ s}^{-1}$ .

Hydroxyl radicals are also found in the natural conditions, actually it was proven that the oxidation of hydrocarbons in troposphere involves the action of hydroxyl radicals as key oxidants<sup>135</sup>. Solar radiations on iron hydroxide complexes<sup>136</sup>, direct photolysis of nitrate and nitrite<sup>137,138</sup> in natural waters and hydrogen peroxide<sup>139</sup> can be natural sources of hydroxyl radicals. But the concentrations of these radicals are low at natural conditions in waters.

Among the most powerful oxidizing agents used in polluted water remediation hydroxyl radicals have been selected as the most suitable one because they fully comply with some important environmental and practice requirements:

They do not introduce secondary pollution problems

They do not manifest any kind of toxicity

They are not corrosive for equipment

They are very powerful oxidizing agent

The control of their production is relative simple, especially in case of EAOPs.

Hydroxyl radical is one of the most oxidizing agents among the oxygenated radicals ( $E^{\circ} = 2.8 \text{ V/SHE}$  in acidic media at  $25^{\circ}\text{C}$ ). In high alkaline medium it is present in the form of its conjugated base  $\text{O}^{\bullet-}$ ,  $\text{pK}_a = 11.9$  (reaction 1)<sup>140</sup>, and reacts slowly as a nucleophile whereas in acidic media it reacts as an electrophile. Its maximum absorption wave-length is at  $225 \text{ nm}$  with a molar extinction coefficient of  $540 \text{ L mol}^{-1} \text{ cm}^{-1}$  at  $188 \text{ nm}$ <sup>140</sup>. These species diffuse very slowly and its diffusion coefficient is of the order of  $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ <sup>140</sup>.



It is considered that hydroxyl radicals react in three types of reactions with organic, organometallic and inorganic materials which will be described further.

#### **1.2.3.1.1. Reaction type and mechanism of hydroxyl radicals**

Advanced oxidation processes, principally are based on the chemistry of hydroxyl radicals ( $\bullet\text{OH}$ ) which are the principal intermediate reactive species responsible of oxidation of organic compounds. They react by three different mode of reaction<sup>141</sup>:

- **Hydrogen abstraction (dehydrogenation)**

Hydroxyl radicals can oxidize the organic compounds by abstraction of hydrogen atoms from saturated hydrocarbon chains creating radical sites. Then these sites can be attacked by oxygen. This process leads to a homolytic split of a C – H bond and the formation of the alkyl radical following to equation 2:

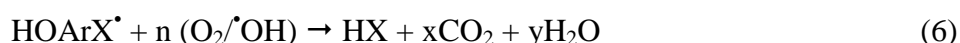


The  $\text{R}\cdot$  radical generated this way react with molecular oxygen to give peroxide radicals  $\text{ROO}\cdot$ , initiating a degradation reaction sequence that leads to the mineralisation of RH d<sup>140</sup>:



- **Electrophilic addition on unsaturated bonds (hydroxylation)**

Hydroxyl radicals attack high electron density regions, like unsaturated bonds of aromatic compounds, alkenes and alkynes:



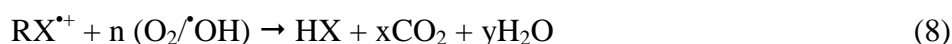
We can predict the possible hydroxylation sites of aromatic organic compounds according to orientation rules of electrophilic aromatic substitution given in the Table 1.

*Table 1. The orientation of hydroxylation reaction by substituents in aromatic compounds<sup>142</sup>.*

Orientation groups on ortho and para positions	Orientation groups on meta positions
Moderate and strong activators	Strong desactivators
-NH <sub>2</sub> , -NHR, -NR <sub>2</sub> , -NHCOR, -OH, -OR	-NO <sub>2</sub> , -CF <sub>3</sub> , -NR <sub>3</sub> <sup>+</sup> , -COOH, -COOR, -COR, -SO <sub>3</sub> H, -CN
Weak activators	Weak deactivators
Alkyles, phenyls	-F, -Cl, -Br, -I

- **Electron transfer (oxydo-reduction)**

The electron transfer leads to the ionisation of the molecule. This mechanism becomes important when hydrogen abstraction and electrophilic addition are inhibited by multiple halogen substitution or steric obstruction. These reactions produce organic radicals which, by addition of O<sub>2</sub>, give peroxy radicals initiating oxidative chain reactions that result in the mineralization of the initial compound:



### 1.2.3.1.2. Reaction rate constant between $\cdot OH$ and organic compounds

The reaction of hydroxyl radicals with organic substrate (S) obeys the second order law of kinetics:



So we can write, for decay rate of S, a differential equation describing the decay of the substrate concentration with the time as follows:

$$-\frac{d[S]}{dt} = k[HO^{\bullet}][S] \quad (10)$$

Where k is the reaction rate constant between hydroxyl radicals and organic substrate, S.

The rate determining step during the process of organics oxidation is the generation of hydroxyl radicals, because this reaction is relatively sluggish in comparison with their consumption by organic molecules and intermediate products created during the degradation of the initial compound. These reactions are very fast with reaction rate constants of  $10^7 \text{ mol}^{-1} \text{ L s}^{-1}$  to  $10^{10} \text{ mol}^{-1} \text{ L s}^{-1}$

Under these conditions the hydroxyl radical concentration can be considered to be quasi-constant with the time so we can write:

$$\frac{d[HO^{\bullet}]}{dt} = 0 \quad (11)$$

The concentration of  $\cdot OH$  being constant we can rewrite the equation (10) in this way:

$$-\frac{d[S]}{dt} = k_{app}[S] \quad (12)$$

where  $k_{app}$  is the apparent rate constant as follows:

$$k_{app} = k[HO^{\bullet}] \quad (13)$$

If we rearrange the equation (12) and integrate it;

$$-\int_{S_0}^S \frac{d[S]}{[S]} = k_{app} \int_0^t dt \quad (14)$$

we obtain the equation which describes the kinetics of degradation of a given substrate S by hydroxyl radicals  $\cdot\text{OH}$ :

$$\ln \frac{[S]}{[S_0]} = -k_{app}t \quad (15)$$

S and  $S_0$  are the concentration of S at time  $t = 0$  and at a giving time t. The plot of  $\ln \frac{[S]}{[S_0]}$  versus t gives a straight line. Then, from the slope of this line we can estimate experimentally the pseudo-first order apparent rate constant  $k_{app}$  for the oxidation reaction of S.

The second order reaction rate constant (the absolute rate constant of the reaction between S and  $\cdot\text{OH}$ ) can be then determined by the competition kinetic method. It is based in the competition for  $\cdot\text{OH}$  radicals between the substrate S with a constant  $k_s$  to be determined versus a reference compound S' for which the rate constant  $k'_s$  is well known<sup>143</sup>. Assuming that the degradation of both compounds S and S' results only from the  $\cdot\text{OH}$  the decrease of concentrations can be given by following equations:

$$-\frac{d[S]}{dt} = k_{app}[HO\cdot][S] \quad (16)$$

$$-\frac{d[S']}{dt} = k'_{app}[HO\cdot][S'] \quad (17)$$

After we have integrated these equations we can combine and arrange them to obtain the following one:

$$\ln \frac{[S_0]}{[S_t]} = \frac{k_s}{k'_s} \ln \frac{[S'_0]}{[S'_t]} \quad (18)$$

Thus, knowing  $k'_s$  the rate constant for substrate S,  $k_s$  can be calculated from the slope of the graph  $\ln \frac{[S_0]}{[S_t]}$  versus  $\ln \frac{[S'_0]}{[S'_t]}$ . This method will be employed to determinate the absolute rate constant for the reaction of pollutant by  $\cdot\text{OH}$ .

Some rate constant values for the reaction of  $\cdot\text{OH}$  with organic compounds are given in the table 2<sup>144</sup>.



Table 2. Rate constants of the reactions of some organic compounds with hydroxyl radicals.

Compound	k (mol <sup>-1</sup> L s <sup>-1</sup> )
2,4,6-Trinitrotoluene (TNT)	2.06x10 <sup>10</sup>
2-Methylphenol	1.1x10 <sup>10</sup>
4-Methylphenole	1.2x10 <sup>10</sup>
N-Phenylhydroxylamine	1.5x10 <sup>10</sup>
Azobenzene	2x10 <sup>10</sup>
Benzene	7.9x10 <sup>9</sup>
Toluene	5.1x10 <sup>9</sup>
Phenol	6.6x10 <sup>9</sup>
4-Nitrophenol	3.8x10 <sup>9</sup>
Aniline	1.5x10 <sup>9</sup>
Atrazine	2.4x10 <sup>9</sup>
Phthalic anhydride Anhydride Phtalique	9.1x10 <sup>8</sup>
Glyoxilic acid	2.3x10 <sup>8</sup>
Oxalic acid	1.4x10 <sup>7</sup>
Formic acid	8.2x10 <sup>7</sup>
Acetic acid	2.8x10 <sup>7</sup>

According to this table, hydroxyl radicals react more rapidly with unsaturated compounds than with aliphatic organic acids that appear in the solution as by-products of the oxidation of compounds with higher molecular mass. The attack of hydroxyl radicals on aromatic compounds results in the formation of cyclohexadienyl radicals. The most easily attacked positions of aromatic ring that contain an electron donor substituent are the ortho and para positions of an electron donor substituent. It is also important to emphasise that hydroxyl radical can react with inorganic substances and water treatment reactive either. But generally the reaction with inorganic compounds is slower than that with organic ones (Table 3).

Table 3<sup>145,146</sup> Reaction rate constants of hydroxyl radicals with some inorganic compounds.

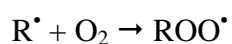
Compound	k (mol <sup>-1</sup> L s <sup>-1</sup> )
HSO <sub>4</sub> <sup>-</sup>	3.5-1.7x10 <sup>9</sup>
Cl <sup>-</sup>	4.3x10 <sup>9</sup>
ClO <sup>-</sup>	8.8x10 <sup>9</sup>
Cu <sup>2+</sup>	3.5x10 <sup>8</sup>
Fe <sup>2+</sup>	3.2x10 <sup>8</sup>
H <sub>2</sub> O <sub>2</sub>	2.7x10 <sup>7</sup>

Moreover, the oxidation pathway of organic compounds is very complex including many types of reactions:

(I) Initiation reaction where radical species R<sup>•</sup> are generated;



(II) Propagation stage where radicals react with other organic molecules or with dissolved oxygen in the solution;



(III) Termination stage when radicals recombine between them;



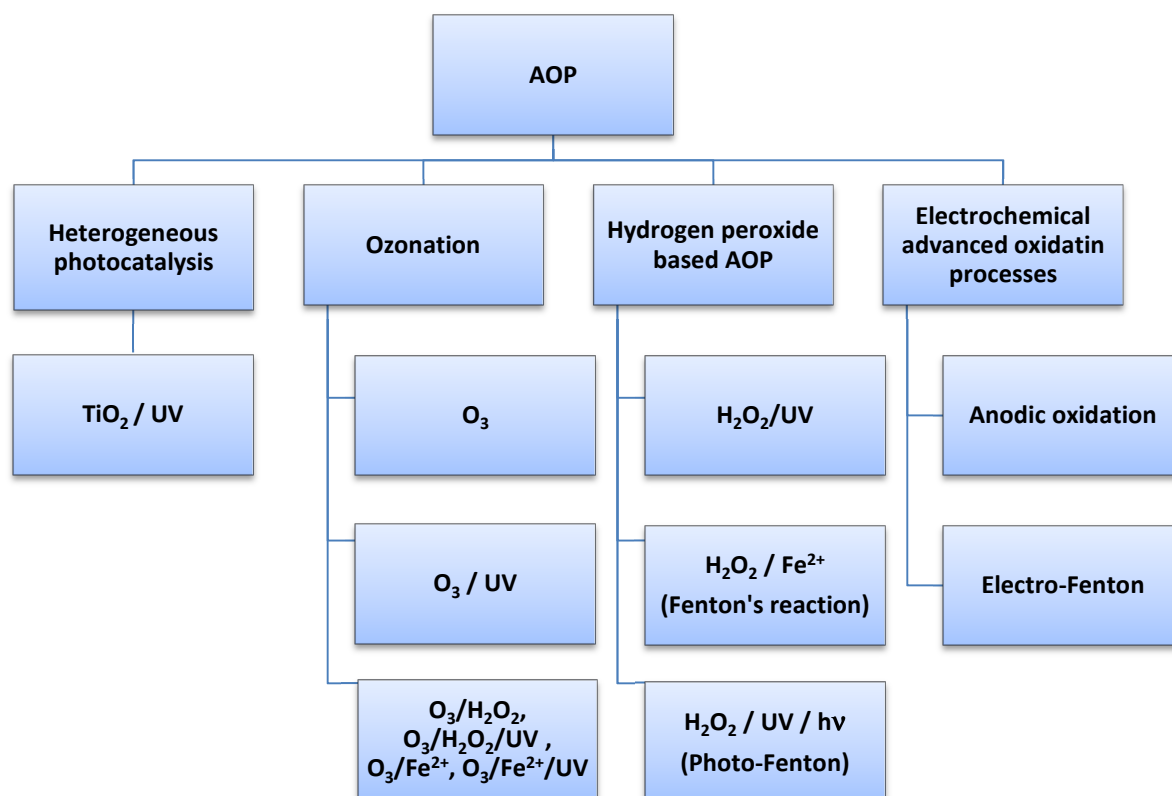
Other oxidants like; H<sub>4</sub>RnO<sub>6</sub>, XeF, OF<sub>2</sub> are extremely reactive, harmful in their reduced state and tend to form carcinogenic trihalomethanes with organic materials<sup>147,148</sup>. Thus only oxygen based oxidants which do not contain neither metal nor halogens are suitable for water treatment.

### 1.2.3.2. METHODS FOR HYDROXYL RADICAL GENERATION: AOPs

As already pointed out, there exist several ways to generate hydroxyl radicals. The possibility to generate  $\cdot\text{OH}$  in different ways makes AOPs very versatile techniques because a proper technique can be applied in order to comply with the specific treatment requirements. Nonetheless, AOPs make generally use of chemical reagents as  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ , more economical ways of treatment must be considered<sup>123</sup>. A combination of AOPs with other economically more acceptable water treatment technologies as with biological techniques can be also applied<sup>149,150,151</sup>.

Concerning the possibility of AOPs application pollution load, generally expressed as chemical oxygen demand (COD), is a very important factor because it indicates if waste water with a given content of COD can be suitably treated by AOPs. In fact, only wastes with relative low COD ( $5.0 \text{ g L}^{-1}$  or less)<sup>123</sup> can be effectively treated by means of AOPs since wastes with higher COD content will consume large amounts of reactants.

A classification scheme of advanced oxidation processes is given below (Fig. 1) and then the description of each AOP model separately, comprising their principles and the reaction mechanisms. AOPs can be divided in four principal groups depicted in the schema below.



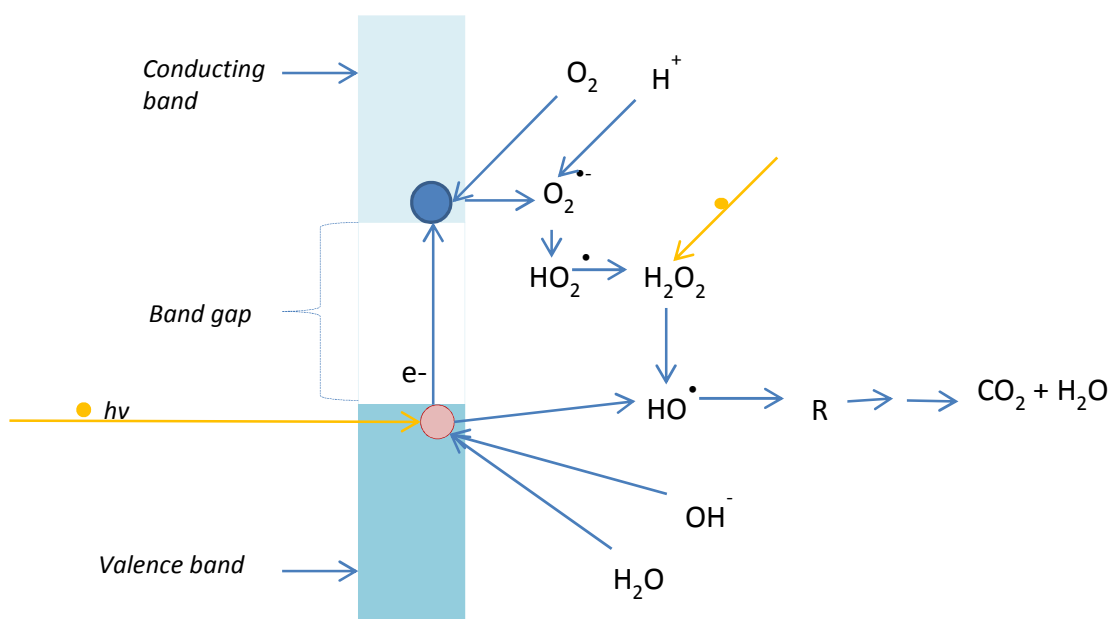
**Fig. 1.** Tentative classification of advanced oxidation processes.

#### **1.2.3.2.1. Heterogeneous photocatalysis (TiO<sub>2</sub>/UV)**

This technique makes use of semi-conductors and UV light to generate hydroxyl radicals ( $\cdot\text{OH}$ ) as active reagent in pollutants degradations<sup>152</sup>. According to the band theory of solids there are available energy levels for electrons in valence band of solids. These bands are created from atomic orbitals such as 1s, 2s, 2p orbitals and so on. If a band is created from partially filled orbitals in separated atoms, the resulting band will be only partially filled too. So, there will be a number of unfilled orbitals in the band for electrons to move into. The electrons can easily move from one orbital to another, and the solid will be an electrical conductor. If the highest occupied band in a crystal is completely filled and the band gap energy is too high, there will be no way for electrons to move and the crystal will be an insulator.

Unlike insulators, in semi-conductors there is a lower band gap between the highest energy of the filled band in the ground state and the lowest energy of the upper band that is empty in the ground state. If the band gap is not larger compared with  $k_{\text{B}}T$  ( $k_{\text{B}}$  Boltzmann constant,  $T$  temperature), some electrons from lower-energy band will occupy states from upper band and the crystal will conduct some electricity. This characteristic of semi-conductors enables them to be suitable for different applications. In this section will be discussed their involvement as catalyst in photo catalytic degradation of pollutants.

Heterogeneous photocatalytic degradation of organic pollutants, as the case of TiO<sub>2</sub>/UV, has been subject of many studies<sup>153,154</sup>. Among many catalysts tested so far, TiO<sub>2</sub> seems to be the most attractive owing to some attributes such as good performance, low cost and high stability<sup>155,156,157</sup>. As mentioned above the electronic structure of semi-conductors is constituted of available energy levels called bands; the lower one which is filled with electrons is called the valence band and the upper one called the conducting band. If the semi-conductor particles are exposed to an energy source as UV radiation exceeding the energy of band gap the electrons will be excited from the valence band to the conducting band leaving a positive hole ( $h^+$ ) in the valence band and an electron ( $e^-$ ) in the conducting band. This process is shown on the figure 2.

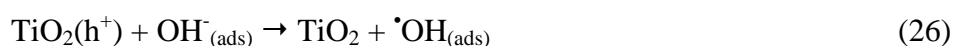
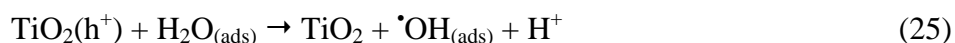


**Fig. 2.** Hole-electron pair generation during heterogeneous photocatalysis with TiO<sub>2</sub> and the mechanism of action on organic molecules.



The photon energy must be exactly of the value needed to excite electron to the conducting band in order to avoid its interaction with other matters in the solution. The band gap energy for TiO<sub>2</sub> is 3.02 eV which is equivalent to a 400 nm radiation wavelength<sup>152</sup>.

The hole in the valence band can react with adsorbed water or hydroxide ions at the surface to form hydroxyl radicals (reactions (25) and (26)). On the other hand, conducting band electron can reduce adsorbed oxygen to form hydroperoxide radicals which further are transformed into hydroxyl radicals<sup>123,158</sup>.



Whereas from the O<sub>2</sub><sup>•-</sup> produced in reaction (27) hydrogen peroxide can also be generated (reaction (29)):



Thus, more hydroxyl radicals can be produced from  $\text{H}_2\text{O}_2$  generated this way<sup>159,160</sup>:



Some adsorbed substrate can be directly oxidized by electron transfer at the catalyst ( $\text{TiO}_2$ ) surface, because the  $\text{e}^-$  and  $\text{h}^+$  potentials are sufficient to oxidise many organic molecules; +0.5 V to -1.5 V versus SHE and +1 to 3.5 V versus SHE respectively<sup>156,161</sup>.



Unfortunately a considerable part of electron-hole pairs recombine reducing the quantum yield.

$\text{TiO}_2$  has been largely studied at concentration of order  $1 \text{ g L}^{-1}$  to  $5 \text{ g L}^{-1}$ . This catalyst can be utilised in suspension form or immobilised<sup>162,163</sup>. It is biologically and chemically inert, insoluble and cheaper than other catalyst as  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CdS}$  and  $\text{ZnS}$ . Currently there are many research on the fixation of  $\text{TiO}_2$  on various support to avoid its separation from water after treatment.

#### 1.2.3.2.2. UV-photolysis

The degradation of organics in solutions can be also realised by exposing the sample to UV irradiation source<sup>164,165</sup>. Direct photolysis involves the interaction of pollutant molecules with light to bring about their fragmentation in intermediates as follows;



It has been shown rapid degradation of organic pollutants in dilute solutions<sup>166</sup>. However, the most of these methods require long residence time and considerable energy consumption.

They are less effective than methods where radiation is combined with hydrogen peroxide, ozone or heterogeneous catalyst.

### 1.2.3.3. METHODES BASED ON OZONE

#### 1.2.3.3.1 Ozonation

The development of large scale ozone generators along with reduced operating cost has enabled its use for the treatment of effluents containing hazardous pollutants<sup>167,168,169,170</sup>. Compared to some other oxidizing agents it is more efficient and not harmful for most of living organisms, because no intruder substances are added in the treated water.

Ozone is an oxygen allotrope (O<sub>3</sub>). It boils at -112 °C and is an explosive and highly reactive endothermic blue gas ( $\Delta_f G^\circ = +163 \text{ kJ mol}^{-1}$ ). It decomposes into molecular oxygen;



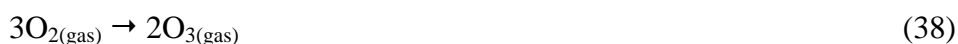
but this reaction is thermodynamically non spontaneous in the absence of UV light or a catalyst since it requires energy to occur.

Ozone has a sharp odour from which is derived its Greek name “Ozein” that means “to smell”. It is a diamagnetic molecule. The ozone molecule is angular and has a bond angle of 117°<sup>171</sup>. Gaseous ozone is blue, liquid ozone is blue-black, and solid ozone is violet-black. Ozone has low water solubility and it is relatively unstable in water undergoing a pretty fast decomposition. Its half life time at 20 °C is between 20-30 min<sup>172</sup>, in basic media this decomposition is accelerated by the presence of OH<sup>-</sup><sup>173</sup>.

Ozone is a very strong oxidant with a redox potential of 2.07 V/SHE (at 25°C). It is exceeded in oxidising power only by F<sub>2</sub>, <sup>•</sup>O, <sup>•</sup>OH and perxenate (XeO<sub>6</sub><sup>4-</sup>) ions. Thus ozone can oxidize many organic compounds and this makes it very useful in water treatment.



But for the usage of ozone it must be produced over site where it will be used in order to avoid the transportation risks as it is explosive. Its formation reaction can be written;



This reaction is endothermic and some energy is required to bring it about. As the ozone is unstable at high temperatures the energy must be provided from a radiation or electricity source. In practice it is produced by electrical discharges.

The degradation mechanism of organics by O<sub>3</sub> in waters depends on the pH. At low pH the direct oxidation will take place whereas at higher pH the indirect process by intermediate of hydroxyl radicals is present<sup>158,160</sup>. If the ozonation is developed under acidic conditions the decomposition of ozone which is caused by OH<sup>-</sup> ions<sup>160,174</sup>, will be slower and consequently the production of hydroxyl radicals will be limited. So the main pathway in organics destruction remains the direct oxidation which is selective and quite slow with kinetic rate constants of 1-10<sup>3</sup> mol<sup>-1</sup> L s<sup>-1</sup>. In direct oxidation, ozone reacts with organic's functional groups through electrophilic, nucleophile, and dipolar addition reactions<sup>160,174</sup>. The indirect oxidation is developed through hydroxyl radical formation which reacts immediately and non-selectively with organic matter. This process is initiated by hydroxide anions (reaction (39)) and is much more rapid than the direct oxidation and occurs at high pH values following a very complex pathway described below<sup>160</sup>;

Initial stage:



Propagation stage:



Termination stage:







Pollutants degradation:



Normally, at  $\text{pH} < 4$  the direct oxidations dominates, at  $4 < \text{pH} < 9$  both mechanism are present, and at  $\text{pH}$  higher than 9 the indirect pathway is the principal reaction. Further, intermediate's nature will depend on that whether the degradation will be brought about by direct or indirect pathway. Ozonation for water treatment is limited by ozone low solubility in water and its explosive nature.

### 1.2.3.3.2. Ozone photolysis (O<sub>3</sub>/UV)

This is an effective method for the abatement of refractory and toxic compounds as many works have shown so far<sup>175,176,177,178,179,180,181</sup>. In this method ozone saturated aqueous solutions are irradiated with UV-C light of  $\lambda = 254 \text{ nm}$  in order to produce the hydroxyl radicals. The molar absorption coefficient of ozone is  $3600 \text{ L mol}^{-1}\text{cm}^{-1}$  much higher than the molar absorption coefficient of hydrogen peroxide, thus allowing a quantitative interaction between ozone and UV radiation.

Photolysis of ozone will lead to the formation of the hydrogen peroxide (reaction (51)) which is decomposed into 2 hydroxyl radicals under UV-C irradiation (reaction (52)):



Moreover, hydrogen peroxide intensifies the ozone decomposition into hydroxyl radicals<sup>160</sup>:



This method depends on the quantity of ozone supplied into the solution and the wave length of radiation<sup>182</sup>. It is limited by the turbidity of the solution since the light will be prevented to come in contact fully with the solution leading to some loss of the radiation.

### 1.2.3.3.3. Ozonation combined with homogeneous catalysis ( $O_3/H_2O_2$ , $O_3/H_2O_2/$ , $O_3/Fe^{2+}$ , $O_3/Fe^{2+}/UV$ )

The oxidizing power of ozone and ozone/UV reagents can be enhanced considerably by the use of some catalysts. The addition of homogeneous catalyst as;  $H_2O_2$ , has led to the shorter residence time for the treatment of pollutants<sup>183,184,185,186,187</sup>. Ozone reacts with  $H_2O_2$  when it is present in solution in the form  $HO_2^-$  to give hydroxyl radicals, whereas its reaction with the undissociated form  $H_2O_2$  is very sluggish ( $k < 0.01 \text{ mol}^{-1} \text{ L s}^{-1}$ ) so it can be neglected.

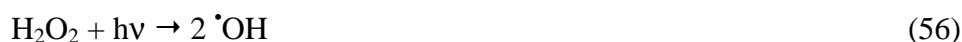


Other interesting catalysts to be combined with ozone are iron (II) and iron (III) in absence or presence of UV light<sup>188,189,190</sup>.

### 1.2.3.4. HYDROGEN PEROXIDE BASED AOPs

#### 1.2.3.4.1. Hydrogen peroxide photolysis ( $H_2O_2/UV$ )

Both,  $H_2O_2$  and UV irradiation can be used separately to achieve the degradation of some contaminants, but their combination gives a more effective mean for water contaminants treatment<sup>191,192</sup>. UV irradiation of 200-280 nm (with  $\lambda_{\text{max}} = 260 \text{ nm}$ ) possesses the necessary energy to induce the homolytic decomposition of hydrogen peroxide<sup>193,194</sup> producing hydroxyl radicals.



In this case the main oxidant acting on pollutants degradation is hydroxyl radical, implying that the rate of oxidation depends on the  $\cdot OH$  production rate. But this reaction is limited by the low absorption coefficient of  $H_2O_2$  ( $\epsilon = 18.6 \text{ mol}^{-1} \text{ L cm}^{-1}$  at  $\lambda_{\text{max}} = 260 \text{ nm}$ ) However, it was found that the rate of  $H_2O_2$  photolysis is pH dependent and it increases at high pH values. This happens because at high pH the peroxide anion  $HO_2^-$  may be formed which shows a higher molar absorption coefficient ( $\epsilon = 240 \text{ mol}^{-1} \text{ L cm}^{-1}$ )<sup>195</sup> at 254 nm than  $H_2O_2$ .



The presence of other species in the solution which absorbs the radiation and turbidity reduce the quantum yield of reactions (56) and (57) and consequently the efficacy of pollutants removal.

This method has already been commercialised because of its relatively low economical cost.

#### 1.2.3.4.2. Fenton's reaction

This technique is based on hydrogen peroxide action including catalytic amounts of Iron (II) salts. The use of this mixture of reagents originates from early works of Fenton<sup>196</sup> concerning the oxidation of tartaric acid. When in the tartaric acid solution was added iron sulphate and hydrogen peroxide followed by alkalisation it got violet coloured. So, Fenton proposed this reaction as an identification test for tartaric acid. But the use of this mixture of reagents, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> nowadays called the Fenton's reagent, is considered for the oxidation of organic compounds began later by 1930s after a radical mechanism for the decomposition of H<sub>2</sub>O<sub>2</sub> was proposed<sup>197</sup>. Afterwards, the Fenton's reagent for the use in destruction of toxic organic compounds became very frequent<sup>132,198,199,200,201,202,203,204</sup>.

It has been accepted that Fenton's reaction includes a series of reactions initiated by the principal reaction between H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> in acid medium given below;

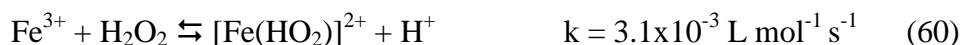


The generation of hydroxyl radicals ( $\cdot\text{OH}$ ) during this reaction has been defined<sup>205</sup> and confirmed by different methods such as chemical probes or spectroscopic techniques namely spin-trapping<sup>206,207</sup>. Also by means of pulse radiolysis, many works concerning rate constants of the reactions involved in Fenton's chemistry have been carried out<sup>208</sup>.

For the Fenton's reaction to take place, only small quantities of iron salts are needed because iron (II) is regenerated from the so-called Fenton-like reaction between excess of hydrogen peroxide and iron (III) formed by reaction (59):



This is not a direct reaction as iron (III) firstly forms an adduct with hydrogen peroxide, reaction (60) and then this species gives the regenerated iron (II) and hydroperoxyl radical HO<sub>2</sub> $\cdot$  (reaction (61)):



Hydroxyperoxyl radicals  $\text{HO}_2^\bullet$  produced in this reaction have less oxidation power compared  $^\bullet\text{OH}$  and do not react strongly with organic molecules<sup>209</sup>. Considering reaction rate constants we can see that reaction (59) is much slower than Fenton's reaction (58), and consequently  $\text{Fe}^{2+}$  regeneration due to this reaction is not very rapid. Anyways,  $\text{Fe}^{2+}$  ion can be regenerated due to some other very rapid reactions: as  $\text{Fe}^{3+}$  reduction by  $\text{HO}_2^\bullet$  reaction (62), a reaction (63) with an organic radical formed during initial organic molecule degradation by  $^\bullet\text{OH}$  and a reaction (64) with a superoxide anion ( $\text{O}_2^{\bullet-}$ )<sup>198,210</sup>.



The species which contribute in  $\text{Fe}^{2+}$  regeneration are produced in reactions denoted below<sup>140,211,212</sup>:

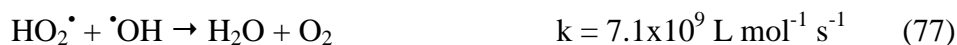


Although these reactions enable the Fenton's reaction to proceed for a period of time, some of them play also a negative role towards the Fenton's reaction rate. In the reactions (59) and (65)  $\text{Fe}^{3+}$  and  $^\bullet\text{OH}$  act as scavengers of  $\text{H}_2\text{O}_2$  destroying it in competition with reaction (58). The organic radical  $\text{R}^\bullet$  participates in  $\text{Fe}^{2+}$  regeneration but also in  $\text{Fe}^{2+}$  oxidation by reaction (70), along with dimerization reaction (71):



Some other reactions involved in Fenton's chemistry are also<sup>141</sup>:



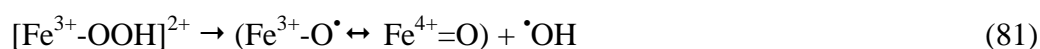


The inhibiting role of these reactions restrict the values of several experimental variables, for instance the occurrence of reaction (72) decreases the concentration of  $\text{Fe}^{2+}$  ions in the medium<sup>213,214</sup> and along with the reaction (65) they are the major parasitic reactions that decrease the oxidation power of Fenton reagent. Other reactions (75-79) are not significant because of the relatively low presence of radical species in the solution in comparison with other non-radical molecules.

It has been proven that radical scavengers play an important role in the rate of Fenton's reaction. Such species are chloride, sulphate and nitrate ions<sup>215</sup>. Anyways, in many studies this behaviour has not been observed. The presence of some other oxidizing agents has also been pointed out<sup>216</sup>. There have been some experimental works which have brought some evidence over the existence of high-oxidation state iron complexes under certain conditions<sup>217</sup>. So, the formation of mononuclear  $\text{Fe}^{4+}$  oxo-complex was proposed<sup>218</sup>, which can oxidise organics only by electron transfer:



Thus, researchers found an agreement between hydroxyl radical and ferryl ion-complex mechanisms predominating one or other depending on the particular operating conditions. The co-generation of  $\cdot\text{OH}$  and high-oxidation state oxo-iron complex has been demonstrated by time-resolved laser flash photolysis spectroscopy<sup>219</sup>:



The  $[\text{Fe}^{3+}\text{-OOH}]^{2+}$  is an excited state species and the overall reaction can be interpreted as an intraligand reaction. On the basis of these results it has been proposed that ferryl formation in secondary reactions under classical Fenton condition cannot be ruled out.

The Fenton process efficiency is depended of many experimental variables<sup>141</sup>, as: pH,  $[\text{Fe}^{2+}]$ ,  $[\text{H}_2\text{O}_2]$  and temperature. The concentrations of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  are the most fundamental parameters. The efficiency of the process is strongly related to the solution pH. The most favourable pH values for the Fenton reaction to proceed are  $2.8 \leq \text{pH} \leq 3.0$  because at these values the majority of the total iron species in the medium are present in the form of  $\text{Fe}^{2+}$ . When the pH is lower than 2.8 the predominant species of iron present in the solution is  $\text{Fe}^{3+}$  as  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  or barely  $\text{Fe}^{3+}$ , deteriorating reaction efficiency. At pH = 1 oxygen concentration does not change, and this probably because of the stabilisation of  $\text{H}_2\text{O}_2$  with  $\text{H}^+$  in  $\text{H}_3\text{O}_2^+$  (solvation of  $\text{H}^+$  with  $\text{H}_2\text{O}_2$ ) which reduces the reaction with  $\text{Fe}^{2+}$ . The Fenton's reaction will also slow down when the pH exceeds the 0 value of pH 3.5. In the case of pH > 5.0, iron ions will precipitate as  $\text{Fe}(\text{OH})_3$  thus the catalyst will be removed from the solution and consequently the Fenton reaction efficiency slows down. At pH = 4.0 hydroperoxy complexes such as  $[\text{Fe}(\text{HO}_2)_2]^+$  and  $[\text{Fe}(\text{OH})(\text{HO}_2)]^+$  are the dominant forms of iron. Temperature is another influencing parameter. The rate of Fenton's reaction increases with the temperature but simultaneously the degradation of hydrogen peroxide in  $\text{O}_2$  and  $\text{H}_2\text{O}$  does. The optimum concentrations of catalyst  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  are depended on each other and experiments are done in the basis of optimisation of their ratio instead of studying them separately.

There are some advantages<sup>141,220,221</sup> related to the Fenton treatment of polluted waters, among them we can mention the following advantages:

- Simple and easy operation.
- Easy to handle chemicals.
- No energy consumption.

Whereas as disadvantages can be highlighted the followings:

- Relatively high cost and risks related to the transport and storage of  $\text{H}_2\text{O}_2$ .
- High amounts of chemicals to acidify the effluents at favourable pH for the Fenton reaction and neutralise the effluent after the treatment.
- High iron sludge quantities at the end of treatment.

- The complete mineralisation is not attained because of the formation of some iron (III) complexes with carboxylic acids that cannot be destroyed by bulk hydroxyl radicals.

Anyways, some of these drawbacks can be reduced. Iron sludge can be prevented by using solid iron-coating catalysts such as zeolites, alumina, iron-modified clays, ion-exchange resins etc. On the other hand to improve the efficiency of Fenton's process can be coupled with other techniques such as biological oxidation, membrane filtration, coagulation and light assisted Fenton (photo-Fenton) process<sup>222,223,224,225,226</sup>.

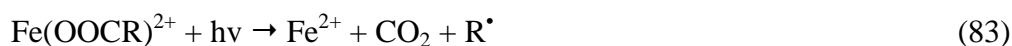
#### 1.2.3.4.3. Photo-Fenton ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}/h\nu$ )

Fenton's process for polluted water treatment can be improved by combining with UV photolysis in order to enhance the degradation reaction rate<sup>227,228,229</sup>. When the solution under treatment with Fenton's reagent is irradiated with UV light, supplementary hydroxyl radicals are obtained from reaction (56) resulting to the formation of more radicals in the medium. Apart this  $\text{Fe}^{2+}$  liberated from  $[\text{Fe}(\text{OH})]^{2+}$  will catalyse the Fenton's reaction (reaction (82))<sup>230</sup>:

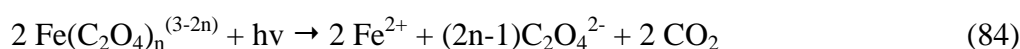


thus avoiding large accumulation of  $\text{Fe}^{3+}$  and providing  $\text{Fe}^{2+}$  necessary. This reaction allows maintaining Fenton's reaction operative for longer time. The quantum yield for the reaction (82) was found to be 0.14-0.19 at 313 nm<sup>136</sup>.

Additionally, UV irradiation can degrade some oxidation by-products or break down the bonds (reaction 83)<sup>230</sup> in complexes formed between iron and carboxylic acids supporting the regeneration of  $\text{Fe}^{2+}$ .



For example complexes that iron(III) can form with carboxylic acids such as  $\text{Fe}(\text{C}_2\text{O}_4)^+$ ,  $\text{Fe}(\text{C}_2\text{O}_4)_2^-$  and  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  can be decomposed by irradiation of wavelengths 250-280 nm according to the reaction (84)<sup>141</sup>:



The use of irradiation lamp (to provide artificial light) with restricted life time is a drawback of this process as well as considerable hydrogen peroxide concentration needed. Its

cost can be reduced if the UV radiation is replaced with solar light as it has been shown in some works<sup>231,232,233</sup>.

### **1.2.3.5. ELECTROCHEMICAL METHODS**

Electrochemical destruction of pollutants in aquatic medium involves, in the destruction process, the action of electrons, coming from a current source. The electrochemical treatment is brought about in an electrochemical cell without the use of specific expensive and relatively dangerous reagents. This permits a very good compliance with environmental requirements. Two electrochemical methods are distinguished:

- I. Direct oxidation of organic molecules on the anode surface which includes two mechanisms<sup>234</sup> (explained below).
- II. Indirect oxidation realized by in-situ generation Fenton's reagent on the cathode compartment called electro-Fenton process<sup>235</sup>.

These two methods constitute the subject of this thesis and will be discussed in the two subsequent sections.

#### **1.2.3.5.1. Anodic oxidation**

During the anodic oxidation of organic pollutants the molecules can be oxidized by two principal mechanisms; direct electrochemical reaction via electron transfer between electrode (anode) and molecule, and indirect oxidation via oxidants generated on the anode, called also mediated oxidation<sup>236</sup>. The direct electrochemical oxidation occurs below the oxygen onset potential and it subsides above it. At the oxygen evolution potential, organics oxidation proceeds in competition with oxygen evolution reaction (OER). Thus, the degradation of pollutants will depend on the mechanism of OER which strongly varies with the electrode (anode) material<sup>237,238,239</sup>. Generally, anodes exhibiting a high overpotential for OER show better efficiency on organics degradation. Many electrode materials have been studied for their electro-catalytic properties towards organics oxidation efficiency<sup>240,241,242,243,244,245,246,247,248,249</sup>. One of the anodes representing low overpotential for OER is iridium dioxide IrO<sub>2</sub> based dimensionally stable anode (DSA)<sup>250</sup>. The evolution of oxygen on these types of anodes is thought to occur in three steps and involves the change of oxidation state of the metal oxide during water discharge according to the simple reactions



(85) - (87)<sup>251</sup>. The first step is the charge transfer by the discharge of water, with the formation of active species on active sites of the anode surface:



The second step is a second electron transfer step with the deprotonation of the adsorbed hydroxy species:



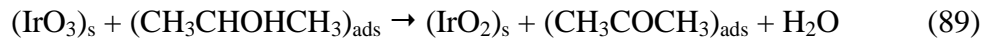
And the third one is the formation of oxygen molecules and the regeneration of two active sites on the surface:



In another work<sup>252</sup> a similar scheme for the oxidation of isopropanol on IrO<sub>2</sub> based anodes was proposed. Firstly the IrO<sub>2</sub> is oxidised to IrO<sub>3</sub> via hydroxyl radicals according to the global reaction (88):



Then the chemical oxidation of adsorbed isopropanol to acetone by the electrogenerated IrO<sub>3</sub>, reaction (89):



And also, oxygen evolution in competition with reaction (89) via decomposition of surface IrO<sub>3</sub> according to the reaction (90):



The OER is the prevailing process leading to low degradation efficiencies and loss of electrical energy.

At high oxygen evolution potential electrodes the organics oxidation process follows a different mechanism. The most remarkable high oxygen evolution overpotential electrode is boron doped diamond (BDD)<sup>253</sup>. This electrode is prepared by chemical vapour deposition of methane mixed with metallic boron or B(OCH<sub>3</sub>)<sub>3</sub> as dopant<sup>254,255</sup>. Titanium, niobium and silicon and other materials can be used as substrate for the diamond deposition<sup>242,256,257</sup>. The water discharge on BDD electrode is thought to occur through a path giving hydroxyl radicals

as intermediate species<sup>258</sup>. A simplified mechanism for the organics oxidation on boron doped diamond electrodes has also been proposed<sup>259</sup>:

First the discharge of water molecules producing hydroxyl radicals physisorbed on BDD surface as very reactive oxidising agents (reaction (91)):



Then the oxidation of organic molecules:



And the competitive oxygen evolution reaction:

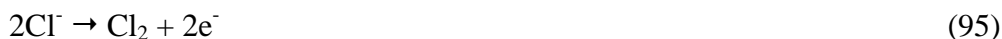


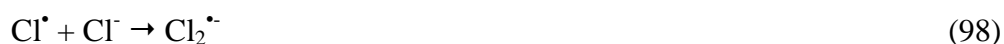
BDD electrode is considered a high overpotential oxygen evolution anode, so the oxygen evolution reaction is much less intensive in comparison with case of DSA type anodes. Nevertheless, a considerable electrical energy is wasted because of OER. Hydroxyl radicals generated cannot oxidize diamond neither they are chemically adsorbed on diamond surface but they are physically adsorbed. The fact that they are loosely adsorbed on the electrode surface let them quasi free so that they can react with other substances which are found in the vicinity of the electrode. So the oxidation of organic pollutants by hydroxyl radicals takes place only at the electrode surface because the diffusion coefficient of hydroxyl radicals is very low<sup>140</sup> (because of its high reactivity).

The pollutant's degradation takes place in the bulk solution also via other oxidants generated on the anode<sup>260,261</sup>. Other oxidants originate from the supporting electrolyte. If sodium sulphate is used as supporting electrolyte the peroxydisulphate anions will be present in the solution, following the reaction (94)<sup>262</sup>:



Whereas when the supporting electrolyte is sodium chloride,  $\text{Cl}^-$  is expected to be oxidized<sup>262</sup> either by direct electron transfer at anode surface or by a reaction with  $\text{HO}^\bullet$  in the vicinity of electrode, reactions (94)-(101):





Therefore BDD electrode has very interesting properties which make it versatile. Its use in polluted water treatment is outstanding and many works have been dedicated on it<sup>263,264,265,266</sup>.

#### 1.2.3.5.2. Electro-Fenton process (Indirect electrochemical oxidation)

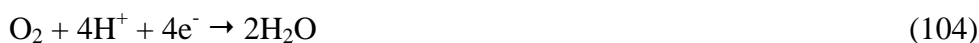
The Electro-Fenton process is an indirect electrochemical method for the destruction of toxic and/or persistent micro-pollutants in contaminated waters<sup>141,235</sup>. This method is based on the Fenton's reaction chemistry<sup>198,266</sup>. As described in one of the previous sections Fenton's reagent ( $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ ) is used to produce very reactive hydroxyl radicals  $\cdot\text{OH}$  that are used to eliminate toxic organic compounds from contaminated waters. In the classical Fenton process,  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  are externally added to the reaction medium and the concentration of target molecules is monitored until the depletion of oxidising agents. As already mentioned the complete mineralisation of pollutants is not achieved because of the  $\text{Fe}^{3+}$  inactivation by ligand action of carboxylic acids<sup>267</sup>, but also because of the mere Fenton's reagent consumption. Whereas in the electro-Fenton method, Fenton's reagent is produced directly in the polluted water to be treated<sup>141,200,201,268,269,270,271,272,273</sup>.  $\text{Fe}^{2+}$  is added in the solution in a catalytic quantity as an iron salt and it is continuously regenerated on the cathode surface via the one electron transfer) (reaction (102)) from  $\text{Fe}^{3+}$  formed during Fenton's reaction (58):



On the other side  $\text{H}_2\text{O}_2$  is also electro-generated at the cathode from the two electron reduction of oxygen in acidic media ( $\text{pH} \approx 3$ ) according to the reaction (103):



Whereas its reduction to water by reaction (104) is avoided by choosing a potential (or current) more positive than that of this second reduction step of  $\text{O}_2$ .



The oxygen needed for this reaction is introduced in the solution by bubbling compressed air (or oxygen). Thus, the oxygen reduction includes the dissolution of oxygen gas in the solution, its transportation to the cathode and finally the reduction to hydrogen peroxide. Some oxygen also comes from the naturally oxygen dissolution in water according to the Henry's law and the oxygen evolution on the anode from water discharge (reaction (107)):



Once  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  produced as described above, they react following to the Fenton's reaction (reaction (58)) to give hydroxyl radicals which in turn oxidize organics. Afterwards,  $\text{Fe}^{3+}$  generated in reaction (58) reduced to  $\text{Fe}^{2+}$  according to reaction (102). On the other hand  $\text{H}_2\text{O}_2$  keeps being produced electrochemically at the cathode. So, the Fenton's reagent is continuously supplied in the electrochemical cell in a catalytic way.

Apart the electrogeneration reactions of Fenton's reagent, parasitic reactions exist too and their intensity depends on electrochemical cell configuration and other operation conditions. For example in an undivided cell  $\text{Fe}^{2+}$  can be electrochemically oxidized to  $\text{Fe}^{3+}$  at the anode:



$\text{Fe}^{3+}$  can precipitate in the very vicinity or in the pores of three dimensional cathodes as  $\text{Fe}(\text{OH})_3$  because of the basic conditions created by water reduction.

Hydrogen peroxide accumulation in the system and its stability depends on working conditions<sup>141</sup>. Some usual parasitic reactions are reactions (104) and itself decomposition to oxygen and water<sup>274</sup> (reaction (109)):



A parasitic reaction related to the cell configuration is its oxidation on the anode if an undivided cell is used. This reaction involves hydroperoxyl radicals as intermediates:



So all possible parasitic reactions make the accumulation of hydrogen peroxide be lower than levels expected from its electrogeneration. Its identification and dosage in the solution can be done by different methods, one of them is the spectrophotometric determination based in the Ti(IV)-H<sub>2</sub>O<sub>2</sub> complex which gives a yellow colour and absorbs at 410 nm<sup>275</sup>.

It is worth noting that all parasitic and regeneration reactions of H<sub>2</sub>O<sub>2</sub> and Fe<sup>3+</sup> involved in the Fenton's chemistry can account for the electro-Fenton process also. However, some parasitic reactions as those between  $\cdot\text{OH}$  and H<sub>2</sub>O<sub>2</sub>,  $\cdot\text{OH}$  and Fe<sup>2+</sup> which are the most important ones are reduced or eliminated.

#### **1.2.3.5.3. Influence of the experimental parameters on the electro-Fenton process**

Many experimental parameters affect the electro-Fenton efficiency process. Among them the most important ones are: solution pH, catalyst concentration, electrode material, applied current, temperature and oxygen or air feed rate.

- **The influence of pH**

Electro-Fenton process efficiency is strongly dependent on solution pH as already discussed for the Fenton's chemistry. Several works have shown that the optimal pH value is 2.8-3 where a maximum generation of hydroxyl radicals was observed<sup>276,277</sup>. For pH > 3.5 the rate of mineralisation of organics starts to slow down because a part of Fe<sup>3+</sup> precipitates as Fe(OH)<sub>3</sub>. At pH < 1 it becomes very slow since Fe<sup>2+</sup> forms complexes with H<sub>2</sub>O<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>. The nature of acid utilised for pH adjustment as well as the nature of supporting electrolyte affects also the rate of pollutants degradation via the acid and salt anions involvement in the oxidation processes<sup>277,278</sup>. At low pH the formation of iron complexes with Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> is also possible whereas SO<sub>4</sub><sup>2-</sup> apart the complexation action scavenges hydroxyl radicals too. It has been found that the removal rate of orange II decreases with the acids utilised for pH adjustment in the order: ClO<sub>4</sub><sup>-</sup> > Cl<sup>-</sup> >> SO<sub>4</sub><sup>2-</sup><sup>279</sup>.

- **Catalyst concentration**

The catalyst is one of two fundamental reagents of the electro-Fenton process and its importance is crucial<sup>213,280</sup>. The rate of degradation reaction increases with the catalyst concentration until a given value owing to the intensification of Fenton's reaction (58). Then

after a certain concentration a reverse effect is observed because of the parasitic reaction (72) which consumes hydroxyl radicals in competition with organics oxidation following the reactions (67)-(68). Thus, an optimal concentration of catalyst is required in order to attain the maximum rate of contaminants oxidation. This optimum concentration depends on the nature of the cathode utilized in the process. If a carbon felt cathode is utilized the optimum concentration for  $\text{Fe}^{2+}$  is 0.1-0.2 mmol  $\text{L}^{-1}$  at  $\text{pH} = 3$ <sup>271,281</sup>, whereas higher concentration is required in case of carbon-PTFE gas diffusion electrodes (GDE), namely 0.5-1.0 mmol  $\text{L}^{-1}$   $\text{Fe}^{2+}$  range is the optimum<sup>276,282</sup>. Greater concentration of catalyst for the GDE electrodes is necessary because of their lower ability of  $\text{Fe}^{2+}$  regeneration in comparison with carbon felt cathodes. Moreover,  $\text{H}_2\text{O}_2$  is produced in greater extent at GDEs so a greater concentration of  $\text{Fe}^{2+}$  is required to intensify reaction (58), otherwise parasitic reaction (65) with the production of  $\text{HO}_2^{\bullet}$  (weak oxidant) can become important.

- **Applied current**

Fenton's reaction driven by electrical current makes electro-Fenton a remarkable method for polluted water treatment. The current applied produces and maintains  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentrations during electrolysis<sup>269,283</sup>. The variation of current affects the production rate and the concentration of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  and consequently the rate of degradation of organic molecules. When the current intensity is increased the quantity of  $\text{H}_2\text{O}_2$  in the solution increases owing to the acceleration of reaction (103). An increase of current intensity results in a more effective  $\text{Fe}^{2+}$  regeneration too (102). Since the concentration of both  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  is increased with the current intensity, the quantity of hydroxyl radicals will be higher and as a consequence faster organics removal are achieved<sup>284,285,286,287</sup>. Nevertheless, the acceleration of organics degradation reaction rises until a certain current intensity beyond which no improvement of the efficacy of process is observed<sup>288,289,290</sup>. This limiting degradation current is a consequence of parasitic reactions which compete with  $\text{O}_2$  reduction to  $\text{H}_2\text{O}_2$  (reaction (103)) namely the hydrogen evolution reaction on cathode. At high current intensities mass transport of  $\text{O}_2$  and  $\text{Fe}^{3+}$  towards cathode becomes the rate determining step of the electrochemical reactions of production of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ , thus any increase in current intensity beyond this limit will lead to a loss of energy without any improvement in the treatment process. Low current intensities give pollutants removal with higher electricity effectiveness but longer electrolysis, and if the current intensity is considerably low no significant remediation of water is attained.

The use of other catalysts other than  $\text{Fe}^{2+}$  is also possible. Among them  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  have been tested showing that optimal concentrations vary from one to other<sup>213,291</sup>.

- **Temperature and oxygen or air feed**<sup>141</sup>

Oxygen is feed continuously in the solution by introducing compressed air or oxygen. This provides a saturated solution with oxygen to reach maximum  $\text{H}_2\text{O}_2$  production. Temperatures up to 35-40°C enhance hydroxyl radical formation, but higher temperatures enhance at the same time hydrogen peroxide decomposition and other parasitic reactions<sup>141</sup>.

- **Electrode material**

Electrode (cathode and anode) material plays a very important role on electro-Fenton process since the principal reagents (oxidants) are generated on. Thus, this thesis is devoted to study the role of electrode material on electro-Fenton treatment of polluted waters. Many cathodes have been studied so far for their performance in the electro-Fenton technology for water treatment, such as: graphite<sup>292,293</sup>, mercury<sup>294</sup>, carbon-PTFE  $\text{O}_2$  gas diffusion<sup>295,296,297</sup>, carbon felt<sup>132,285,298</sup>, reticulated vitreous carbon (RVC)<sup>299</sup>, carbon sponge<sup>283</sup> and carbon nanotubes<sup>300,301</sup>. However, to the best of our knowledge, there has been no a systematic study to compare the performance of these materials to find the better one for the process. Therefore, such a study constitutes the subject of this thesis.

A cathode material for electrochemical water treatment must have some characteristics that make them fit to the electro-Fenton process. A cathode must have high hydrogen evolution overpotential in order to provide high hydrogen peroxide yield with high current efficiencies, low catalytic activity for hydrogen peroxide decomposition, chemical and physical stability, good electrical conductivity and low economical cost. Some materials like mercury support  $\text{H}_2\text{O}_2$  production, however they are very toxic so not useful for water treatment.

Carbon is a very appropriate material for environmental application as it does not show any toxic effect towards living beings and represents all the characteristics required for electrochemical water remediation. Considering the fact that oxygen is poorly soluble in water three dimensional large surface area cathodes are needed to obtain reasonable current efficiencies in pollutants removal. Such electrodes are GDEs with thin and porous structure favouring the circulation of injected oxygen through its pores until the solution electrode

interface. These electrodes allow fast O<sub>2</sub> reduction to have H<sub>2</sub>O<sub>2</sub> accumulation owing to high number of active sites on their surface. GDEs are constituted of carbon particles bonded with PTFE in a cohesive layer.

Carbon felt is a three dimensional large specific surface cathode where the Fenton's reagent generation takes place very rapidly. In comparison with GDEs there is a lower accumulation of the H<sub>2</sub>O<sub>2</sub> because its H<sub>2</sub>O<sub>2</sub> generation ability is lower than that of GDEs<sup>235,295</sup>. Contrarily, the regeneration of Fe<sup>2+</sup> at carbon felt is faster than at GDEs<sup>286</sup> leading to lower accumulation of H<sub>2</sub>O<sub>2</sub> because hydroxyl radicals are immediately produced through Fenton's reaction.

Anode material is another source of oxidants that participate in oxidation of organic matter. Different anodes used in direct anodic oxidation can be used for electro-Fenton. When a high overpotential oxygen evolution anode is used hydroxyl radicals can be generated from the water discharge along with other oxidants like S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, ClO<sup>-</sup> etc. depending on the supporting electrolyte present in the solution. In fact, the supporting electrolyte plays always an important role in pollutant degradation<sup>279</sup> in extents varying from anode material. An anode providing high concentration of hydroxyl radicals is boron doped diamond (BDD) which is widely being used in environmental studies and also for the particular case of electro-Fenton<sup>145,288,302,303,304,305</sup>, thanks to its distinguished performance for water remediation. Noble metals represent interesting materials to be used for water remediation owing to their resistivity in the very oxidising medium in the electrochemical reactor for organic contaminants destruction. Platinum is one of the preferred anodes as it does not leave toxic ions in the solution<sup>200,235,306,307</sup>. Organics are oxidized directly on its surface by electron transfer or by hydroxyl radicals generated in low quantities, or by other oxidants in the bulk. Parasitic reactions restrict the efficiency of oxidation on anodes too. Beyond a given potential, O<sub>2</sub> evolution prevails greatly, reducing the organics oxidation at the anode.

In this work, for the comparative study on the degradation efficiency of different electrodes tested, two organic molecules namely amoxicillin (AMX) and Sulfamethazine are taken as models which will be described in the following sub-section.



### 1.3. MODEL MOLECULES

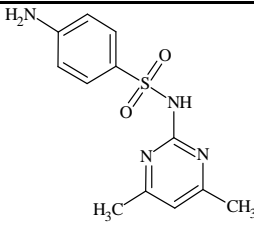
Sulfamethazine [SMT] and amoxicillin [AMX] has been taken as model pollutants to estimate the effectiveness of their removal from aqueous solution when a certain electrode system is utilized.

The occurrence of antibiotics in the environment has been firmly reported in several papers<sup>40,41,308,309,310</sup>. World production and consumption of pharmaceuticals has been steadily increasing. After the metabolic cycle in humans or animal's organisms that have been treated metabolites of medicaments pass in the environment<sup>40,41</sup>. As medicaments remains partially unchanged during their metabolism in the organism, they leave the body and can be found in the environment as well<sup>40,308</sup>. The main source of antibiotics in the environment is anthropogenic input from wastewater discharge, manure disposal and aquaculture<sup>308</sup>. Classical waste water treatment plants sometimes are not sufficient enough thus becoming a source of contamination. Some authors<sup>311</sup> have reported that 80% of used antibiotics enter the environment despite the use of various processes in waste water treatment plants. Once they are released, they come in contact with living organisms threatening their normal life course. A very serious effect is that the continuous exposure of bacteria to antibiotics can provoke genetic transformation leading to the antibiotic resistant bacterial species<sup>312,313,314</sup> being harmful for human's health and the natural order, and difficult to treat.

#### 1.3.1. Sulfamethazine

Sulfamethazine (SMT) is an antibiotic of sulphonamides class and is used in human and veterinary medicine. Sulphonamides are synthetic antibiotics with a broad spectrum of action against Gram-positive and Gram-negative bacteria. They have also been used as animals feed as growth promoters<sup>315</sup>. SMT is one of the most commonly used sulphonamides thus widely present in natural systems<sup>308,316,317,318</sup>. It has been observed that SMT represents toxic effects to daphnia magna and synergism in the presence of sulfametazine<sup>55</sup>, fertility effects in mice<sup>319</sup> and thyroid hormone homeostasis in rats<sup>320</sup>. Physicochemical properties of SMT are given in the table 4 below. The EC<sub>50</sub> and LC<sub>50</sub> are the effects observed at times given in the table.

Table 4. General properties of sulfamethazine

Chemical structure			
Molecular weight	278.33 gmol <sup>-1</sup>		
CAS No	57-68-1		
Solubility	1.5 gl <sup>-1</sup> <sup>321</sup>		
pKa <sub>1</sub>	2.65 (aromatic amine) <sup>322</sup>		
pKa <sub>2</sub>	7.65 (sulfonamide nitrogen)		
Log K <sub>ow</sub>	0.89 <sup>322</sup>		
K <sub>oc</sub>	60-208.3 <sup>322</sup>		
Vapor pressure	8.62x10 <sup>-9</sup> mm Hg at 25°C <sup>323</sup>		
Half-life in environment	1% after 64 days in loamy sand and clay silt <sup>324</sup>		
Toxicity (acute) (mg L <sup>-1</sup> )	Vibrio fischeri (bacteria)	5 min luminescence inhibition EC <sub>50</sub>	303.0 <sup>325</sup>
	Algae (pseudokirchneriella subcapitata)	72 h growth EC <sub>50</sub>	8.7 <sup>326</sup>
	Duckweed (lemna gibba)	7 days wet weight EC <sub>50</sub>	1.277 <sup>327</sup>
	Invertebrate (daphina manga)	48 h immobilization EC <sub>50</sub>	105 <sup>328</sup>
	Fish (oryzias latipes)	48 h survival LC <sub>50</sub>	>100 <sup>325</sup>

The removal of SMT from waters has been studied in several works. Its adsorption on coal and coconut based activated carbon has been studied where similar removal efficiencies were deduced for both types of activated carbon<sup>329</sup>. Treatment of SMT by aerobic sludge and isolated *Achromobacter* sp. S-3 <sup>330</sup> showed relative good removal efficiency and COD, depending on sludge retention time where it increased from 25.9% SMT and 25% COD to 83.9% SMT and 59.1% COD when retention time increased from 0.5 h to 4.0 h. Garcia-Galan studied the removal of SMT from sewage sludge by the white-rot fungus *Trametes versicolor*<sup>331</sup>. Chemical oxidation<sup>332</sup> and electro-Fenton biodegradability improvement have been also considered<sup>333</sup>.

### 1.3.2. Amoxicillin

Amoxicillin (AMX) is an antimicrobial proscribed for the treatment of different disease and is considered as the most important  $\beta$ -lactam antibiotics. About 80% of the AMX leaves the body unmetabolised<sup>334</sup> whereby it is expected to be found frequently in municipal waters. Watkinson<sup>335</sup> reported its presence in hospital effluents, WWTP influents, WWTP effluents and environmental waters at maximal concentrations of 0.9, 6.94, 0.05 and 0.2  $\mu\text{g L}^{-1}$  respectively. AMX presence in the environment<sup>336,337,338,339,340,341,342</sup> and its fate<sup>343,344,345,346,347</sup> has been reported in several other papers. Diverse effects on *Synechocystis* sp. (algae) have been reported<sup>348</sup>; addition of AMX at the levels of  $\text{mg L}^{-1}$  significantly inhibited  $\text{O}_2$  evolution of *Synechocystis* sp., where treatment with 150  $\text{mg L}^{-1}$  AMX for 24 h led to 80.5% inhibition in  $\text{O}_2$  evolution. Toxicity towards several other non-targeted species is evident and has been considered up now in several studies<sup>349,350,351,352</sup>. The phenomenon of genetic modifications due to the AMX presence, in bacteria which results with antibiotic resistance, has been observed as well<sup>353</sup>.

Several AMX removal methods from aqueous solution have been studied. Watkinson assessed the removal of 28 human antibiotics by mean of activated sludge and microfiltration/reverse osmosis where he remarked that low quantities of antibiotics remained in the solution after treatment<sup>354</sup>. Photocatalytic degradation using UV/ $\text{TiO}_2$  could remove only partially the initial concentration of AMX<sup>355</sup>. Whereas  $\text{H}_2\text{O}_2$  addition (UV/ $\text{H}_2\text{O}_2$ / $\text{TiO}_2$ ) improved significantly the efficacy leading to complete removal after 20 min treatment, but leaving still high COD. It has been demonstrated that biodegradability of AMX can be improved if it is pre-treated by the photo-Fenton process<sup>356</sup>. Some other methods for AMX removal include Fenton process<sup>357</sup>, sulphate radicals under ultrasound irradiation<sup>358</sup>, Ozonation<sup>359</sup>.

Table 5.<sup>360</sup> General properties of amoxicillin.

Chemical structure (C <sub>16</sub> H <sub>19</sub> N <sub>3</sub> O <sub>5</sub> S)			
Molecular weight	365.4 g mol <sup>-1</sup>		
CAS No	26787-78-0		
Solubility in water	3430 mg L <sup>-1</sup> at 35 °C		
pKa	2.8		
Log K <sub>ow</sub>	0.87		
K <sub>oc</sub>	8650.5		
Vapor pressure	4.69 E-14 (mm Hg)		
Half life time in environment	30% degradation after 3 months in laying hen feces		
	34% degradation after 8 day broiler feces		
Toxicity (acute) (mg L <sup>-1</sup> )	Microcystic aeruginosa	Growth EC <sub>50</sub>	0.0037
	Oncorhynchus mykiss	Hepatocyte toxicity 24 h EC <sub>50</sub>	182.7
	Lemna gibba	Wet weight, chlorophyll l seven day LOEC	1
	Vibrio fischeri	IC <sub>50</sub> 5 min	1.32
	Daphnia magna	EC <sub>50</sub> 24 h	>1.000
	Moina marocopa	EC <sub>50</sub> 24 h	>1.000
	Oryzias latipes	EC <sub>50</sub> 24 h	>1.000

## **CHAPTER 2**

### **MATERIALS AND ANALYTICAL METHODS**

## 2.1. CHEMICALS

Chemicals used in this work were all analytical grades and has been used without further purification. Pure water obtained from a Millipore Mill-Q system with resistivity  $> 18 \text{ M}\Omega \text{ cm}^{-1}$  at room temperature was used for the preparation of all investigated solutions and for HPLC measurements. A list of all chemicals used during this work is given in the table 6.

*Table 2.1. List of chemicals used in this thesis work.*

Chemical	Marque	CAS N°	Molar masse (g/mol)
Sulfamehazine $\geq 99 \%$	Sigma	57-68-1	278.33
Amoxicilline $\geq 97 \%$	Fluka	26787-78-0	365.41
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 99 %	Acros	7782-63-0	278.01
$\text{Na}_2\text{SO}_4 \geq 99 \%$	Sigma-Aldrich	7757-82-6	142.04
$\text{K}_2\text{SO}_4 \geq 99 \%$	Chimie-Plus	7778-80-5	174.26
$\text{NaOH} \geq 98 \%$	Fluka	1310-73-2	40.00
$\text{NaCl} \geq 99.5 \%$	Fluka	7647-14-5	58.44
$\text{KC} \geq 99 \%$	Fluka	7447-40-7	74.56
$\text{FeCl}_3$ 97 %	Sigma-Aldrich	7705-08-0	162.21
$\text{Na}_2\text{CO}_3 \geq 99.8 \%$	Riedel-de Haën	497-19-8	105.99
$\text{NaHCO}_3 \geq 99.7 \%$	Fluka	144-55-8	84.007
$(\text{NH}_4)_2\text{C}_2\text{O}_4$ 99 %	Acros	1113-38-8	124.10
$\text{NaNO}_3 \geq 99.0 \%$	Sigma-Aldrich	7631-99-4	84.99
$\text{H}_2\text{O}_2 \geq 30 \%$	Fluka	7722-84-1	34.02
$\text{TiCl}_4$ 99.9 %	Acros	7550-45-0	189.71
$\text{H}_2\text{SO}_4$ 98 %	Acros	7664-93-9	98.08
$\text{H}_3\text{PO}_4 \geq 85 \%$	Fluka	7664-38-2	98.00
$\text{HCl}$ 37 %	Fluka	7647-01-0	36.46
Acetic acid 99.8 %	Riedel-de Haën	64-19-9	60.05
Benzoic acid 99.7 %	Prolabo	65-85-0	122.12
Glycolic acid 99 %	Acros	79-14-1	76.05
Glyoxylic acid 98 %	Acros	563-96-2	92.05
Formic acid 99 %	Acros	64-18-6	46.02
Fumaric acid 99 %	Acros	110-17-8	116.07
Oxalic acid 97 %	Fluka	144-62-7	90.03
Oxamic acid 98 %	Alfa Aesar	471-47-6	89.05
Pyruvic acid 98 %	Aldrich	127-17-3	98
Malic acid 99 %	Acros	617-48-1	134.09
Maleic acid 99 %	Sigma	110-16-7	116.07

Malonic acid 99 %	Fluka	141-80-2	104.06
Succinic acid 99 %	Acros	110-15-6	118.09
Tartronic acid 97 %	Fluka	80-69-3	120.06
Methanol 99.9 %	Sigma Aldrich	67-56-1	32.04
2-propanol 99.8 %	Sigma Aldrich	67-63-0	60.1

## 2.2. ELECTROCHEMICAL CELL

Three electrochemical cells of different volumes have been used to perform the electrolysis experiments: a 300 mL glass of 7.7 cm diameter, 250 mL of 6.6 cm and 250 mL of 5.7 cm. In each case the cell was equipped with two electrodes, and the stirring magnetic bar to provide good mass transport conditions. A glass tube was put in the cell to purge compressed air to maintain the solution saturated with oxygen during the experiment. For anode testing experiments, a carbon felt cathode (Carbone Lorraine) of dimensions 23 cm x 7 cm x 0.5 cm was used to test the comparative efficiency of the anodes: boron doped diamond (BDD), Platinum, (Pt) DSA/RuO<sub>2</sub>-IrO<sub>2</sub> and carbon felt of 2 x 24 cm<sup>2</sup>. The carbon felt cathode covered the inside walls of the cell whereas the anode was situated in the centre of the cell. For cathode tests, a platinum anode was used and cathodes (Carbon sponge 6 cm x 3.5 cm x 1 cm and carbon felt 6 cm x 3.5 cm x 0.5 cm) were altered. Amoxicillin oxidation trials were performed using a stainless steel cathode of 24 cm<sup>2</sup> and the corresponding anode of the same surface area placed in the electrolytic cell in a distance of 3.5 cm between them.

Solutions of SMT of 0.2 mM concentrations were prepared for electro-Fenton experiments. 0.2 mM catalyst (Fe<sup>2+</sup>) was added as iron sulphate (Fe<sub>2</sub>SO<sub>4</sub>) as well as 50 mM sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) as supporting electrolyte. In the case of SO<sub>4</sub><sup>2-</sup> analysis by ionic chromatography Na<sub>2</sub>SO<sub>4</sub> was replaced by NaCl and Fe<sub>2</sub>SO<sub>4</sub> by FeCl<sub>3</sub> in order to avoid the SO<sub>4</sub><sup>2-</sup> interference which comes from the supporting electrolyte. Similarly for the analysis of NH<sub>4</sub><sup>+</sup>, K<sub>2</sub>SO<sub>4</sub> was added instead of Na<sub>2</sub>SO<sub>4</sub> as the retention times of NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> are close and some possible overlap of NH<sub>4</sub><sup>+</sup> peak by the Na<sup>+</sup> peak is possible because of the high concentration of the Na<sup>+</sup> of the supporting electrolyte. Once the solution prepared it was acidified at pH = 3 (optimal conditions for Fenton's reaction) with sulphuric or hydrochloric acid solution.

AMX solutions for anodic oxidation experiments were prepared at 0.1 mM concentration whereas supporting electrolyte Na<sub>2</sub>SO<sub>4</sub> was 50 mM without pH adjustment.

These solutions were electrolysed for different current intensities using an electric power supply model Hameg Triple Power Supply HM804030. Samples to be analysed were withdrawn in regularly time scales.

## **2.3. ANALYTICAL TECHNIQUES**

In order to follow the kinetics of degradation of targeted model chemical and the composition of the solution during electrolysis several analytical techniques have been employed.

### **2.3.1. High Performance Liquid Chromatography (HPLC)**

High performance liquid chromatography is a separation analytical technique largely applied for the analysis of organic substances. It is based on different interactions of molecules with a solid phase, called stationary phase, fixed in a column and a liquid phase which flows through the column and is called the mobile phase. The separation of different molecules of a mixture is related to their affinity versus stationary and mobile phases. If the column is packed with a nonpolar stationary phase and the sample is eluted with a polar eluent, molecules of higher polarity will be attracted more by the eluent and those less polar will be retained on the stationary phase. This means the analyte species will be retarded to pass through the column depending on the retention time in the column. This differential affinity of phases in contact towards different polarity molecules leads to the separation so they will come out of the column one after other. Then separated molecules enter the detector and the signal is presented with a chromatogram where separated peaks at different retention times are observed for all the sample constituents. In this way good separation and analysis can be achieved by varying the composition of mobile phase (eluent).

### **2.3.2. Analysis of SMT and AMX**

The samples withdrawn regularly were analysed by a Merc-Hitachi high performance liquid chromatograph, Lachrom-Elite model, controlled by EZchrom elite software. It was composed of a quaternary pump MH L-7100, a diode array detector L-7455 and a thermostated Merck column L-7360 with thermostat.



Injections of aliquots of 20  $\mu\text{L}$  were done in the column which was thermostated at 40°C. Conditions of HPLC analysis for SMT and AMX are summarised in the table 7.

*Table 2.2. HPLC conditions for the analysis of sulfamethazine and amoxicillin.*

	SMT	AMX
Column	C <sub>18</sub> Purosphere RP 18 (5mm, 250 mm x 4.6 mm)	C <sub>18</sub> Purosphere RP 18 (5mm, 250 mm x 4.6 mm)
Detector	DAD-UV-VIS L-7455	DAD-UV-VIS L-7455
Pump	L-7100	L-7100
Temperature	40 °C	40 °C
Flow	0.8 mL min <sup>-1</sup>	0.5 mL min <sup>-1</sup>
Mobile phase	CH <sub>3</sub> OH: 10% (H <sub>2</sub> O 99-H <sub>3</sub> PO <sub>4</sub> 1): 90%	(H <sub>2</sub> O 99% + CH <sub>3</sub> COOH 1%)97 % CH <sub>3</sub> OH 3 %
Pressure	156 bar	
Injection volume	20 ml	20 ml
Wave length	244 nm	233 nm
Retention time	13.8 min	8.4 min

### 2.3.3. Analysis of Carboxylic acids

The evolution of carboxylic acids has been followed by ion exclusion chromatography. An HPLC chromatograph equipped with pump Alltech (Model 426) and a column Supelcogel H, 25 cl x 4.66 mm coupled to a detector Dionex AD20 was used. The eluent was a solution of sulphuric acid 9 mM. Flow rate was adjusted to 0.25 mL min<sup>-1</sup>. Detection wave length for carboxylic acids was 220 nm and measures were done at 30 °C The system is connected with an acquisition and data treatment unit commanded by analytical Chromeleon SE software.

### 2.3.4. Analysis of inorganic ions

Ionic chromatography is a separation analytic method which allows the separation of ions and polar molecules based on their charge. The stationary phase in ion chromatography is an electrically charged material so the separation of ions depends on their density charge. Usually the stationary phase is an ion exchange resin that contains charged functional groups

that interact with oppositely charged ions of the sample. Ions with different charge density will be retained more or less in the column what makes them emerge in different scale times from the column.

In this work ion chromatography was used to identify and quantify inorganic ions evolved from the heteroatoms contained in the structure of the molecule which are electrolyzed. These ions are  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . The ion chromatograph was a system Dionex ICS-1000. The data acquisition was done by Chromeleon software. This system is equipped either with a column cationic (CS12A) or anionic (AS4A-SC) of 4 mm diameter and 25 cm length coupled with a conductometric detector DS6. In the case of cation detection the mobile phase was 9 mM sulphuric acid, the flow rate was  $1 \text{ mL min}^{-1}$ . The applied current in the suppressor SRS (Self Regenerating Suppressor) needed to prevent the influence of the eluent ions in the detector signal was 30 mA. The suppressor acts in the way that cancel the conductivity of the eluent which otherwise is very high and disturbs seriously the analysis. For anions measurements the mobile phase contained 1.8 mM  $\text{Na}_2\text{CO}_3$  and 1.7 mM  $\text{NaHCO}_3$ . The flow rate was fixed to  $2 \text{ mL min}^{-1}$ . The suppressor current was 30 mA.

The analysis of ions coming in the solution because of the decomposition of the initial organic compound during electrolysis was done by standard curves prepared with: ammonium oxalate for ammonium determination, sodium nitrate for nitrate and sodium sulphate for sulphate anion determination.

## **2.4. TOTAL ORGANIC CARBON**

Total organic carbon (TOC) is a very important parameter for the estimation of the level of pollutant abatement in the aquatic solution. Namely, it represents the quantity in mg of carbon present only in organic molecules. If the oxidation of the organic matter proceeds until carbon dioxide the gas will escape from the solution resulting to a diminution of TOC content.



**Fig. 2.1.** Total organic carbon analyzer – TOC-V<sub>CSH</sub>.

The principle of TOC analysis of a sample consists on complete conversion of atoms of an organic molecule in CO<sub>2</sub> which is then measured. The combustion of organic matter is realized in high temperature chamber (680 °C) in the presence of platinum containing catalyst under pure oxygen gas flux. The combustion of the organics produces carbon dioxide which is measured by infrared spectroscopy at the exit of the oven where the combustion takes place.

For the TOC analysis in this study a Shimadzu VCSH TOC *analyzer* equipped with a manual injector was used. Samples were acidified with 1% hydrochloric acid to remove the mineral CO<sub>2</sub> coming from sources other than organic molecules under investigation. The total volume injected was 50 µL. The apparatus did three measures for each sample and gave the average value. Calibration curves were prepared from standard solutions of potassium hydrogen phthalate.

## **2.5. HYDROGEN PEROXIDE DOSAGE**

Hydrogen peroxide production was studied for the cathodes tested for their performance in electro-Fenton process. Spectrophotometry was used as method for H<sub>2</sub>O<sub>2</sub> analysis. This technique refers to the absorption of light in the ultraviolet visible region (UV-

VIS) by analyte molecules. The absorption of UV-VIS light causes electronic transitions in molecules. The logarithm of fraction of incident light intensity and transmitted light intensity is called absorbance (A). A is linearly related to the concentration and is expressed by the Beer-Lambert law.

$$A = \epsilon c l \quad (2.1)$$

Where  $c$  is the concentration of analyte  $l$  is the length of the path which light passes through and  $\epsilon$  is molar absorptivity or extinction coefficient.

The spectrophotometric dosage of  $H_2O_2$  was realized by the method of titanium. The reaction between  $Ti^{4+}$  and  $H_2O_2$  gives a yellow complex in the acidic media, the pertitanic acid, the absorbance of which is measured by means of a spectrophotometer.

The experiments were done in an electrolytic cell containing a platinum anode and the cathode to be investigated, in pure aqueous medium in the presence of  $Na_2SO_4$  as supporting electrolyte. Aliquots of 5 ml were withdrawn at given time scales and were put in a flask of 25 mL. In each aliquot were added 2 mL of  $TiCl_4$  solution previously prepared in a 1 M  $H_2SO_4$  (10 mL  $TiCl_4$  in L of  $H_2SO_4$  1M), 2 mL of concentrated  $H_2SO_4$  (18 M) and the rest was filled with the pure water. Then the sample was measured at the maximum wave length of adsorption at 423 nm in a quartz vessel of 1 cm optic path. The absorptivity coefficient of complex formed between  $H_2O_2$  and  $Ti^{4+}$  was calculated from the slope of the calibration curve prepared with standard solutions of  $H_2O_2$ . Finally, the concentration was calculated according to the Beer-lambert law. The spectrophotometer for analysis was PERKIN ELMER UV/VIS spectrometer Lambda 10.

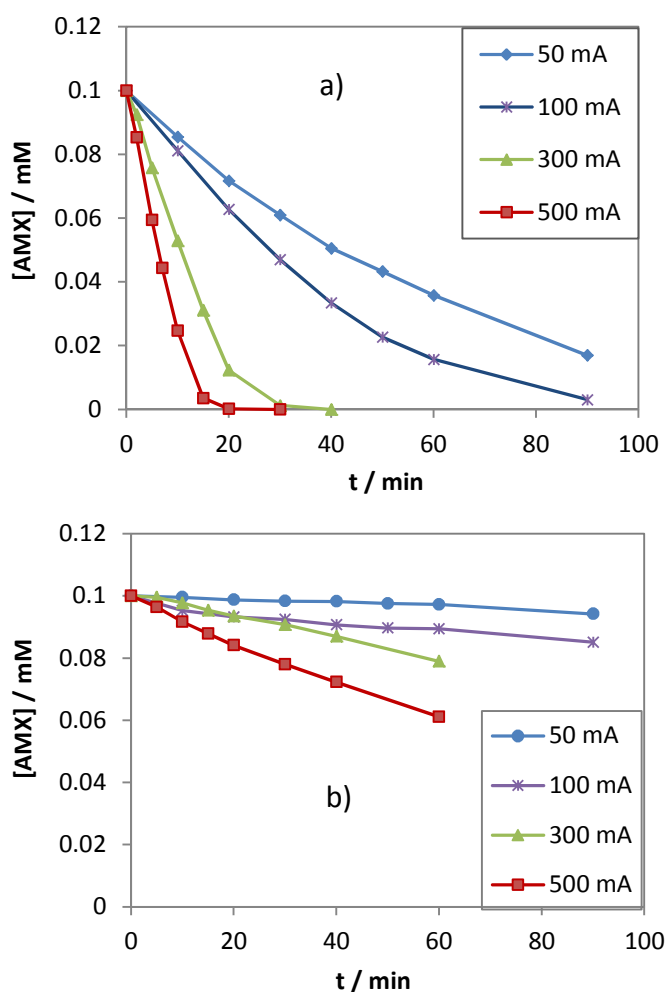
## **CHAPTER 3**

### **EFFECT OF THE ANODE MATERIAL ON THE ELECTROCHEMICAL OXIDATION OF AMOXICILLIN (AMX)**

### 3.1. KINETICS OF THE DEGRADATION AND MINERALIZATION OF AMX

#### 3.1.1 Effect of the current intensity

The electrochemical data with different anode materials were obtained in an aqueous solution of 0.1 mM (36.54 mg L<sup>-1</sup>) AMX and 50 mM Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte. A stainless steel cathode was used in order to avoid hydrogen peroxide production (as stainless steel cathode is known to produce very little quantities of H<sub>2</sub>O<sub>2</sub>) which could contribute in the whole oxidation of AMX, Figure 3.1 shows the decay in the concentration of AMX with time during the electrolysis of an AMX solution with DSA and BDD anodes at different current intensities ranging from 50 to 500 mA.

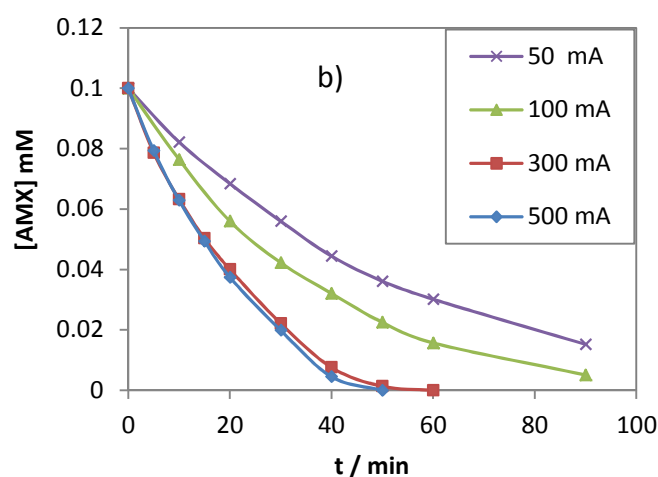
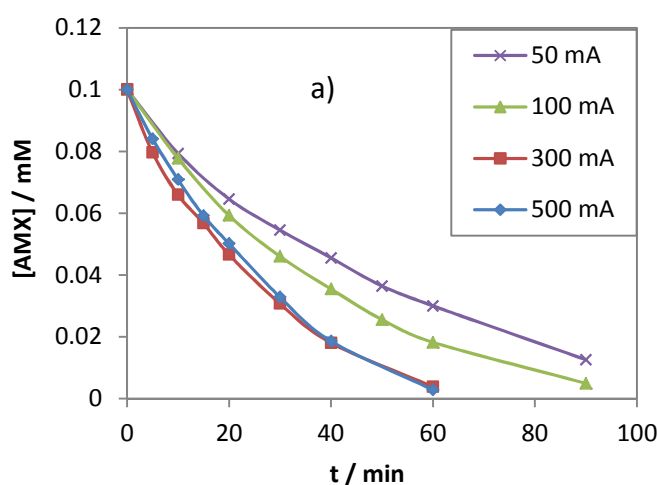


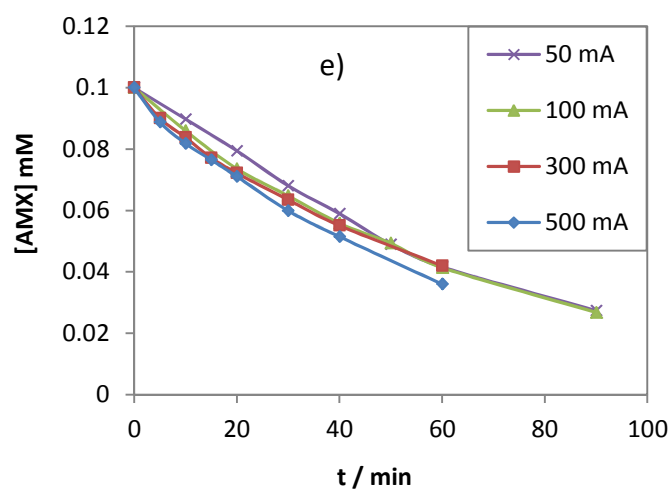
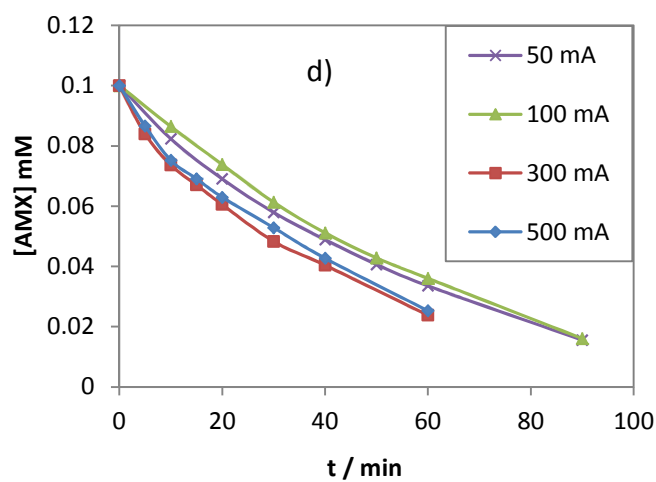
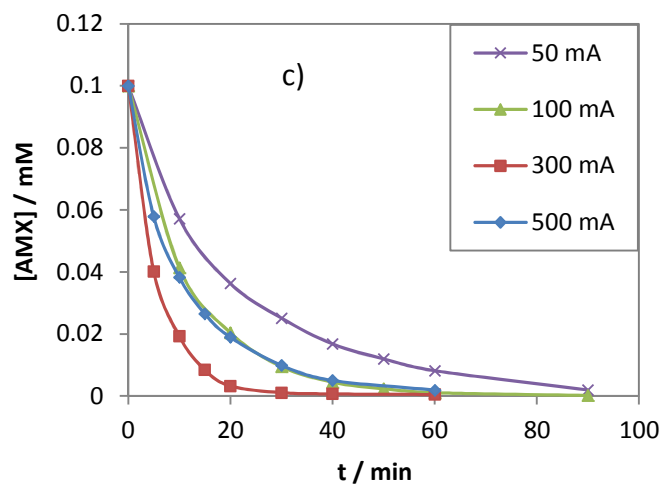
**Fig. 3.1.** Effect of current intensity on the oxidation of 0.1 mM AMX at room temperature with BDD (a) and DSA (b) anodes. Cathode: S Steel,  $V_s = 250$  mL,  $[Na_2SO_4] = 50$  mM.

As it can be observed in figure 3.1, there is a strong influence of the anode material on the oxidation rate of AMX, being the BDD anode much faster than the DSA in the oxidation of AMX. In fact, the total depletion of AMX is attained with the BDD electrode at 20 and 40

min with applied current intensity of 500 and 300 mA respectively and almost complete depletion at 90 min with 100 mA. Whereas the AMX concentration decay is less than 40% of initial concentration at 60 min even for the higher current value of 500 mA under same operating conditions in the case of DSA anode. As expected, the higher the current density, the higher the oxidation rate of AMX for both electrodes.

In the figure 3.2 are presented the degradation curves  $[AMX] = f(t)$  for five other anodes. It can be seen that  $PbO_2$  and Pt are faster than carbon fiber and graphite, whereas carbon felt is the fastest. AMX degradation percentage, under 300 mA constant current, for other anodes is: Pt (96.1),  $PbO_2$  (99.14), Carbon fiber (76.2), Graphite (58) and Carbon felt (99.5). From these values of abatement it can be observed that in addition to the very fast initial decay of the concentration of model pollutant with carbon felt, very small quantities still remain in the solution after 60 min electrolysis with other anodes. Similar tendency of AMX depletion is observed also for other currents. For carbon fiber and graphite the rates of AMX removal are lower than all other anodes apart from DSA type anode for which the concentration decay is the lowest one.



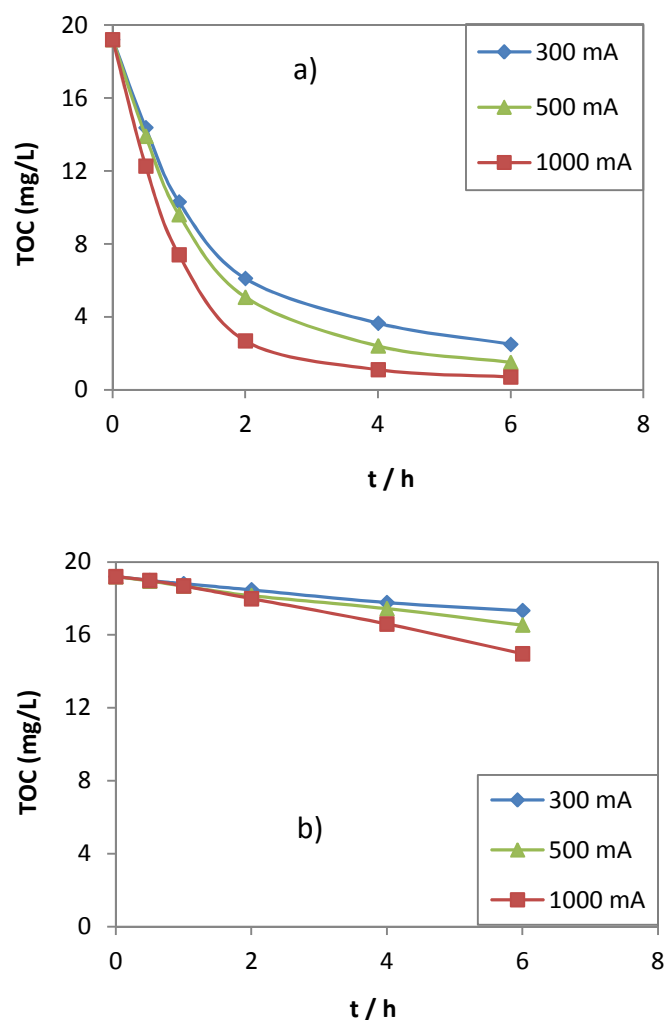


**Fig. 3.2.** Effect of applied current intensity on the oxidation of 0.1 mM AMX with (a) Pt, (b)  $\text{PbO}_2$ , (c) carbon felt, (d) carbon fiber, and (e) graphite anodes. Cathode: S Steel,  $V_s = 250$  mL,  $[\text{Na}_2\text{SO}_4] = 50$  mM.



Changes in the concentration of AMX are important, but it is worth to take into account that depletion of AMX does not mean total removal of the pollution problem. It only means an oxidation of the mother molecule (addition of  $-OH$  group or electron transfer) to its oxidation intermediates. For this reason the TOC removal is a much more significant parameter, because it clearly indicates the mineralization of the pollutants, that is, the complete destruction of the starting molecule and its transformation into carbon dioxide and water.

Figure 3.3 informs about the mineralization of the AMX aqueous solutions. As it can be seen, the reaction times (and, consequently, current charges passed) required are much higher in these experiments than in the electrolysis shown in Fig. 3.1 and 3.2.



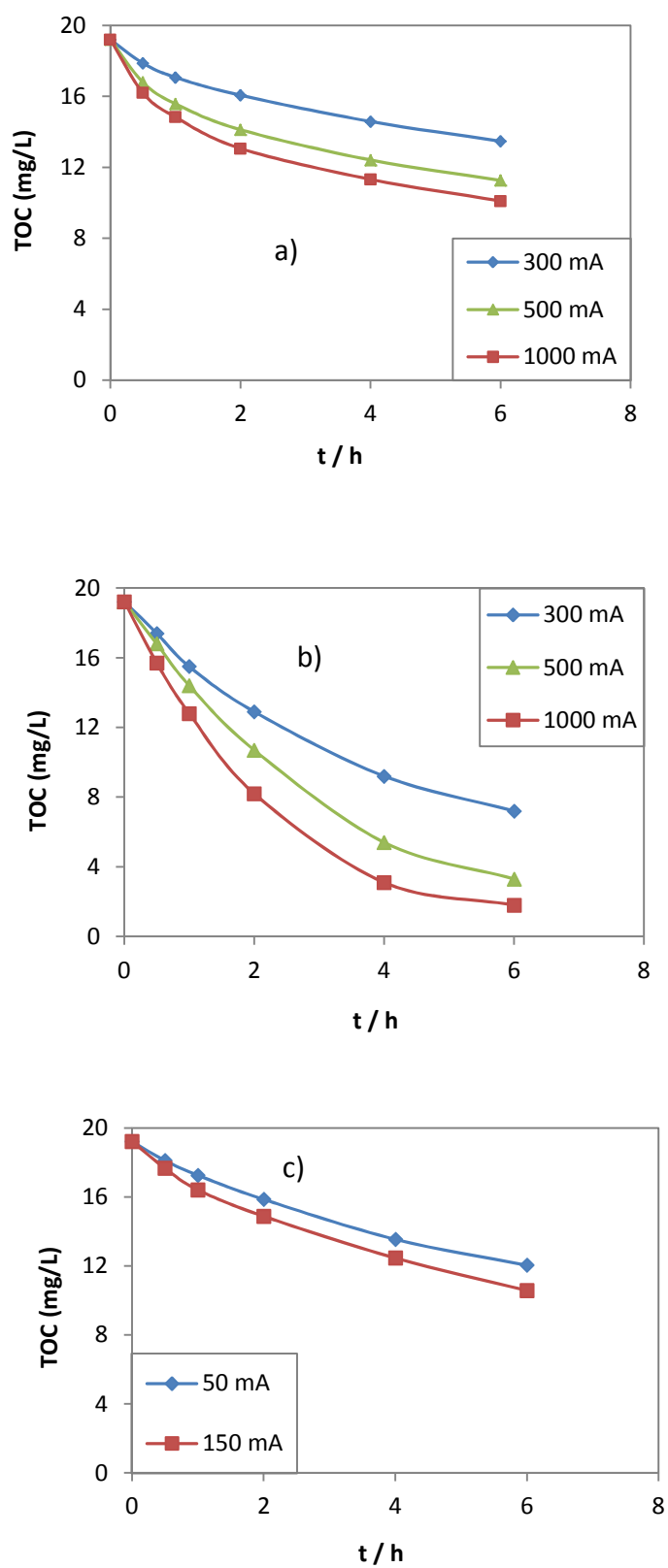
**Fig. 3.3.** Effect of current intensity on the mineralization degree of AMX with BDD and (a) and DSA (b) anodes at room temperature. Cathode: S Steel,  $V_s = 250$  mL,  $[Na_2SO_4] = 50$  mM.

Thus, in the case of AMX, 98 electrons are needed for the mineralization of the molecule up to carbon dioxide (Eq. (3.1)), while a simple one-electron transfer can transform the AMX into another molecule, and this explains the largest electrolysis times in the case of the mineralization study.



Figure. 3.1a clearly indicates that BDD anode is faster than DSA in the mineralization of the AMX, and that for both anodes the higher the current density, the faster is the mineralization rate. However, effect of current density is much less significant than in the case of the simple oxidation of AMX (shown in Fig. 3.1), suggesting that much more complex processes may be occurring during the mineralization process. Reaction times required to mineralize completely the AMX are above 6 h for BDD anode. However, for this reaction time, less than 25% of mineralization is obtained for the electrolysis with DSA anode under the highest current density.

The rest of results on mineralization with other anodes are given below in the figure 3.4. At the difference of the simple oxidation of the molecule, where among all the anodes tested (each of them showing different oxidation capacities), all of them could not be used for the mineralization where much longer time of treatment is required. Thus, only BDD, DSA,  $\text{PbO}_2$  and Pt electrodes gave significant mineralization results in the range of current intensities applied, whereas graphite could be used only for current intensities of 150 mA and lower. Two other carbon based anodes, carbon felt and carbon fiber burned at the beginning of electrolysis and led to the failure of the electrochemical cell.



**Fig. 3.4.** Effect of current intensity on the mineralization of AMX with Pt (a), PbO<sub>2</sub> (b) and graphite (c) anodes. Cathode: S Steel, V<sub>s</sub> = 250 ml, [Na<sub>2</sub>SO<sub>4</sub>] = 50 mM.

BDD and DSA are usually employed as model anodes to perform the electrolysis of many organic pollutants because they use to show two opposite behaviors. Thus, BDD behaves as a high-efficiency electrode for the oxidation of organics. It promotes the mineralization of the organics with high efficiency, and usually few intermediates are observed during the treatment. In addition, it promotes the production of high amount of hydroxyl radicals due its high O<sub>2</sub> evolution overvoltage. On the contrary, DSA electrodes are known as low-efficiency electrodes for the oxidation of organics. These anodes promote a soft oxidation of organics, with a great amount of intermediates (most aromatics treated by these anodes are slowly degraded due to the generation of hardly oxidizable carboxylic acids), small mineralization and in some cases (particularly, under high concentration of pollutants) with production of polymers<sup>236</sup>. They produce a very low current efficiency and consequently small perspectives of application. On the other hand these anodes promote the formation of oxidant HClO if the solution contains chlorine ions. The use of the platinum and carbon based electrodes as anode in electro-oxidation to be included into this second type of electrodes because they usually exhibit low-efficiency for the oxidation of organics compared to BDD electrode. Low efficiencies are even more significant with the use of carbon-based materials as anode because during the electrochemical process they can also be electrochemically incinerated (transformed into carbon dioxide) when using high voltages or currents to oxidize organic pollutants. On the other side, the lead dioxide behaves as BDD and performs high efficiency oxidations.

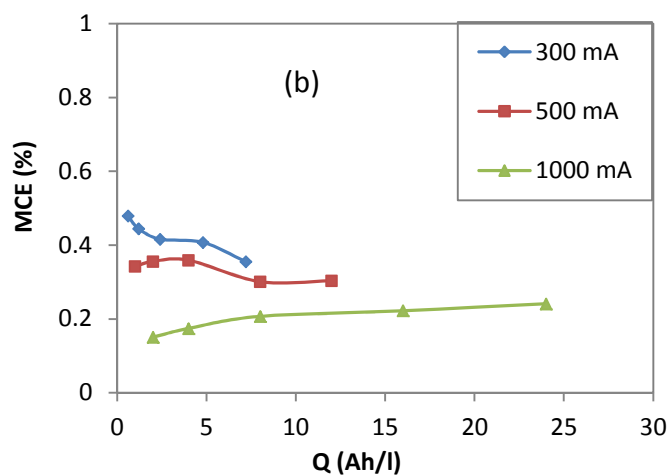
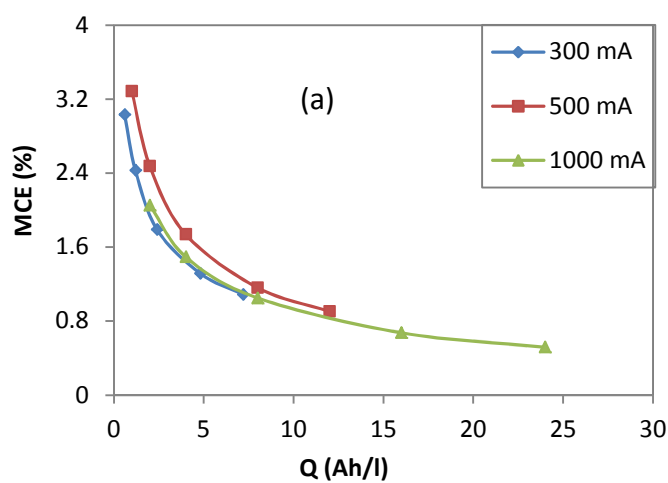
### 3.2. Mineralization current efficiency

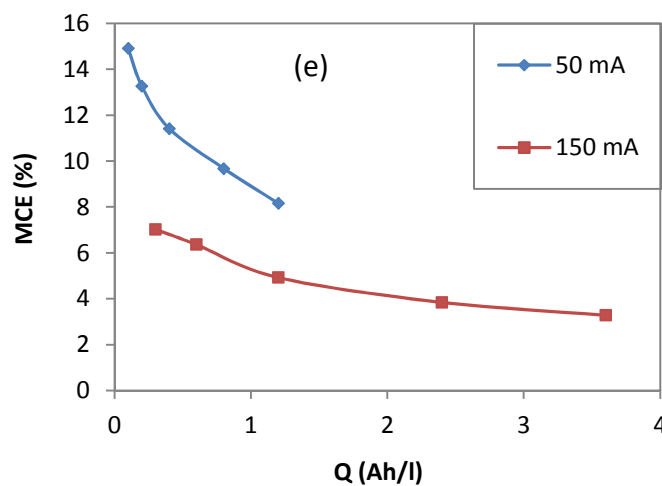
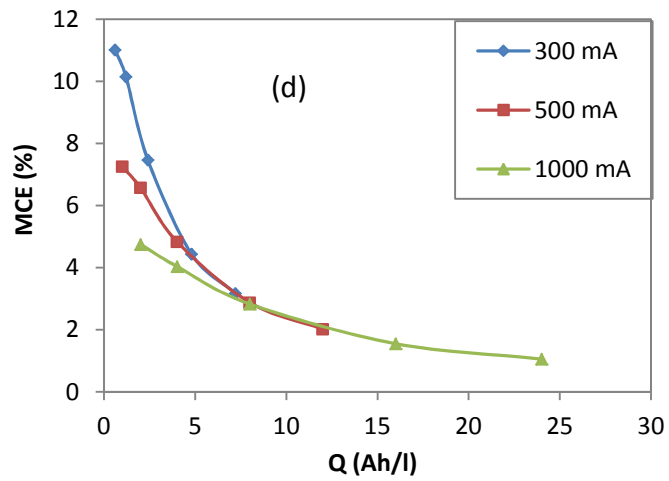
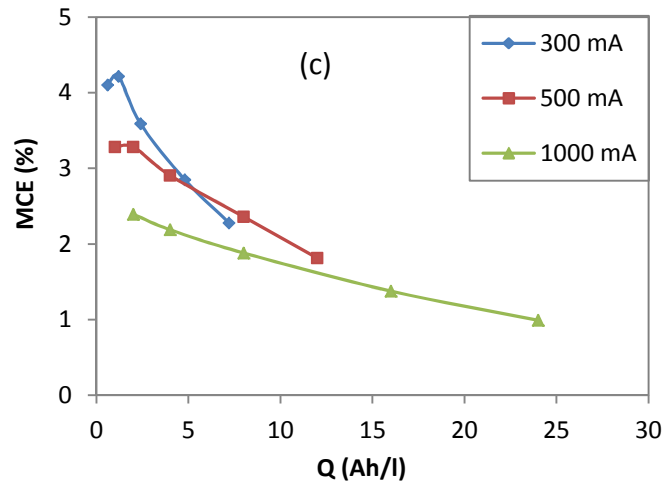
An estimation of energy consumption during electrochemical mineralization of organic pollutants can be done by calculating the mineralization current efficiency (MCE). MCE in percentage can be calculated from the following equation<sup>305</sup>:

$$\text{MCE \%} = \frac{nFV_s\Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 \text{ mIt}} \times 100 \quad (3.2)$$

Where  $n$  is the number of electrons exchanged per molecule (following equation 3.1),  $F$  is the faraday constant,  $V_s$  the solution volume,  $\Delta(\text{TOC})$  the experimental TOC decay,  $4.32 \times 10^7$  is

the conversion factor to homogenize the units ( $= 3600 \text{ s h}^{-1} \times 12.000 \text{ mg of C mol}^{-1}$ ),  $m$  the number of carbon that the molecule contains,  $I$  is the current intensity applied and  $t$  is time when sample was withdrawn. For the mineralization of 1 mol of AMX, 98 mole of electron ( $n$ ) are needed for its complete transformation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and after substituting other constants and experimental variables the MCE were calculated and plotted against specific charge  $Q$  (Ah/L). The percentage of MCE versus specific charge is given in the figure 3.5.





**Fig. 3.5.** Mineralization current efficiencies for the mineralization of AMX (a) Pt/S Steel, (b) DSA/S Steel, (c) PbO<sub>2</sub>/S Steel, (d) BDD/S Steel, (e) Graphite/S steel, V<sub>s</sub> = 250 ml, [Na<sub>2</sub>SO<sub>4</sub>] = 50 mM.

It is obvious that MCE has higher values at lower current intensities as less energy is consumed by wasting reactions. When current intensity is increased more TOC is removed for a given time interval since more charge passes through the cell, but this leads also to the lowering of MCE. The most efficient anode for AMX oxidation was BDD. For example, we can see that the highest MCE value is 11% at 0.5 h electrolysis for 300 mA (Fig. 3. 5). The mineralization efficiency undergoes a continuous decay as electrolysis is prolonged as a result of the formation intermediate species more difficult to oxidize, particularly carboxylic acids. The MCE decay is also a result of simple pollutant depletion in the solution, so that according to the fundamental kinetic considerations the rate of a reaction decreases as reactant concentration is lowered. When the concentration of AMX is low, for a constant current intensity a smaller part of charge will be used for its oxidation as less of AMX molecules are available to be degraded. The MCE decreases with the current intensity too; in the case of BDD we can see lower initial MCE values (11, 7.2 and 4.7 for 300, 500 and 1000 mA respectively). This decay is as a consequence of energy wasting rations such as O<sub>2</sub> release on the anode instead of  $\cdot$ OH formation. Moreover, OER will compete with the formation of other oxidizing agents lowering their contribution to mineralization.

The MCE varies significantly with the anode material. MCE is very low for the DSA anode (Fig. 3.5a) whereas Pt and PbO<sub>2</sub> (Figs. 3.5a and 3.5c) give medium efficiency compared to BDD ((Fig. 3.5d) and DSA (Fig. 3.5a). Such extremely low MCE values for the DSA anode are explained by the mechanism of organics oxidation on Ir(VI) oxide formed on DSA surface as a weak oxidant. This oxide allows very easily the release of oxygen (as DSA is low oxygen evolution overpotential anode) and at higher current intensities it becomes the main reaction leading to smaller values of MCE. As already seen, graphite could only be used for 150 mA and lower. However better mineralization current efficiencies and even better TOC removal was achieved with graphite (Fig. 3.5e) than with Pt and DSA.

### **3.3. Comparison of the oxidation capacity of different anode materials**

To compare the performance of different anodes studied in this work namely BDD, DSA, PbO<sub>2</sub>, Pt, carbon-felt, carbon-graphite and carbon-fiber for the particular case of the oxidation of AMX, the time course during electrolysis were fitted to a pseudo-first order kinetic model. Table 3.1 shows the apparent (or observed) rate constants ( $k_{app}$ ) for electro-oxidation of AMX obtained by mathematical fitting of experimental results, respectively. It

has to be remarked that the linear approach was only for the initial stage of the oxidation, where AMX oxidation does not compete with the oxidation of intermediates. Thus, in the semi-logarithmic plot, it can be clearly observed two zones (not shown in Figures) corresponding to the electrolysis in which AMX does not compete and the zone in which significant concentration of intermediates are present in the system and compete with AMX for  $\bullet\text{OH}$ . The later cannot be used in the calculation of the  $k_{\text{app}}$ .

Regarding the oxidation rate constants, it can be clearly observed that the reaction rate increases with the current intensity in every case (except for the carbon-felt in which a strange shape can be observed), but the slopes ( $k_{\text{app}}$ ) are very different depending on the nature of the anode material tested.

*Table 3.1. Apparent rate constants of the degradation of AMX by anodic oxydation with different anode materials.*

Anode	BDD	Pt	DSA	PbO <sub>2</sub>	Graphite	Carbon Felt	Carbon fibre
I (mA)	$k_{\text{app}}$ (min <sup>-1</sup> )						
50	0.02	0.02	0.0006	0.02	0.01	0.05	0.02
100	0.03	0.03	0.003	0.03	0.01	0.08	0.02
300	0.06	0.04	0.003	0.05	0.02	0.2	0.03
500	0.11	0.03	0.008	0.04	0.02	0.09	0.02

The rate of oxidation of AMX with the current intensity is increased as more electrons are transferred from anode to the pollutant molecule. But more significant is the role of heterogeneous hydroxyl radicals  $\text{M}(\bullet\text{OH})$  which are generated at the anode surface on AMX oxidation, their quantity increases with the current intensity and consequently the oxidation rate of pollutant too. The ability of an anode to produce  $\bullet\text{OH}$  is related to its oxygen overpotential evolution. An anode showing high oxygen evolution overpotential provides high quantity of  $\bullet\text{OH}$  even for higher current intensities whereby higher oxidation rate constants. Thus, this explains the order of abatement efficiencies for anodes tested (table 3.1), being the BDD the most powerful one and DSA the weakest one.

As oxidant species like  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , are generated on the anode, but the later ( $\text{H}_2\text{O}_2$ ) is essentially generated at the cathode, their contribution in the overall value of the rate constant cannot be neglected. So the modification of  $k_{\text{app}}$  with current intensity can be explained also by an increase in the concentration of oxidants at the pseudo-steady state or by



the action of more powerful oxidants with higher kinetic constants. This means that differences between the oxidation rates of AMX shown in Table 3.1 should not be explained only in terms of the direct electro-oxidation of AMX but also by the action of mediated electro-reagents formed on the surface of the electrode. According to this, the production of these electro-reagents promoted at large current densities with most materials except for graphite and carbon-fiber (in which not a clear increase is observed). Likewise, it can be observed that production of oxidants that can oxidize the AMX is promoted with carbon-felt, BDD and Pt anodes, but this production is almost negligible for DSA anode. Therefore, it is worth to remind that no chlorides are present in the reaction media and that mediated oxidation of organics with DSA is only promoted in the presence of chlorides. Graphite and carbon-fiber electrodes have behaviors something in between both behaviors, maybe because of the production of a softer oxidants and the possibility of film formation as light orange color could be observed on the surface.

Compared with other works in literature, the huge reaction rates observed for carbon-felt electrode are surprising, especially if one takes into account that it consists of  $sp^2$ -carbon. These values are not in agreement with the low mineralization rates observed for this material and can only be explained in terms of a double effect: the enhanced direct-like processes because of the higher surface area of carbon felt (as compared with the other electrodes assessed) and also the production of a soft oxidant (most probably hydrogen peroxide), activating the oxidation of AMX but not enough strong for depletion till carbon dioxide of  $sp^2$ -carbon of the electrode. The decrease in the kinetics constant observed for larger current densities is due to the destruction of the electrode (it will be discussed later).

Changes of the oxidation power of anodes are important for the initial oxidation of the AMX but they should be even more important for the complete mineralization process. In this case, very different results are obtained with respect to the oxidation of AMX as it is shown in Table 3.2. The percentages of AMX abatement at 6 h treatment in  $sp^2$ -carbon based materials (including carbon-felt) fall to an almost nil values and only diamond, platinum and lead dioxide exhibit appreciable values of both parameters.

*Table 3.2. TOC removal percentages at 6 h electrolysis.*

Anode	BDD	Pt	DSA	PbO <sub>2</sub>	Graph	C Felt	C Fibre
I (mA)	TOC removal (%)						
300	86.9	29.8	9.7	62.5	0	0	0
500	92.2	41.3	13.8	81.2	0	0	0
1000	96.3	47.4	22.0	90.6	0	0	0

Comparing the abatement percentages of the oxidation and mineralization of AMX, it can be observed that the oxidation of AMX is easier to be achieved than mineralization. This is important because it clearly exhibits that these parameters with a very different meaning, mineralization being the main goal in the efficient removal of pollutants from wastewaters, and much more difficult to attain that depletion of the AMX by transformation into its oxidation intermediates. The high efficiencies obtained for BDD, apart from hydroxyl radicals, should be explained in terms of the production of large amount of oxidant as it has been widely described in literature. Hence in addition to hydrogen peroxide and ozone, persulfates are expected to play an important role in the oxidation of organic pollutants. Production of the persulfates is also possible with Pt and PbO<sub>2</sub> anodes but in a lesser extent.

*Table 3.3. TOC removal percentages at 6 h for low current intensities with carbon anodes.*

Anode	Graphite	Carbon felt	Carbon fibre
I (mA)	TOC removal (%)		
50	37.3	0	0
150	42.9	0	0

Table 3.3 shows percentages of the mineralization obtained at low current densities with sp<sup>2</sup>-carbon based electrodes indicating that only graphite is robust enough against incineration in the range of low current densities. This is important because carbon-fiber and carbon-felt are not able to mineralize the AMX while they oxidize AMX to its intermediates. That means oxidation intermediates are recalcitrant to the mineralization with these anode materials. In the case of carbon-felt, the difference is remarkable. It performs very well in the initial oxidation of the AMX but it is not able to attain a higher oxidation. This confirms the significance of the active area of the electrode and the potential formation of soft oxidants

(such as hydrogen peroxide) which help in the initial stages but are not able to mineralize this complex pollutant. An important fact is that graphite can mineralize AMX almost with the same efficiency as Pt and is almost two times better than DSA, applying much lower current intensities, what means less energy consumed for same or more TOC removal. Previous results obtained with BDD electrodes with different ratios  $sp^3/sp^2$  during the degradation of enrofloxacin showed that  $sp^2$  carbon in diamond promoted the formation of intermediates<sup>361</sup>.

### 3.4. Conclusions

A systematic study on the efficiency of the electrode materials such as carbon-felt, carbon-fiber, carbon-graphite, Pt, DSA (Ti/RuO<sub>2</sub>-IrO<sub>2</sub>), PbO<sub>2</sub>, and BDD was studied through different electrochemical parameters in the oxidative degradation of the drug AMX. First it was evidenced that BDD electrode is more efficient than that of DSA to oxidize AMX achieving the total mineralization of the antibiotic in less than 100 min while less than half of the initial AMX was mineralized with DSA anode in the same period for the best experimental conditions. Then, the apparent rate constants of the oxidation reaction of AMX were determined in function of current intensity for several anodes. The results showed that apart from BDD electrode, carbon-felt exhibits a better performance for low and moderate current density values. On the other side, in particular in terms of mineralization, obtained results highlighted that the BDD anode is the best anode material for the large current densities due to generation of large amount of different oxidants: hydroxyl radicals, but also hydrogen peroxide, ozone and persulfates, that permits not only the oxidation of AMX but also its complete mineralization.

## **CHAPTER 4**

### **EFFECT OF THE ANODE MATERIAL ON THE ELECTRO-FENTON PROCESS EFFICIENCY**

# KINETIC STUDY OF THE DEGRADATION AND MINERALIZATION OF SULFAMETHAZINE (SMT) BY ELECTRO-FENTON PROCESS USING DIFFERENT ANODE MATERIALS

To estimate the effect of anode material on the electro-Fenton process efficiency as an electrochemical advanced oxidation processes (EAOPs), the SMT was chosen as a model pollutant. Degradation of SMT was performed under different current intensities and the apparent rate constants  $k_{app}$  and TOC removal percentages are studied for each anode, the cathode being always the carbon-felt.

## 4.1. Kinetics of SMT oxidation during electro-Fenton treatment

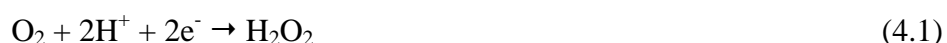
Electrochemical oxidative degradation of SMT was brought about in an electrolytic cell of 300 mL capacity and equipped with two electrodes. The cathode was a carbon felt piece of dimensions 23 cm x 6 cm x 0.5 cm whereas the anodes were Pt, BDD, DSA ( $\text{RuO}_2\text{-IrO}_2$ ) and C F (carbon felt) of 24 cm<sup>2</sup> area each side. The pH of the solution was adjusted with sulfuric acid to 3, the optimal pH for electro-Fenton process.  $\text{Na}_2\text{SO}_4$  (50 mM) was added as supporting electrolyte to provide a good conductivity in the electrolytic cell. The concentration decay with time was followed by withdrawing samples at regularly time intervals and analyzing by HPLC.

During the analysis of electrolyzed samples, SMT showed a well-defined chromatographic peak at 13.8 min which diminished progressively with the time until complete disappearance. After electrolysis begins, the chromatogram showed also other peaks indicating the formation of many intermediate products during the degradation of the initial compound. The intermediate's peaks continued to increase until a certain moment and then they started to diminish until their disappearance.

Fig. 4.1 shows the effect of current intensity on the concentration decrease of SMT with time in the Pt/Carbon felt system. It can clearly be observed that the concentration diminishes with time exponentially, following a pseudo-first order reaction kinetics almost until the complete disappearance of the target molecule. The pseudo-first order kinetics for the pollutant degradation can be adopted taking in consideration the fact that for a given current intensity, the quantity of hydroxyl radicals  $\cdot\text{OH}$  produced in the solution by time unit ( $\cdot\text{OH}$

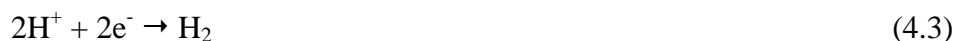
formation rate) is constant. The experimental degradation curves seem to fit very well this consideration.

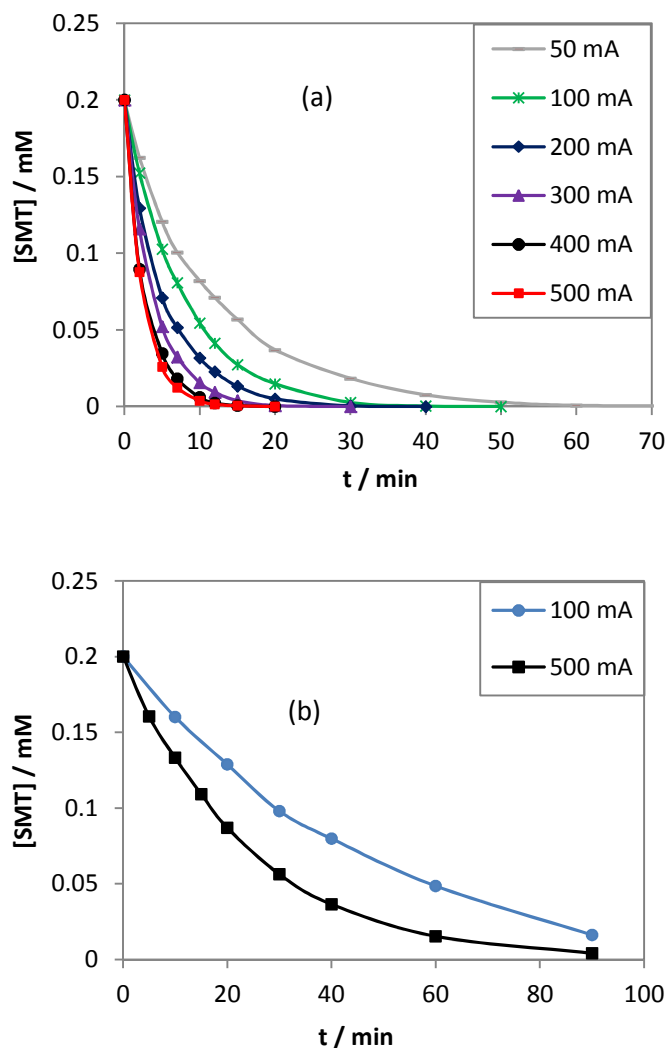
The plot below Fig 4.1(a) depicts the variation of degradation rate in a range of current intensities from 50 to 500 mA. An increase in the current intensity leads neatly to an increase in the decay rate of the SMT concentration. The acceleration of the degradation reactions comes due to the intensification of the electrochemical reactions of hydrogen peroxide production (reaction 3.1) and catalyst ( $\text{Fe}^{2+}$ ) generation (reaction 4.2) on the cathode:



As  $\text{H}_2\text{O}_2$  concentration increases with the current and the catalyst is faster regenerated, the Fenton's reaction accelerates too, resulting in a higher  $\cdot\text{OH}$  production rate in the medium which leads to a faster degradation of the pollutant. Another important fact to be observed is that the improvement of degradation can only be achieved until a certain current value. In this case we can see that an optimal abatement current is attained at 300 mA. For 400 and 500 mA no more increase on degradation rate is gained, indicating that side wasting reactions begins to become prevalent. There are two principal parasitic reactions that waste the current for high potentials:

Oxygen reduction on the cathode until  $\text{H}_2\text{O}$  according to the reaction (104) (chapter 1) which leads to less production of  $\text{H}_2\text{O}_2$  and hydrogen evolution (reaction (4.3)) which compete with oxygen reduction and oxygen evolution on the anode (reaction (4.4)) which compete with the production of  $\text{M}(\cdot\text{OH})$  and SMT direct oxidation on the anode surface:





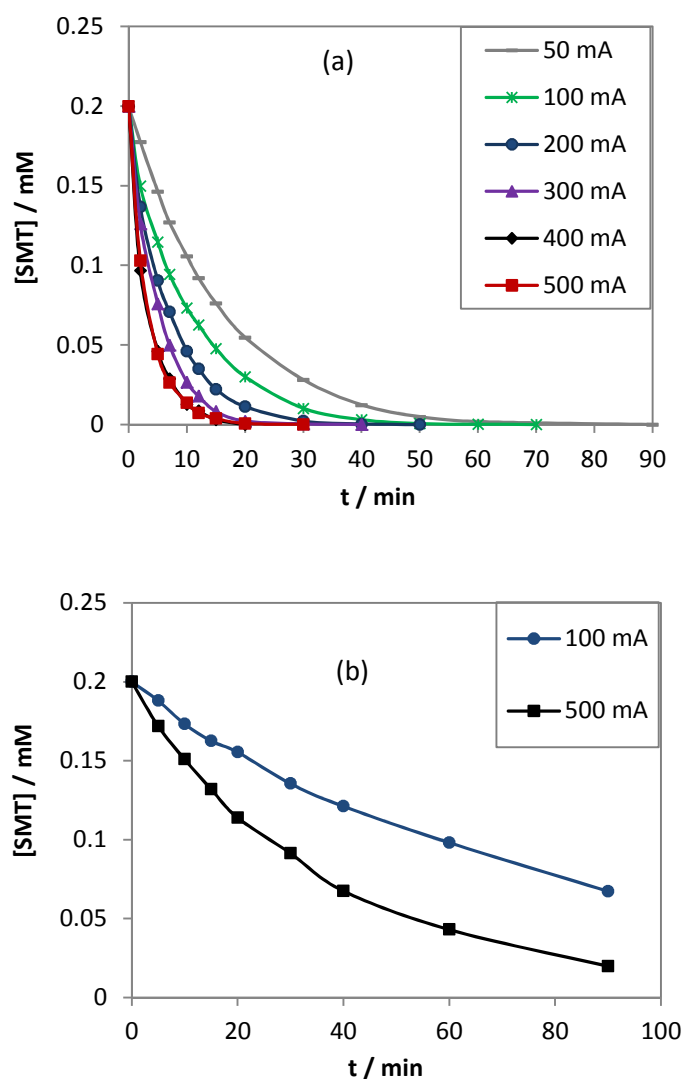
**Fig. 4.1.** The effect of current intensity on the kinetics of degradation of SMT using the Pt/Carbon felt electrode couple. (a) electro-Fenton and (b) anodic oxidation.  $V_s = 300$  mL,  $\text{pH} = 3$ ,  $[\text{Na}_2\text{SO}_4] = 50$  mM,  $[\text{Fe}^{2+}] = 0.2$  mM for electro-Fenton and 0.0 mM for anodic oxidation.

To see the contribution of direct oxidation without the effect of electro-Fenton process in the whole result, two experiments without adding the catalyst  $\text{Fe}^{2+}$  were done and they are presented in figure 3.1b. As can be seen, much more longer time are needed to reach complete oxidation (disappearance) of SMT. Actually even after 90 min of electrolysis at 500 mA there are still some traces of the SMT remaining in the solution. In contrast, in the case of electro-Fenton process, in only 20 min treatment no SMT could be detected in the solution under same experimental conditions. Whereas at 100 mA applied current, 91.8% of SMT was oxidized at 90 min by anodic oxidation against 100% by electro-Fenton process.



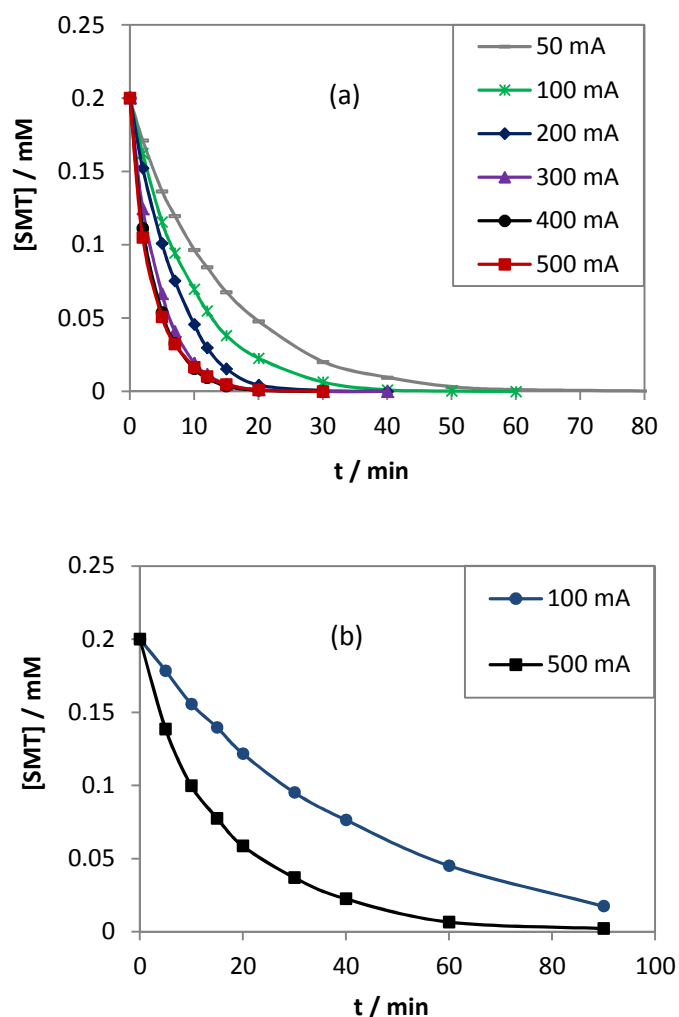
The DSA/Carbon felt electrolytic cell was tested in the same conditions and results are presented in the Fig. 4.2. Similarly, for higher current intensities the rate of oxidation increases until a limiting value is attained at 400 mA. The degradation efficiency seems to be similar to that of Pt/Carbon felt system (slightly slower) for the case of electro-Fenton treatment of the solution, but it changes more for the direct anodic oxidation. 70 and 30 minutes are needed for complete transformation of SMT from the solution when current intensities were 100 and 500 mA, respectively, during the electro-Fenton process. But, by applying a current intensity of 100 mA for the anodic oxidation only 66.4% of SMT could be oxidized after 90 min, while for a 500 mA current intensity this process is enhanced and reaches the value of 90.1% of oxidation of SMT.

A better performance of Pt anode in comparison with DSA can be explained with the oxygen evolution overpotential. As the overpotential of oxygen evolution is higher for Pt for DSA, generation of hydroxyl radicals is better for the former anode. It means also that for a given operation potential the quantity of oxygen evolution is lower on Pt electrode so more organics can be transformed on the anode. Moreover, polymeric films can be created on the DSA anode which inhibits the organics oxidation. When the catalyst is added to the medium, hydroxyl radicals will be generated and they will attack the polymeric film releasing more active sites on the anode surface. DSA anode is more efficient on organics oxidation only in the presence of chlorides, when a chloride containing salt is used as supporting electrolyte or when the pollutant under treatment contains chlorine as heteroatoms.



**Fig. 4.2.** The effect of current intensity on the kinetics of degradation of SMT using the DSA/Carbon felt electrode couple: (a) electro-Fenton, (b) anodic oxidation.  $V_s = 300$  mL,  $\text{pH} = 3$ ,  $[\text{Na}_2\text{SO}_4] = 50$  mM,  $[\text{Fe}^{2+}] = 0.2$  mM (electro-Fenton only).

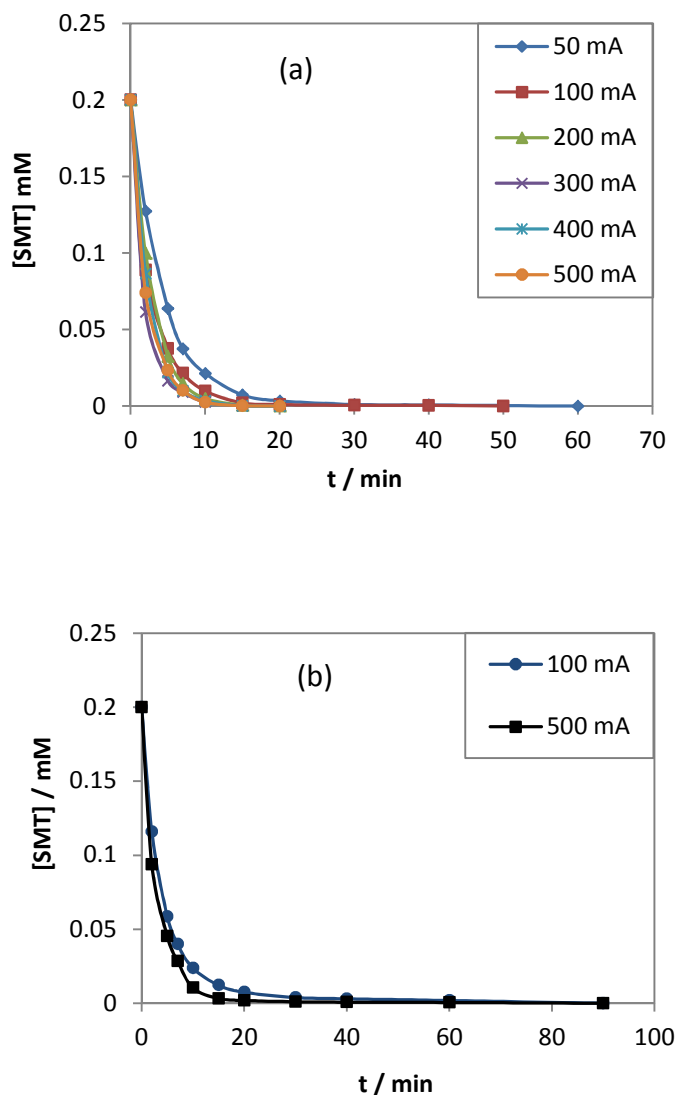
In figure 4.3, is presented the concentration decay of SMT for the electrolytic system BDD/Carbon felt with time for different current intensities for both electro-Fenton and anodic oxidation. There is always an exponential pseudo-first order kinetic decay of concentration for the whole range of applied currents.



**Fig. 4.3.** The effect of current intensity on the kinetics of degradation of SMT using the BDD/Carbon felt electrode couple: (a) electro-Fenton, (b) anodic oxidation.  $V_s = 300$  mL,  $\text{pH} = 3$ ,  $[\text{Na}_2\text{SO}_4] = 50$  mM,  $[\text{Fe}^{2+}] = 0.2$  mM (only for electro-Fenton).

The rate of SMT abatement still increases until the optimal current intensity that is about 300 mA. If we do a comparison between electro-Fenton and direct anodic oxidation, a remarkable difference is observed. For the electro-Fenton treatment the complete depletion in SMT is attained at 30 min for 500 mA and at 60 min for 100 mA. For the anodic oxidation there still remain traces of SMT at 90 min for 500 mA, whereas 91.3% of SMT is oxidized with 100 mA at the same time. According to the degradation curves, BDD is slightly faster than DSA for 50, 100, 200 and 300 mA but it is slightly slower than Pt for the whole range of current intensities.

The results obtained with carbon felt as anode and carbon felt again as cathode, show a much more different compartment. These results are shown in the Fig. 4.4.



**Fig. 4.4.** The effect of current intensity on the kinetics of degradation of SMT using the Carbon Felt /Carbon felt electrode couple: (a) electro-Fenton, (b) anodic oxidation  $V_s = 300$  mL, pH = 3,  $[Na_2SO_4] = 50$  mM,  $[Fe^{2+}] = 0.2$  mM (for electro-Fenton only).

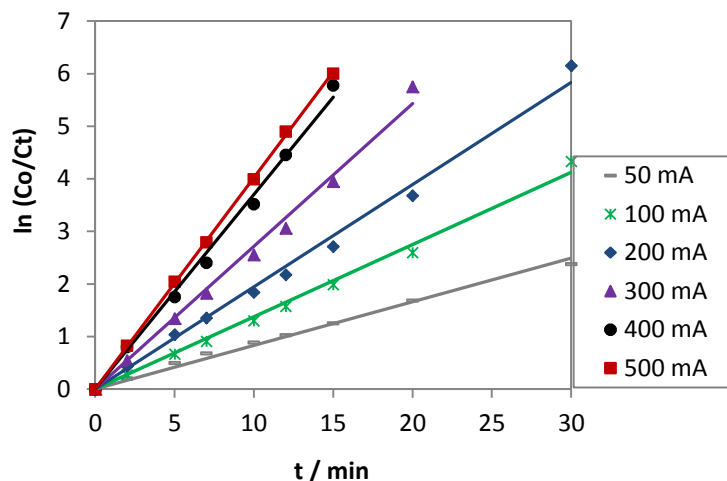
Figure 4.4a shows that in the electro-Fenton process, once the current starts to pass through the circuit, the concentration of the pollutant (here SMT) decreases rapidly up to zero value at about 15 min for the current higher than 100 mA while traces of the pollutant can be found until 50 min or more for the current intensity of 50 mA and 100 mA. For 300-500 mA, SMT disappearance kinetics curves have similar shapes, since the anode underwent combustion reactions for high current values. Thus the effect of increasing current was inhibited by the loss in the electrode surface from its partial combustion.

When anodic oxidation only is brought about, the oxidation of SMT is slower what lets more time for oxidation of anode (carbon-felt) to advance. At a moment the anode has been considerably damaged and SMT concentration lowered, oxidation rate of SMT became very slow. This is probably manifested with the prolongation of degradation curves until 90 min, despite that it descends almost to zero in 20 min.

Hydroxyl radicals are known for their extreme reactivity and non-selectivity towards organic molecules. Once created in the solution they react immediately with whatever molecule that they come across first. This very short life time prevents them to accumulate in the medium. For a constant current intensity a constant rate of  $\cdot\text{OH}$  production is obtained, so a quasi-stationary state is attained for their concentration, whereby a pseudo-first order kinetics can be established for the reaction of oxidation of organics. Now considering the section dealing with the reactivity of hydroxyl radicals, for the reaction of the degradation of SMT we can write:

$$\ln \frac{[\text{SMT}]_0}{[\text{SMT}]_t} = k_{app} \cdot t \quad (4.5)$$

So the slope of the plot of  $\ln \frac{[\text{SMT}]_0}{[\text{SMT}]_t} = f(t)$  gives a straight line with the slope equal to  $k_{app}$ (apparent rate constant) for the reaction of the oxidation of sulfamethazine with hydroxyl radicals. In the figure 4.5 is given the example for the system Pt/Carbon felt, and the same method was applied for all the other electrolytic cells.



**Fig 4.5.** Semi-logarithmic plots for the determination of apparent rate constants ( $k_{app}$ ) of the reaction of degradation of SMT with  $\cdot\text{OH}$  in the Pt/Carbon felt electrolytic cell:  $V_s = 300$  mL,  $\text{pH} = 3$ ,  $[\text{Fe}^{2+}] = 0.2$  mM,  $[\text{Na}_2\text{SO}_4] = 50$  mM.

The apparent rate constants calculated from pseudo-first order kinetics are given in the Table 4.1

*Table 4.1. Apparent rate constants in function of anode material and current intensity for electro-Fenton process with carbon felt cathode.*

Cell	Pt	DSA	BDD	C F
I (mA)	$k_{app}/\text{min}^{-1}$			
50	0.08	0.06	0.07	0.22
100	0.15	0.09	0.12	0.31
200	0.19	0.14	0.18	0.37
300	0.27	0.20	0.24	0.44
400	0.37	0.27	0.27	0.43
500	0.40	0.27	0.25	0.43

Table 4.2. Apparent rate constants in function of anode material and current intensity for anodic oxidation. The cathode is carbon felt.

Cell	Pt	DSA	BDD	C F
I (mA)	$k_{app}/\text{min}^{-1}$			
100	0.02	0.01	0.02	0.22
500	0.04	0.02	0.06	0.29

According to apparent rate constants obtained for the SMT oxidation in different electro-Fenton electrolytic systems, no very important difference exist between them, except for the carbon felt anode which represents considerably high  $k_{app}$  values. If we consider this difference towards the organic molecules oxidation between anodes studied, kinetic data range the DSA anode as the weakest one followed by BDD which is a little more efficient, then Pt and finally carbon felt as the most powerful one. In all cases the degradation rate increases with the current until an optimal current intensity of about 300-400 mA. Concerning the optimal current intensity, a more characteristic behavior is observed for the carbon felt anode, for which an optimal current intensity is attained at 300 mA. Namely when current intensity increases from 50 mA to the optimal value 300 mA, the  $k_{app}$  increases less than for other anodes and kinetic curves stay closer to each other. This behavior can be explained by partial combustion of the anode material. When the current intensity is lower the oxidation of anode itself is less intensive, whereas the increase of I favors the Fenton's reaction but at the same time accelerates the anode oxidation. These two opposite actions cancel at certain degree each other making the  $k_{app}$  increase slower with the current intensity.

The anodic oxidation rate constants given in the table 4.1 and also the graphs of anodic oxidation given below to every electro-Fenton plot (figs. 4.1-4.4), show a difference in the order of  $k_{app}$  values for BDD and Pt anodes alone when compared to electro-Fenton. Unlike in electro-Fenton process, in direct anodic oxidation, BDD anode oxidizes faster SMT than Pt. This trend is normally expected for the BDD anode having a higher overpotential for OER makes more possible generation of higher hydroxyl radical and other oxidizing species than Pt. In the case of electro-Fenton process, the electrogenerated oxidizing agents formed in the solution can play a slight negative role too. Since  $\text{Na}_2\text{SO}_4$  was used as supporting electrolyte in electrolysis experiments, the main electrogenerated oxidizing specie created on the anode is the persulphate anion  $\text{S}_2\text{O}_8^{2-}$  which can oxidize the catalyst  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (reaction (4. 6))<sup>286</sup> which do not react with  $\text{H}_2\text{O}_2$  in the same way as  $\text{Fe}^{2+}$ .



Actually  $\text{Fe}^{3+}$  ions reacts with  $\text{H}_2\text{O}_2$  giving hydroxyperoxyl radicals  $\text{HO}_2^\bullet$  according to the reaction (59) which are relatively weaker oxidants compared to  $^\bullet\text{OH}$ , and do not oxidize effectively the organic molecules. Another reason might be the higher potential of BDD than Pt for a given constant current which also contributes to higher oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . In fact it has been confirmed that  $\text{Fe}^{2+}$  accumulates much more in a cell employing Pt as anode than in that of BDD<sup>286</sup>. Accordingly we can say that the slightly better performance of Pt than BDD is because of the removal of a part of catalyst from the electro-Fenton cycle in the BDD/Carbon felt cell.

Finally, the slight difference between  $k_{\text{app}}$  for Pt/Carbon felt, BD/Carbon felt and DSA/Carbon felt, in electro-Fenton process, can be explained with the overwhelming effect of hydroxyl radicals generated from electro-Fenton process (as kinetic curves show, the contribution of only anodic oxidation is far lower from that of electro-Fenton). High quantities of  $^\bullet\text{OH}$  are formed in the bulk of solution and rapidly degrade the organic molecules resulting in high degradation rate constants. Thus, a part of anode effect is hidden by the dominating electro-Fenton action, in particular at high applied current intensities.

The best performance of Carbon felt/Carbon felt cell is a result of much more larger surface area of the carbon felt material owing to its high porosity and three dimensional geometry. A high surface area enhances the rate of electrochemical reactions (formation of  $\text{H}_2\text{O}_2$  and regeneration of  $\text{Fe}^{2+}$ ) and also facilitates the contact of organic molecules with the anode due to better mass transport conditions leading to a greater contribution to the overall oxidation rate of pollutant to be degraded. It is important to emphasize that the carbon felt anode provides good oxidation efficiency at low current densities but it is not suitable for high currents densities that lead to its combustion.

In order to determine the absolute rate constant of the oxidation of SMT, we have used as before the method of competition kinetics<sup>277</sup> and the experiment was done in the Pt/Carbon felt cell at current intensity of 50 mA. As we have emphasized before this method consists on simultaneously degradation of the compound of concern and a standard compound (competitor) with a known absolute rate constant of its reaction with hydroxyl radicals.



p-Hydroxy benzoic (pHBA) acid was used as standard competitor for the determination of the absolute rate constant of SMT oxidation by hydroxyl radicals. Assuming that hydroxyl radicals react only with SMT and pHBA we can write:

$$-\frac{d[SMT]}{dt} = k_{SMT}[SMT][HO^{\bullet}] \quad (4.7)$$

$$-\frac{d[pHBA]}{dt} = k_S[pHBA][HO^{\bullet}] \quad (4.8)$$

As the hydroxyl radicals are very reactive they have a very short life and a stationary state for their concentration can be considered. After integrating and arranging equations (4.7) and (4.8) we obtain:

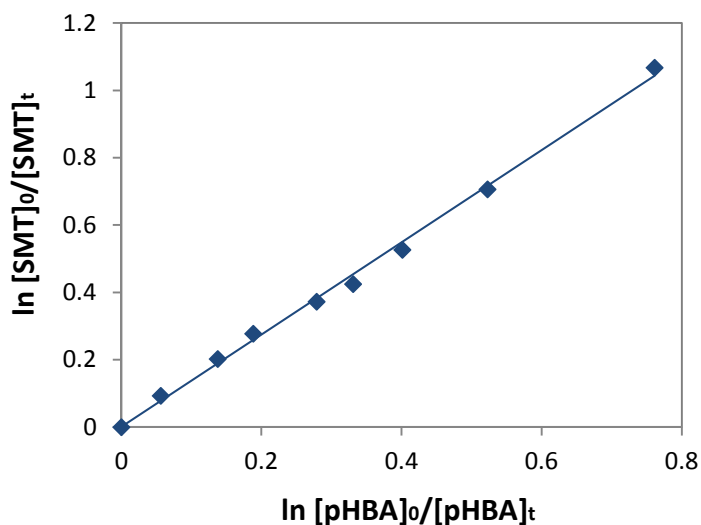
$$\ln \frac{[SMT]_0}{[SMT]_t} = \frac{k_{SMT}}{k_{pHBA}} \ln \frac{[pHBA]_0}{[pHBA]_t} \quad (4.9)$$

where  $[SMT]_0$  and  $[pHBA]_0$  are the concentrations of sulfamethazine and p-hydroxy benzoic acid before the beginning of electrolysis.  $[SMT]_t$  and  $[pHBA]_t$  are the concentration of the sulfamethazine and the p-hydroxy benzoic acid after a time  $t$  of electrolysis.

Therefore knowing that the absolute rate constant of pHBA with hydroxyl radicals is  $k_{pHBA} = 2.19 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , we can calculate that for the oxidative degradation of SMT from the slope of the graph  $\ln \frac{[SMT]_0}{[SMT]_t} = f\left(\ln \frac{[pHBA]_0}{[pHBA]_t}\right)$ .

The concentration decay of SMT and pHBA was followed and measured by high performance liquid chromatography at a given time. The above written function for the absolute rate constant determination of SMT is presented in Fig. 4.6.

The slope of the linear curve shown in the Fig. 4.6, multiplying it by  $k_{pHBA} = 2.19 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  we obtain the absolute rate constant of SMT oxidation by hydroxyl radicals which results to be  $k_{SMT} = 2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . It is a high value indicating high reactivity of  $\bullet\text{OH}$  towards SMT. This value is of the same order as absolute rate constants for oxidation of several aromatic organic compounds by hydroxylation with  $\bullet\text{OH}$ , indicated in the Table 1 (chapter 1).

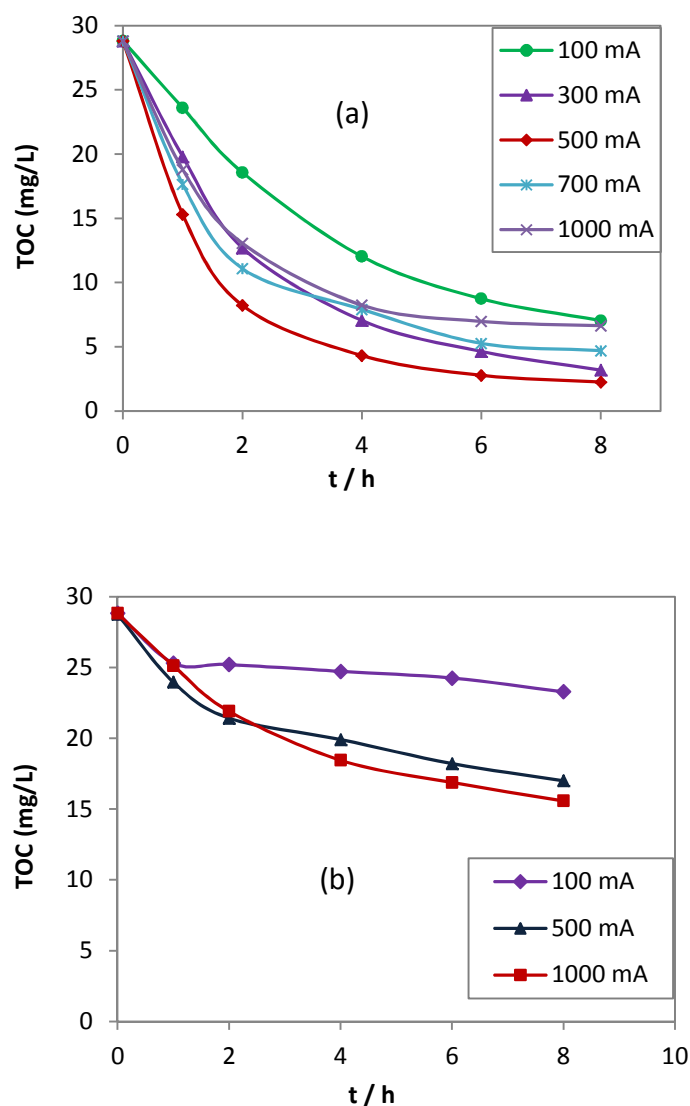


**Fig. 4.6.** Kinetic analysis for the absolute reaction rate constant for oxidation of SMT with  $\cdot\text{OH}$ . Electro-Fenton cell: Pt/Carbon felt,  $V_s = 300$  mL,  $[\text{Fe}^{2+}] = 0.2$  mM,  $[\text{Na}_2\text{SO}_4] = 50$  mM,  $I = 50$  mA,  $\text{pH} = 3$ .

#### 4.2. Comparison of the mineralization efficiency

The degradation of organic pollutants is necessary because they have various adverse effects on the environment. When an initial organic pollutant degrades during an AOPs, it can produce other molecular species which may be more or less harmful or not harmful at all for the environment. Unfortunately the byproducts of the degradation by AOPs are very often even more dangerous for the living organisms than the mother pollutant. For this reason the oxidative degradation of the toxic chemicals must continue until their complete transformation on  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (mineralization). The complete mineralization of organics is a complicated oxidation process and a level of depollution is considerably hard to be achieved. Probably one of the most powerful methods to mineralize the organic matter in aqueous solution is the electro-Fenton process that provides high total organic carbon removal (TOC). Furthermore the extent of the organics mineralization with electro-Fenton technology depends on several parameters, one of the most crucial being the anode material. This section will give an insight on the effect of anode material on the mineralization degree by explaining the results gained with anode materials tested for the degradation of SMT in the previous parts of this chapter.

As it can be seen in figure 4.7a) the mineralization of SMT is improved with the current intensity for the Pt/Carbon felt cell.



**Fig. 4.7.** Effect of applied current intensity on the extent of TOC removal of SMT aqueous solution in the cell Pt/Carbon felt during (a) Electro-Fenton and (b) anodic oxidation.  $V_s = 300$  ml,  $\text{pH} = 3$ ,  $[\text{Na}_2\text{SO}_4] = 50$ ,  $\text{mM}[\text{Fe}^{2+}] = 0.2$  mM (for electro-Fenton).

The mineralization rate increases with the current intensity until 500 mA where the TOC removal efficiency from the solution reaches a maximum. After this optimal current intensity contrarily the TOC abatement is even lower. At current intensities of 700 and 1000 mA, TOC removal curves had almost the same slope as 300 mA, and the 1000 mA curve is even worse after 4 h electrolysis ending with the TOC removal as low as for 100 mA.

Fig. 4.7b) shows mineralization curves for anodic oxidation; it indicates clearly that the TOC abatement is very weak compared with the electro-Fenton. Otherwise the anodic oxidation follows a similar course except that the slope of the curve for 1000 mA is not very

much lower than that for 500 mA, as it happens in the case of electro-Fenton, but it is slightly less stepper.

When working under electro-Fenton conditions at 1000 mA, parasitic reactions such as H<sub>2</sub> evolution on the cathode, O<sub>2</sub> evolution on the anode and four electron reduction of O<sub>2</sub> on the cathode, diminish significantly the rate of hydroxyl radical generation. So the TOC removal kinetics tends to be less effective. At 500 mA there is still considerable H<sub>2</sub>O<sub>2</sub> production high TOC removal values than at 1000 mA in electro-Fenton, and of course, much more effective than 500 mA in anodic oxidation.

During electro-Fenton treatment a very steep decay of the mineralization curve is observed for the first part of electrolysis until 4 h, and then it becomes more flat because the mineralization slows down. This sluggish mineralization reaction by the end of treatment is considered to be due to the carboxylic acids as they accumulate in the solution and react slowly with hydroxyl radicals. Carboxylic acids not only are more refractive but they also can form complexes with iron inhibiting its role of catalyst. An effect on this sluggishness of the mineralization process may have also the diminution of concentration of catalyst due to its precipitation in the basic medium created in the pores of carbon felt because of hydrogen evolution. This can be visibly detected as very small yellow precipitate particles can be seen on the carbon felt cathode.

For comparison between electro-Fenton and anodic oxidation we can take the percentage of the TOC removal at the end of experiment for the optimal current intensity of 500 mA. For the mineralization with electro-Fenton we have 92.2% of TOC removed at 8 h, whereas only 41% TOC removal could be achieved at the same conditions at 8 h with anodic oxidation.

To understand the efficiency of electric current used, mineralization current efficiency was calculated for each experiment following the following mineralization reaction of SMT:

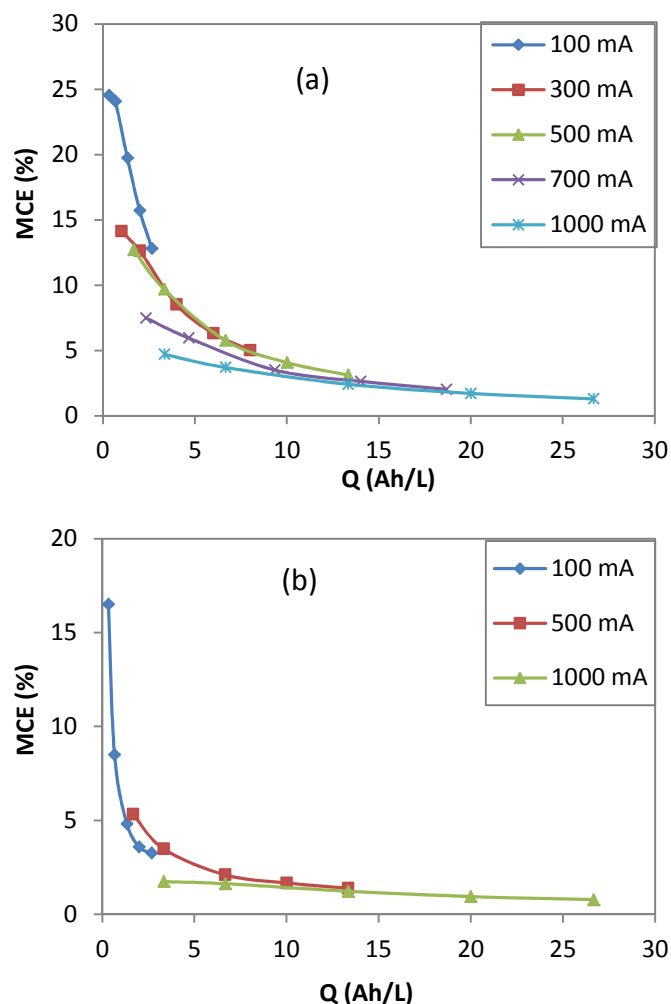


than the MCE can be obtained from the equation :

$$\text{MCE } \% = \frac{n F V_s \Delta(\text{TOC})_{\text{exp}}}{4.32 \times 10^7 \text{ m I t}} \times 100 \quad (4.11)$$

with units given in precedent chapter.

The mineralization current efficiencies in percentage MCE% for the cell Pt/Carbon felt are given in the figure 4.7.

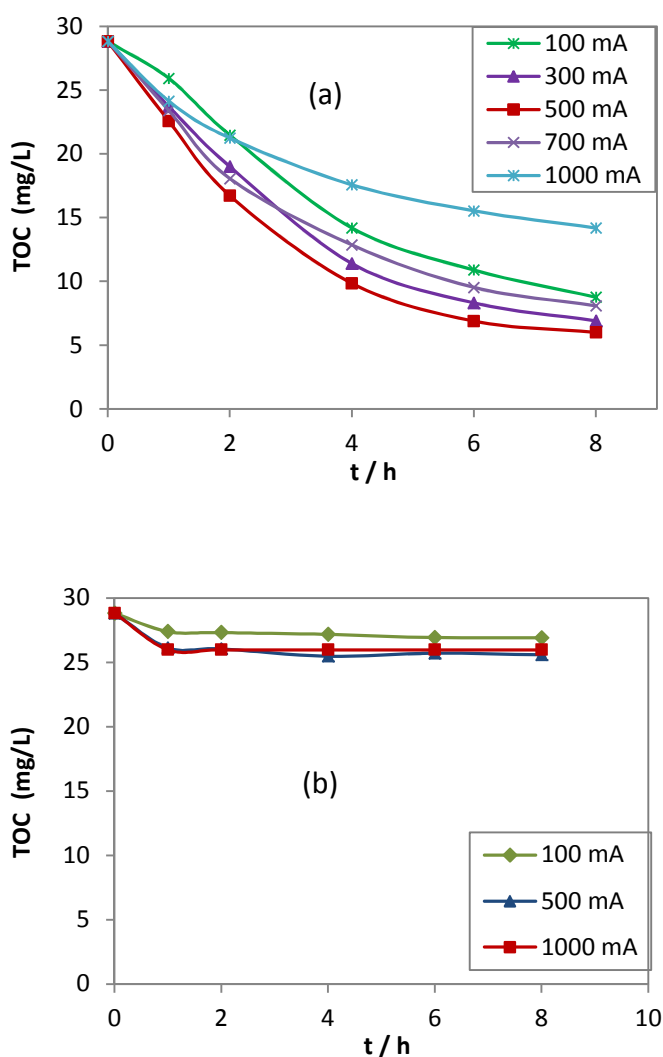


**Fig. 4.8.** Mineralization current efficiency versus specific charge per volume unit passed through the cell, Pt/Carbon felt: (a) Electro-Fenton, (b) anodic oxidation processes.  $V_s = 300$  ml,  $\text{pH} = 3$ ,  $[\text{Fe}^{2+}] = 0.2$  mM,  $[\text{Na}_2\text{SO}_4] = 50$  mM,  $[\text{Fe}^{2+}] = 0.2$  mM (for electro-Fenton)

It can be clearly seen that MCE% decreases drastically with the specific charge passed (and indirectly with treatment time). At the beginning there is more organic matter in the cell to be degraded resulting in higher MCE% values. When the concentration of organic matter decreases during electrolysis, the parasitic reactions occur simultaneously and after a certain time they become dominant compared to SMT and by products oxidation. Consequently, as

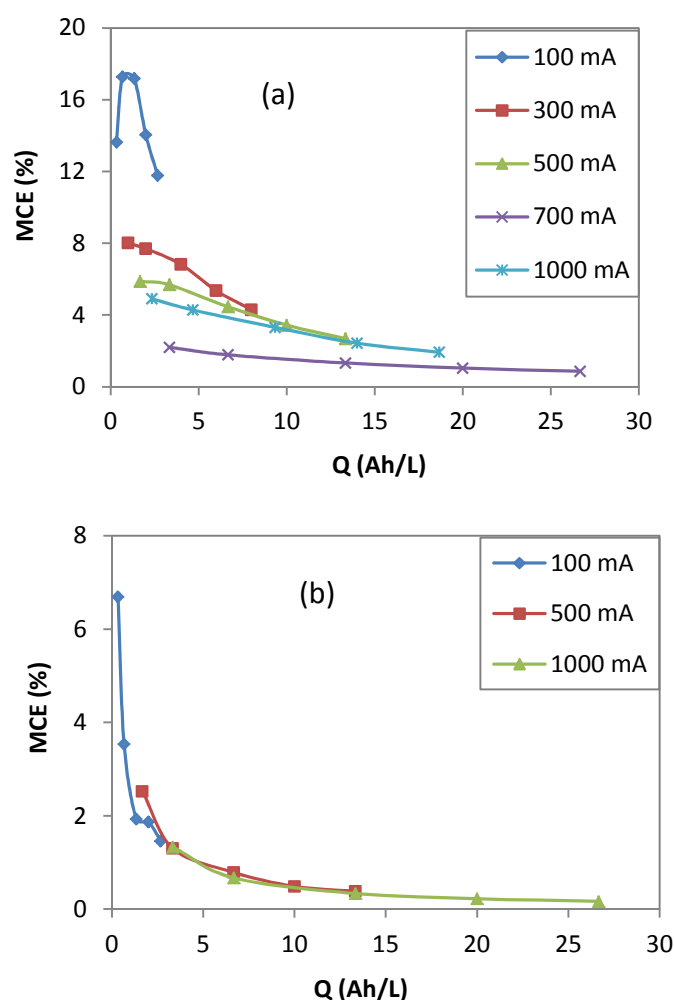
the specific charge increases with time, the quantity of organic matter to be oxidized decreases continuously making the MCE% falls progressively.

In the case of electro-Fenton, the MCE% are very high compared to anodic oxidation, for example the starting value for electro-Fenton at 100 mA is 24.5 %, but it is 16.5% for the anodic oxidation which is not surprising. This explains the additional role of hydroxyl radicals formed in the solution bulk in the presence of the  $\text{Fe}^{2+}$ . Now, for the same current more reactive oxidants are formed giving higher TOC abatement per unit specific charge.



**Fig. 4.9.** Effect of current intensity on the extent of TOC removal in the cell DSA/Carbon felt. a) Electro-Fenton,  $V_s = 300$  ml,  $\text{pH} = 3$ ,  $[\text{Fe}^{2+}] = 0.2$  mM,  $[\text{Na}_2\text{SO}_4] = 50$  mM. b) Anodic mineralization of SMT:  $V_s = 300$  ml,  $\text{pH} = 3$ ,  $[\text{Na}_2\text{SO}_4] = 50$  mM.

The experiments with the DSA/Carbon felt system revealed a poorer TOC abatement than with Pt/carbon felt. As Fig. 4.9a indicates the TOC decay is improved with the current intensity so that 100, 300 and 500 mA curves are closer to each other than when Pt was used as anode. This means that the optimal current is attained for lower values for the DSA indicating that the OER dominates the SMT oxidation easier than on Pt. Despite this, the TOC removal is still good for the electro-Fenton treatment. Anodic oxidation with DSA is very low and there is almost no difference between current intensities, Fig. 4.9b). A positive effect of higher current on SMT mineralization when electro-Fenton is operating can be attributed to the bulk hydroxyl radicals which can destroy organic layers that possibly formed on the DSA surface.



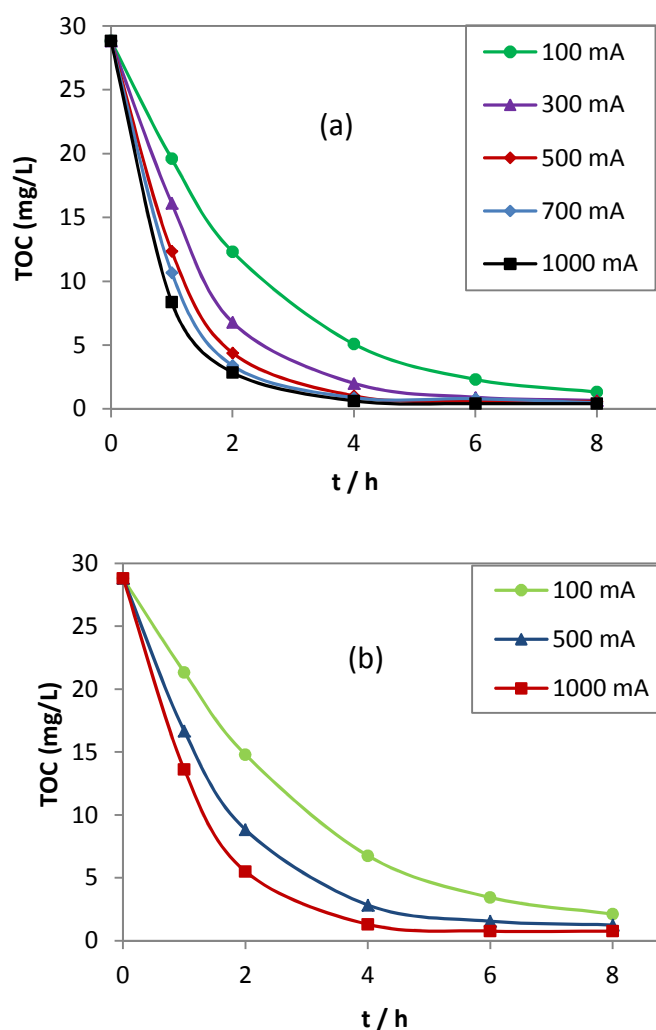
**Fig. 4.10.** Mineralization current efficiency versus specific charge passed through the cell, DSA/Carbon felt. (a) Electro-Fenton and b) anodic oxidation processes.  $V_s = 300$  ml, pH = 3,  $[\text{Fe}^{2+}] = 0.2$  mM (for electro-Fenton only),  $[\text{Na}_2\text{SO}_4] = 50$  mM.

Just like TOC, the MCE% with DSA electrode is smaller than that of Pt (see Fig. 4.8a). When the solution is treated with electro-Fenton process using DSA anode (Fig. 4.10a), the MCE% have more important values than in the case of anodic oxidation. For the current intensity of 100 mA, MCE% increases for the early stages of electrolysis because more SMT is oxidized, and then after 2 h it decreases sharply with the specific charge. As the oxidation of SMT is not efficient with DSA anode, higher currents results mostly in energy loss.

Contrarily to oxidation of SMT on BDD anode which was slower than on that of Pt, the mineralization process is performed remarkably better on the former one. The oxidation of an organic molecule is easier than the mineralization because the mineralization process requires several steps and a great number of hydroxyl radicals contrarily to oxidation which necessitates the reaction with one mole of this oxidant. As most of the SMT molecules are in the bulk they will react quickly with the hydroxyl radicals that are generated from electro-Fenton process. Taking into account the fact that the concentration of oxidizing species other than  $\cdot\text{OH}$  (as mentioned earlier) in the BDD system is much higher than in Pt system, a lower bulk concentration of  $\cdot\text{OH}$  is expected because of the removal of a quantity  $\text{Fe}^{2+}$  by these species. That's why the Pt/Carbon felt is a bit faster in degrading SMT than BDD/Carbon felt. When the initial molecule is broken it is transformed in smaller intermediates that react less with the hydroxyl radicals in the bulk in the case of Pt/Carbon felt, but when a BDD anode is employed high amounts BDD( $\cdot\text{OH}$ ) are formed on its surface which destroy the organic matter. This does not happen with Pt and DSA anodes as they do not generate appreciable hydroxyl radical quantities, so the mineralization rate subsides for longer electrolysis time.

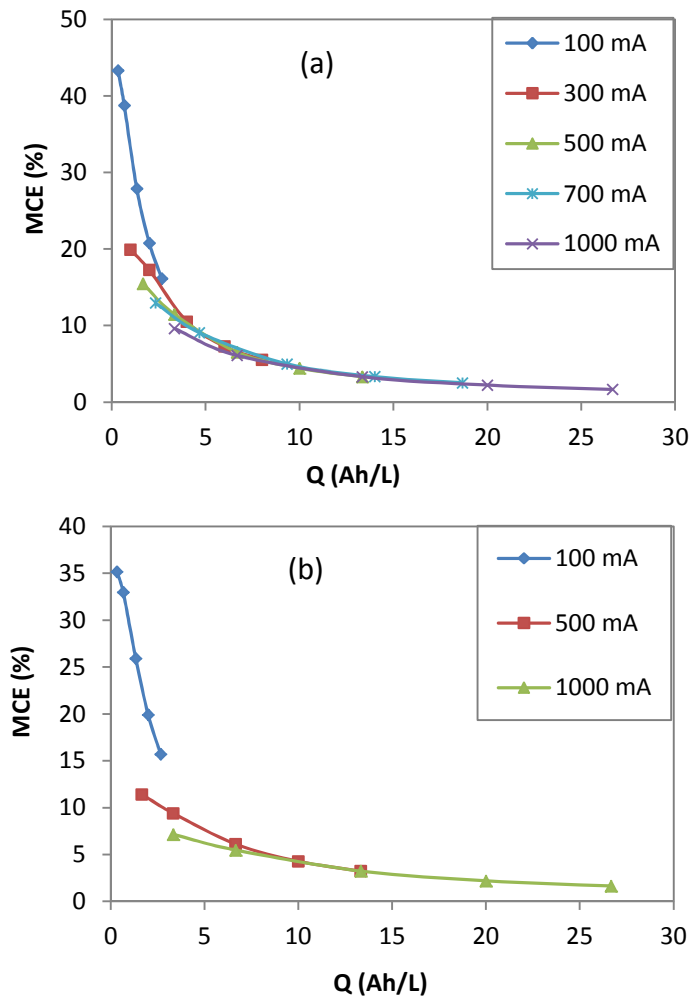
The effect of current intensity on mineralization of SMT is given in the figure 4.11, where a new trend is observed. Unlike with the precedent anodes, in the case of BDD anode, the range of current intensities where the oxidation of organic molecule can be accelerated is extended. For Pt and DSA anodes the limit of the optimal current intensity was 500 mA, whereas for BDD anode, the mineralization efficiency can be improved even at 1000 mA.





**Fig. 4.11.** Effect of current intensity on the extent of TOC removal in the cell BDD/Carbon felt during mineralization of SMT aqueous solution by (a) Electro-Fenton and (b) anodic oxidation.  $V_s = 300$  ml,  $\text{pH} = 3$ ,  $[\text{Fe}^{2+}] = 0.2$  mM (for electro-Fenton only),  $[\text{Na}_2\text{SO}_4] = 50$  mM. .

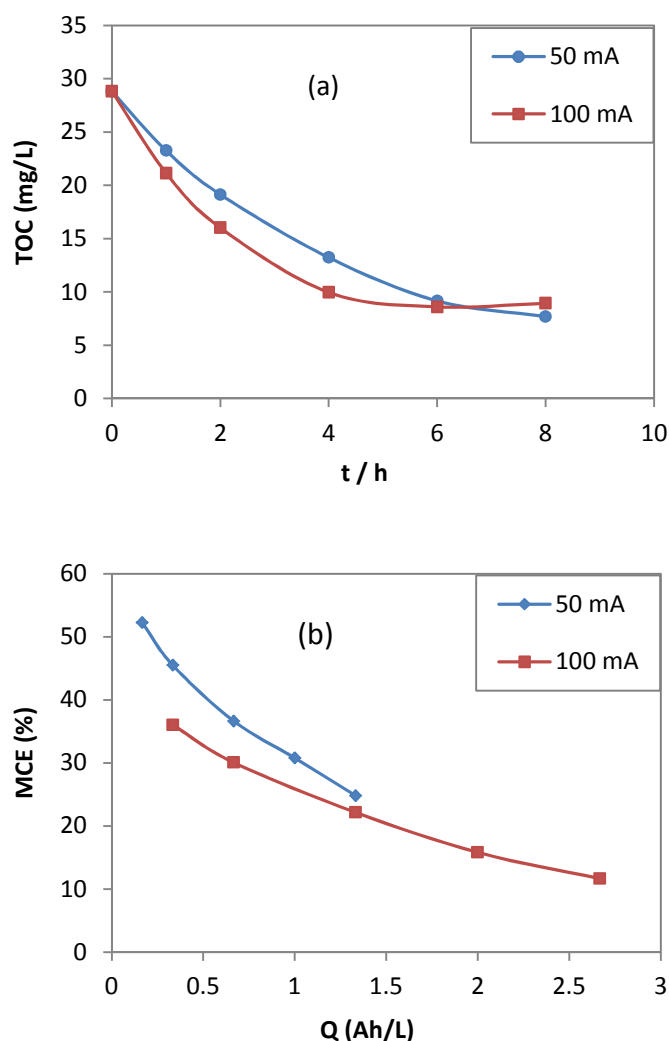
This is possible thanks to the high overpotential of OER on BDD which enables the generation and accumulation of hydroxyl radicals on its surface. Comparing electro-Fenton and anodic oxidation still another different compartment appears for BDD that is not seen for Pt and DSA. The TOC abatement does not change much from electro-Fenton to anodic oxidation. This result can be related to the fact that in the mineralization process BDD( $\cdot\text{OH}$ ) play a predominant role compared homogeneous  $\cdot\text{OH}$  in the bulk solution. Basing on this consideration and experimental data, the contribution of anodic oxidation on mineralization process plays the principal role.



**Fig. 4.12.** Mineralization current efficiency versus specific charge passed per volume unit during mineralization of SMT aqueous solution in BDD/Carbon felt cell (a) Electro-Fenton and (b) anodic oxidation processes.  $V_s = 300$  ml,  $\text{pH} = 3$ ,  $[\text{Fe}^{2+}] = 0.2$  mM (for electro-Fenton only),  $[\text{Na}_2\text{SO}_4] = 50$  mM.

Obviously MCE% is higher than for the previous experiments because the wasting reactions such as oxygen evolution are not so present (thanks to the high  $\text{O}_2$  overpotential of this anode material) and more TOC is removed per unit specific charge passed in the solution. The best mineralization current efficiency is obtained for the current intensity of 100 mA and its initial value is 43.3% for electro-Fenton and 35.1% for anodic oxidation, than it falls steeply down to 16.1% and 15.6% respectively for electro-Fenton and anodic oxidation. MCE% is lower when higher current intensities are applied, due to enhancement of wasting reactions.

Despite the high overpotential for OER on BDD, oxygen evolution is always a very competitive parasitic reaction at high current values.



**Fig. 4.13.** Effect of current intensity on the extent of TOC removal in the cell Carbon felt/Carbon felt. (a) Electro-Fenton and (b) MCE.  $V_s = 300$  ml,  $\text{pH} = 3$ ,  $[\text{Fe}^{2+}] = 0.2$  mM (in electro-Fenton),  $[\text{Na}_2\text{SO}_4] = 50$  mM.

The mineralization with carbon felt is not enhanced with high current densities. We can see that the mineralization is relatively good for 50 mA. At 100 mA the TOC decays quickly from the beginning until 4 h electrolysis, it is almost constant at 6 h and finally it is higher at 8 h than at 6 h. This result is something surprising but considering the results obtained during degradation experiments, the carbon increase may come from carbon felt burning. Also, when the carbon felt is burned this causes more heating in the system which

leads to water vaporization and volume diminution resulting in an increase of the total carbon concentration.

Anyways carbon felt can be an interesting anode material because relatively good TOC removal values can be reached using low current intensity. Then a low current intensity gives higher mineralization current efficiency as shown in figure 4.12b).

Table 4.3 gives some summarized data about the mineralization of SMT with different anodes.

*Table 4.3. TOC removal percentages during electro-Fenton treatment as function of anode material and current intensity at a treatment time of 2 and 6 h.*

Cell	Pt	DSA	BDD	C F
I (mA)	% TOC removal 2h / 6h			
50				33.6/68.2
100	35.5/69.6	25.5/62.2	57.2/91.9	44.4/70.2
300	55.9/83.9	34.1/71.1	76.4/96.8	
500	71.5/90.3	41.9/76.1	84.7/97.9	
700	61.4/81.7	14.8/75.2	88.2/97.2	
1000	54.7/75.8	26.3/46.1	90.1/98.5	

*Table 4.4. TOC removal percentages as a function of anode material and current intensity during anodic oxidation.*

Cell	Pt	DSA	BDD	C F
I (mA)	% TOC removal 2 h/6 h			
100	12.5/15.8	5.2/8.3	48.7/88.1	0/0
500	25.7/36.8	9.6/10.8	69.4/94.6	0/0
1000	24.0/41.4	9.8/9.8	80.9/97.4	0/0

The mineralization power of anodes according to the %TOC removal values given in the table 4.3 can be ranged as following: BDD > Pt > DSA, whereas carbon felt is only effective for currents smaller than 50 mA being always more efficient than DSA. The TOC abatement improves with current intensity up to 500 mA for Pt and DSA whereas for BDD

we can obtain higher percentages of TOC abatement even for that of 1000 mA. It is also important to note that although the TOC removal efficiency increases with current intensity until 1000 mA, the slope of the curves starting from 500 mA are very close to each other.

TOC removal percentages for anodic oxidation are lower than those for electro-Fenton. This effect is more pronounced for Pt and particularly for DSA electrode and it is less observed for BDD electrode.

The outstanding oxidation power of BDD comes, as we have stated before, from the generation of additional hydroxyl radicals on its surface which are weakly physio-sorbed and are free to react. In the case of DSA anode, the electronic structure permits higher oxidation states for iridium without free hydroxyl radical formation. Thus Ir (IV) in  $\text{IrO}_2$  passes to Ir (VI) as  $\text{IrO}_3$ , now the iridium trioxide oxidizes the organic matter which is rather a slow chemical reaction. At high current intensities (or high potentials) the  $\text{O}_2$  evolution rate from  $\text{IrO}_3$  according to the reaction (90) becomes faster than SMT oxidation by  $\text{IrO}_3$  lowering its oxidation efficiency. Higher oxidation states have been proposed for Pt also<sup>362</sup>, but as oxygen evolution overpotential is higher than on DSA, small quantities of hydroxyl radicals are possible.

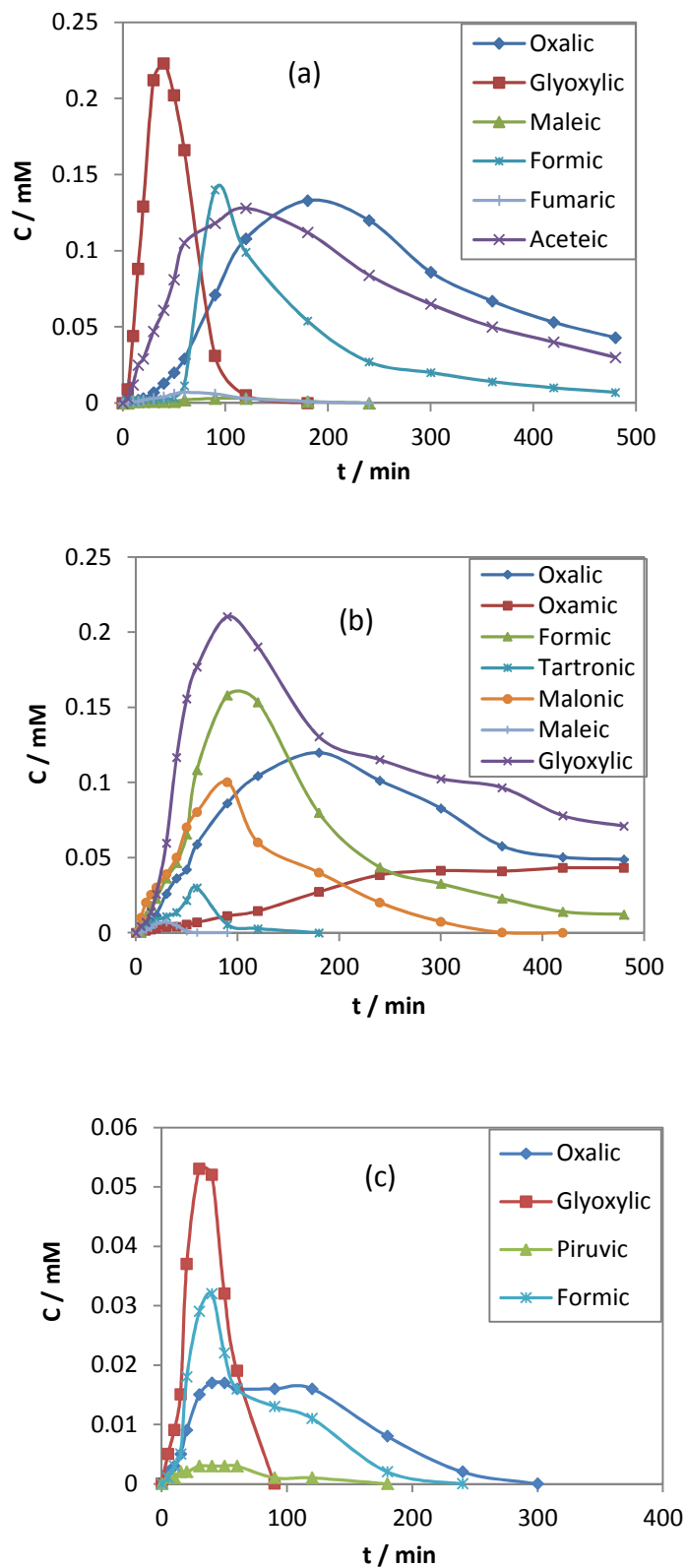
#### **4.3. Determination and evolution of carboxylic acids during electro-Fenton treatment of SMT**

The electrochemical degradation of organic compounds is accompanied with the intermediate product formation<sup>268,363,364</sup>. Short chain carboxylic acids<sup>214,277</sup> and probably some aliphatics, are the lowest organic molecular species formed before complete transformation of organic compounds in  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic ions (if the molecule contains heteroatoms). Depending on the structure of the molecule to be degraded many carboxylic acids can be formed. The electrode material that is used for the oxidation of the pristine compound has also an important impact on the carboxylic acids that will be present in the solution as well as their concentrations.

Figure 4.14 shows the experimental curves of different carboxylic acids that are obtained during the degradation of the initial product on Pt, DSA and BDD cells. Short chain carboxylic acids were identified and quantified for three electrolytic systems. Six of them could be quantified for the Pt/Carbon felt cell namely oxalic, glyoxylic, maleic, formic fumaric and acetic acids. Some other could not be identified or quantified either because their

chromatographic peaks were very close or they were at very low concentration and could not be determined. For the BDD/Carbon felt cell oxalic, glyoxylic, pyruvic and formic acids were quantified. The DSA/carbon felt system gave more carboxylic acids than two others and in that case we have quantified oxalic, oxamic, formic, tartronic, malonic, maleic and glyoxylic acid.

It can be seen that carboxylic acids starts to be generated immediately from the beginning of the electrolysis In the case of BDD and Pt anode a smaller number of carboxylic acids could be determined because of the more oxidizing capabilities of these anodes compared to DSA. The concentrations of carboxylic acids accumulated in different systems are not the same. The lowest concentrations were measured for the BDD/carbon felt system, what explains also the better mineralization efficiency of this couple. In the Pt/Carbon felt system there is still some oxalic, acetic and fumaric acid that remains in the solution, whereas for the BDD/Carbon felt anodes these acids could not be detected after 300 minutes of electrolysis. However some unidentified peaks remained at the end of electro-Fenton treatment of SMT, only two/three of them for the BDD whereas their number and area were more important for Pt and much more for DSA.



**Fig 4.14.** Time course of carboxylic acids formed during electro-Fenton treatment of SMT with different electrolytic cells: (a) Pt/Carbon felt, (b) DSA/Carbon felt and (c) BDD/Carbon felt.  $V_s = 300$  ml,  $[SMT] = 0.2$  mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM,  $I = 300$  mA,  $pH = 3$ .

Glyoxylic acid appears very quickly and then disappears being transformed in other carboxylic acids like oxalic and formic<sup>365</sup>. Oxalic and formic acids stays longer in the solutions because they can be formed from oxidation of other's acids (glyoxylic, glycolic, pyruvic, malonic, succinic, maleic, fumaric etc.) as reported by Oturan et al<sup>365</sup>. The poorer mineralization obtained with DSA/Carbon felt system is manifested with higher carboxylic acids accumulation as is shown in Fig 4.13b). There are four remaining carboxylic acids that could be quantified in the solution at the end of electrolysis at 8 hours, namely glyoxylic, oxalic, oxamic and formic acid.

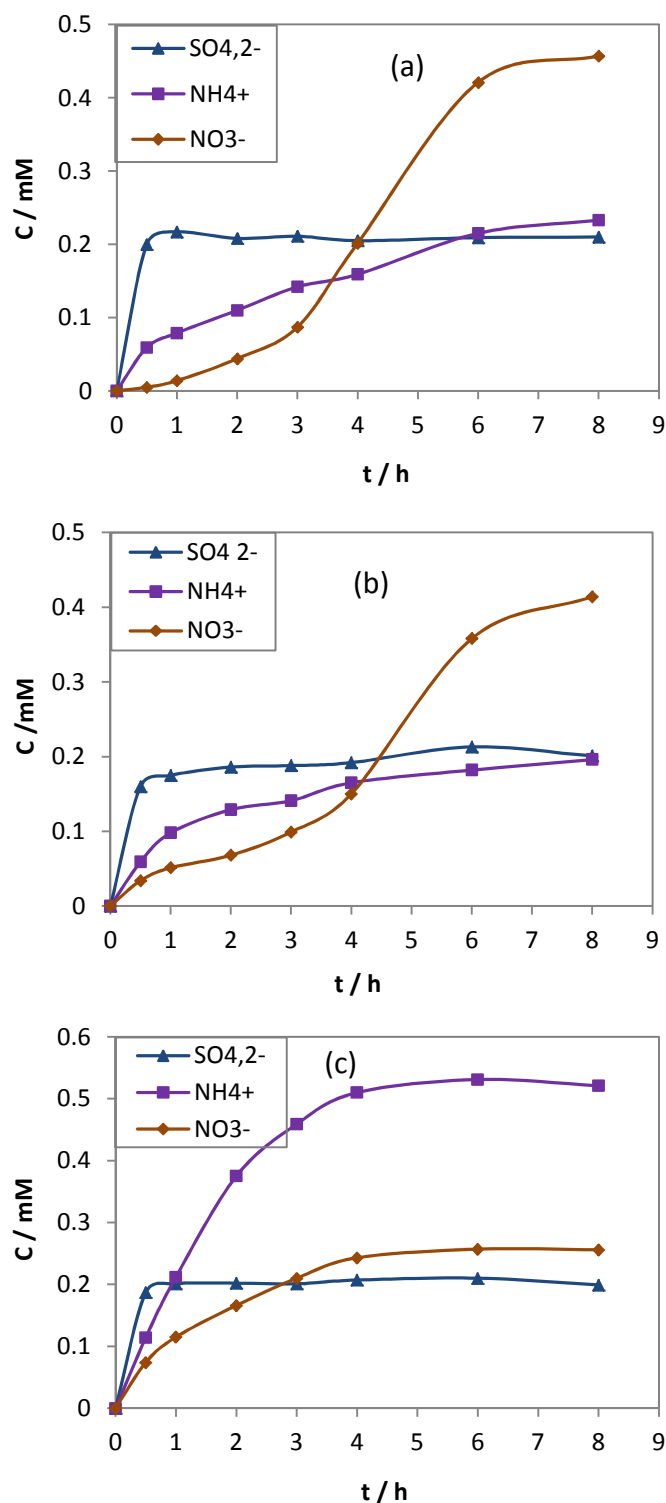
#### **4.4. Evolution of inorganic ions during the mineralization of SMT**

When the organic molecule contains heteroatoms in its structure, then during mineralization, the corresponding inorganic ions will be released to the solution<sup>143,144,366,367</sup>. The release of inorganic ions is another proof that the organic molecule has been mineralized.

Sulfamethazine is a sulfonamide antibiotic which contains two hetero atoms: Nitrogen N and sulfur S. Consequently at least three inorganic ions are expected to be detected in the solution: nitrate  $\text{NO}_3^-$ , ammonium  $\text{NH}_4^+$  and sulphate  $\text{SO}_4^{2-}$ . The analysis of inorganic ions during mineralization has been realized by ionic chromatography in the conditions described in the second chapter. The evolution of inorganic ions is presented in the Fig. 4.15 below.

As the molecule of SMT contains one sulfur atom and four nitrogen atoms, 0.2 mM concentration of  $\text{SO}_4^{2-}$  and 0.8 mM as the sum of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are expected to be formed in the solution for a complete mineralization. In three cases it can be noticed the characteristic of immediate evolution of  $\text{SO}_4^{2-}$  attaining 100% of its expected value in thirtieth first minutes. The very rapid appearance of the quantitative  $\text{SO}_4^{2-}$  suggests that the SMT degradation starts mostly by sulfur extrusion from the molecule.





**Fig. 4.15.** Time course of inorganic ions formed during electro-Fenton treatment of SMT with electrolytic cells: (a) Pt/Carbon felt, (b) DSA/Carbon felt and (c) BDD/Carbon felt. For NO<sub>3</sub><sup>-</sup>: V<sub>s</sub> = 300 mL, [SMT]<sub>0</sub> = 0.2 mM, [Fe<sup>2+</sup>] = 0.2 mM, [Na<sub>2</sub>SO<sub>4</sub>] = 50 mM, I = 500 mA, pH = 3. For NH<sub>4</sub><sup>+</sup>: V<sub>s</sub> = 300 mL, [SMT] = 0.2 mM, [Fe<sup>2+</sup>] = 0.2 mM, [K<sub>2</sub>SO<sub>4</sub>] = 50 mM, I = 500 mA.

pH = 3. For  $\text{SO}_4^{2-}$  :  $V_s = 300$  mL,  $[\text{SMT}] = 0.2$  mM,  $[\text{Fe}^{2+}] = 0.2$  mM,  $[\text{KCl}] = 50$  mM,  $I = 500$  mA, pH = 3.

Nitrogen is released in different quantities and rates from SMT, depending on the anode used. For the Pt anode the sum of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  determined in the cell represents 90.2% of the nitrogen theoretically calculated for the sulfamethazine molecule. At the beginning of the experiment  $\text{NO}_3^-$  is slowly evolved than between three and six hours the most if it is released. After six hours the curve is almost flat.  $\text{NH}_4^+$  is released at lower concentration and it continues to increase very slowly after six hours. The nitrogen released as  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the DSA/Carbon felt cell is the lowest as expected from its mineralization extent achieved for SMT. A part of it remains in the solution in the form of oxamic acid as it is shown in the figure 4.14b. 62% of the theoretic nitrogen could be determined in the electrolyzed solution with this system. The highest nitrogen concentration was measured in the BDD/Carbon felt cell, where 96.7% of the value expected was determined. The  $\text{NO}_3^-$  and  $\text{NH}_4^+$  are released quickly until 4 h and then a plateau is reached. This value corresponds to the high removal percentage of TOC with this anode. Small amounts of nitrogen can also be escaped from the solution as ammonia for all three cells.

## 4.5. Conclusions

In this chapter, the effect of four anode materials; Pt, DSA, BDD and Carbon felt, on the electro-Fenton efficiency has been treated. Apparent rate constants calculated as a function of current intensity revealed that a small difference on the degradation efficiency exist between the anodes tested. According to apparent rate constant values the best anode for SMT degradation was Carbon felt followed by Pt > BDD > DSA. The absolute rate constant of the reaction of hydroxyl radicals with SMT is significantly high and of the order of many aromatic compounds. In contrast this order was not observed for the mineralization of SMT where it was; BDD > Pt > DSA, where Carbon felt could only be used for low current intensity of 50 mA because it burned for higher currents. When BDD was used as anode an adverse effect could be observed on the electro-Fenton process because of the oxidation of Fe<sup>2+</sup> in Fe<sup>3+</sup>. That is why even that the electro-Fenton supported anodic oxidation with BDD is not much more effective than anodic oxidation only (as it is for the case of other anodes).

Despite the reduced effect of electro-Fenton process when BDD is used, the best mineralization current efficiencies were achieved for the BDD/Carbon felt system. This is due to the more TOC removal for the unit specific charge owing to the high production of hydroxyl radicals and other oxidants on BDD surface.

The analysis of short-chain carboxylic acids showed that a smaller number of them were accumulated in a significant quantity to be quantified when a BDD anode was employed than for other systems. In the BDD/Carbon felt cell, no more acids could be measured after 300 min electrolysis, whereas even after 8 h electrolysis there remained still carboxylic acids for the Pt/Carbon felt and much more for the DSA/Carbon felt cell.

The release of inorganic ions also showed that the BDD anode was the most performing anode where nitrogen was released almost quantitatively. Sulphur was released completely in all cells and very quickly suggesting the SMT degradation proceeded extensively by sulphur extrusion.

## **CHAPTER 5**

### **THE INFLUENCE OF CATHODE MATERIAL ON ELECTRO-FENTON PROCESS EFFICIENCY**

## **5. KINETICS OF DEGRADATION AND MINERALIZATION OF SMT WITH DIFFERENT CATHODES**

Since in the electro-Fenton process the Fenton's reagent that lead to the formation of the main oxidizing species, namely  $\cdot\text{OH}$  is generated on the cathode surface, as discussed in the bibliographic section, its nature plays a crucial role on the destruction of organic pollutants. In this chapter will be presented the experimental data obtained with different cathodes, namely: carbon sponge of five different porosity, carbon felt, and stainless steel. Degradation and mineralization experiments were realized using platinum as anode for each cathode studied. We have also done the dosage of hydrogen peroxide during electrolysis and its dependence on current intensity for all the cathodes.

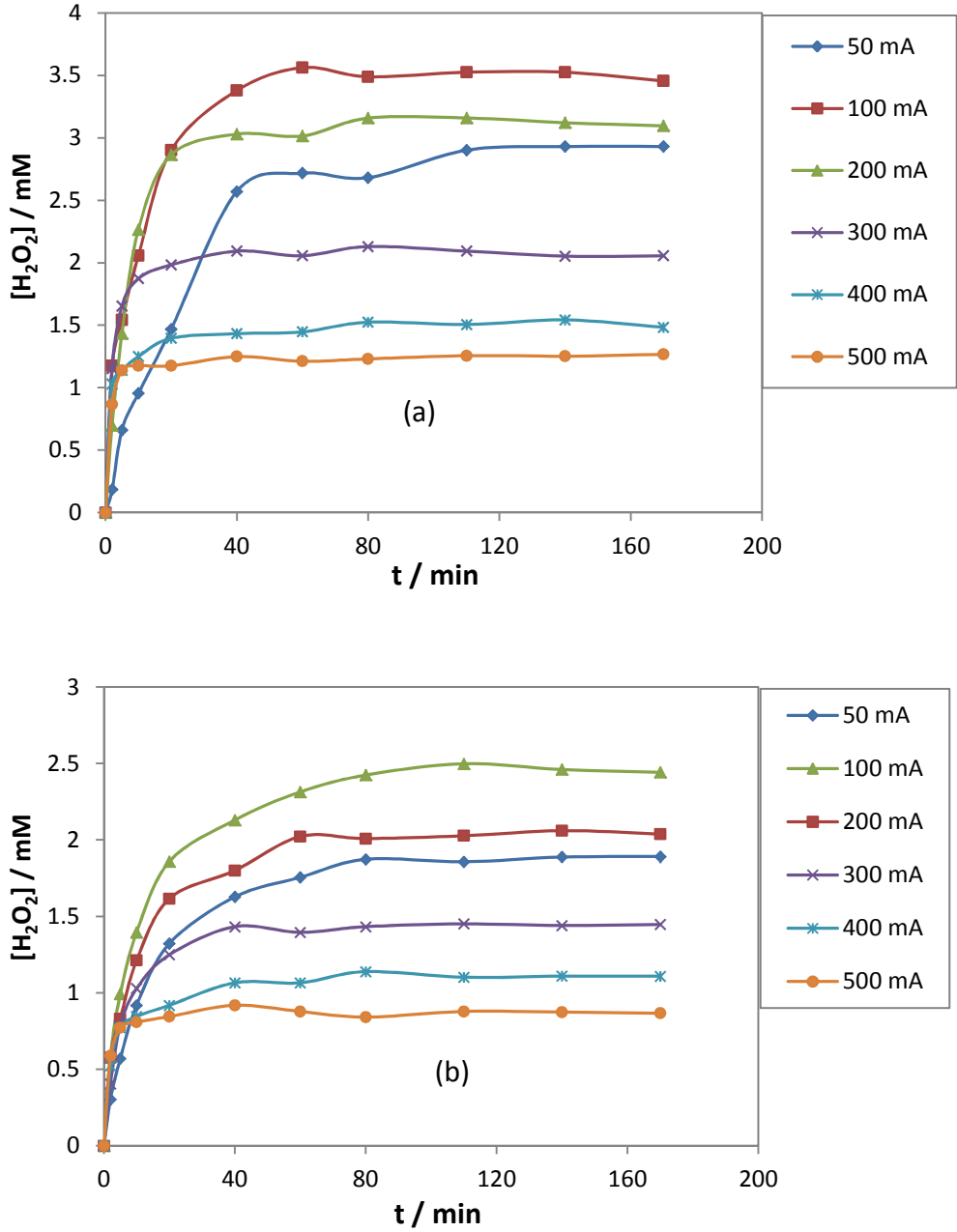
### **5.1. Hydrogen peroxide dosage in different electrolytic cells**

Hydrogen peroxide is a fundamental reagent in the electro-Fenton technology for polluted water treatment. Its concentration in the solution influences directly the oxidation rate of the organic pollutants.

The dosage of hydrogen peroxide in the electrolytic cells equipped with different cathodes has been realized to estimate their capacity in Fenton's reagent production. This data will also help to explain better the results discussed in the proceeding section on degradation and mineralization of sulfamethazine as a model pollutant.

Experiments were realized in 250 mL electrolytic cell, the same used for the study of the kinetics of oxidative degradation. It is equipped of the cathode to be studied and the Pt anode. Sodium sulphate was added as supporting electrolyte and the pH was adjusted at 3. The compressed air was bubbled through the solution for 10 min before starting the electrolysis, in order to attain an oxygen saturated solution, the bubbling continued during all the experiment as usually.

Figure 5.1 shows the  $\text{H}_2\text{O}_2$  evolution with the time ( $[\text{H}_2\text{O}_2] = f(t)$ ) for the carbon sponge cathodes of 45 ppi and 80 ppi porosities.



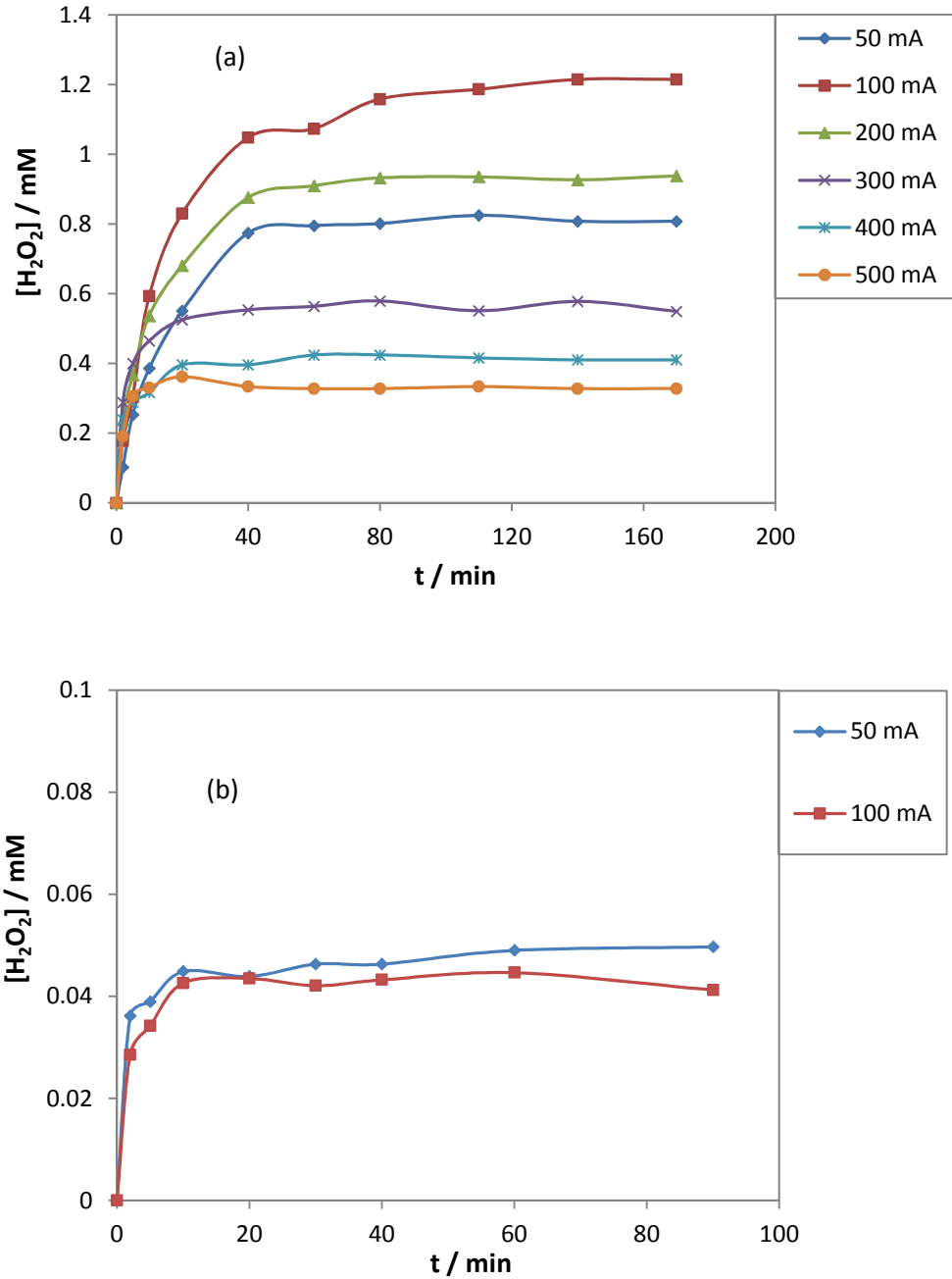
**Fig. 5.1.** Evolution of hydrogen peroxide in the cells containing carbon sponge cathode of (a) 45 ppi and (b) 80 ppi porosity under continuous compressed air bubbling conditions.  $V_s = 250$  mL,  $[\text{Na}_2\text{SO}_4] = 50$  mM,  $\text{pH} = 3$ .

As soon as the electrical current passes through the cell,  $\text{H}_2\text{O}_2$  starts to be generated. At the beginning of electrolysis the rate of generation of hydrogen peroxide is very rapid until reaching plateau and then remains almost constant. The plateau is attained when the rate of its production at cathode equals the rate of destruction according to the reactions 109, 110, 111.

For lower current intensities of 50, 100 and 200 mA the plateau is reached at around 1 h whereas for 300, 400 and 500 mA it is reached early at 20 minutes. As can be seen in the Fig. 5.1 the evolution of  $\text{H}_2\text{O}_2$  is very rapid, in fact at 20 minutes the most part of hydrogen peroxide is formed for all currents. The curves are very close for 10 first minutes where the maximum of hydrogen peroxide is already reached for higher currents and they continue to increase until 1 h for lower currents. Clearly carbon sponge of 45 ppi gave higher amounts of  $\text{H}_2\text{O}_2$  than that of the 80 ppi porosity, and this owing to its more favorable macrostructure which provides better mass transport conditions. The maximal concentration for both cathodes is reached for 100 mA whereas current intensities higher than this value led to inferior hydrogen peroxide production. This is because of the enhancement of four electron  $\text{O}_2$  reduction to water (reaction 104) with high current (or potential). Maximal  $\text{H}_2\text{O}_2$  concentrations accumulated in the cell were 3.5 mM for 45 ppi and 2.4 mM for the 80 ppi carbon sponge cathodes.

The results obtained with carbon felt and stainless steel cathodes are given in the Fig. 5.2. Similarly, the hydrogen production improved with the increasing current from 50 mA to 100 mA then it was poorer for higher currents. Here also a very important quantity of hydrogen peroxide is produced at early stage of electrolysis and after 20 min or 1 h the plateau was attained. Carbon felt capacity for  $\text{H}_2\text{O}_2$  production was much lower than that of carbon sponge cathode, the maximal concentration accumulated for the optimal current intensity of 100 mA was 1.2 mM. For stainless steel cathode very low concentrations were measured for 50 and 100 mA, beyond 100 mA current intensity hydrogen peroxide only could be detected but not quantified because of very low concentrations.

There is something to be noted when analyzing the hydrogen peroxide evolution and degradation of organic compound curves. It is clear that the maximum concentration of  $\text{H}_2\text{O}_2$  is reached at 100 mA; nevertheless the degradation of SMT accelerates until 300 mA or 400 mA. According to the maximal hydrogen peroxide accumulation in the solution, the maximal degradation rate should be achieved at 100 mA. In fact this does not happen because the degradation of SMT proceeds until 300 mA. The  $\text{H}_2\text{O}_2$  generated at higher currents decomposes on cathode and anode and also by the effect of heat, where by lower  $\text{H}_2\text{O}_2$  accumulation. In the case of SMT degradation the  $\text{H}_2\text{O}_2$  generated reacts immediately with the catalyst  $\text{Fe}^{2+}$  resulting in  $\cdot\text{OH}$  production, so, there is not much time left for its decomposition in other ways. The anodic oxidation improves beyond 100 mA too. This leads to higher degradation of SMT at 300 mA.



**Fig. 5.2.** Evolution of the concentration hydrogen peroxide in the cells containing (a) Carbon felt and (b) Stainless steel cathodes under continuous compressed air bubbling conditions.  $V_s = 250$  mL,  $[Na_2SO_4] = 50$  mM,  $pH = 3$ .

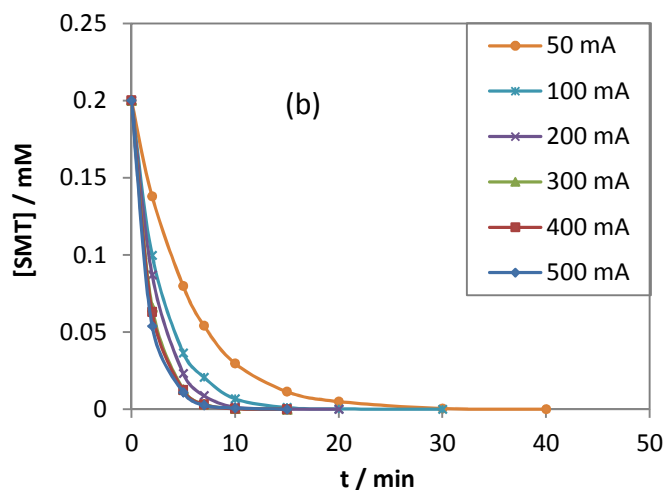
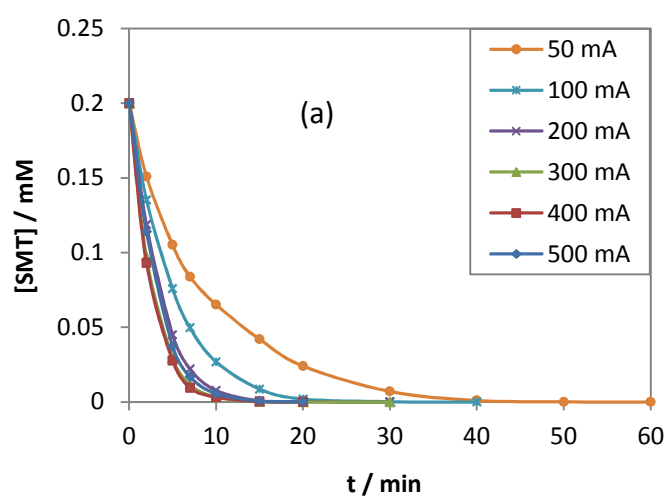
## 5.2. The effect of current intensity and cathode material on the degradation rate of SMT

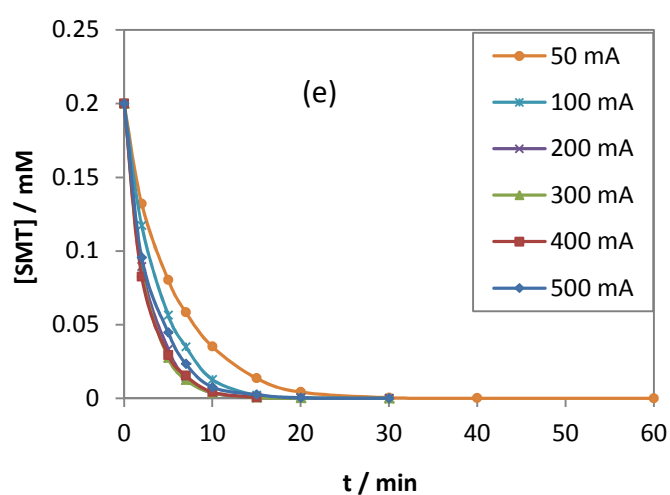
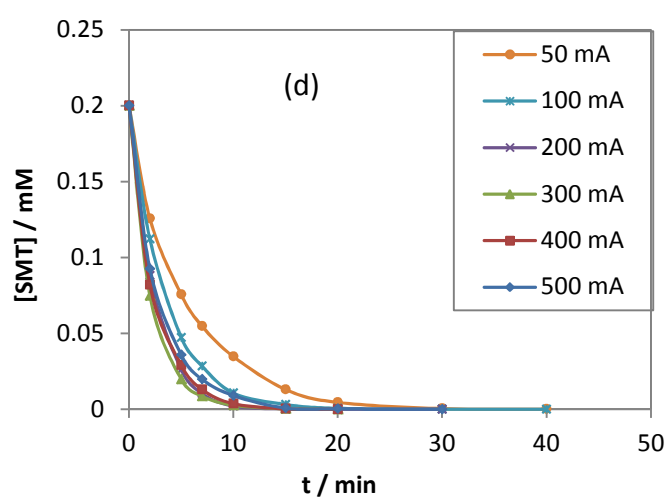
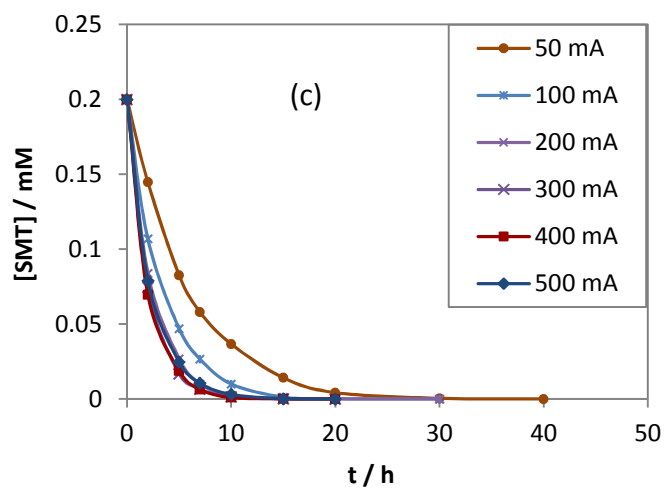
To evaluate the effect of cathode material on electro-Fenton process efficiency, degradation experiments of SMT were brought about in an electrolytic cell of 250 mL. The



cathode dimensions were 6 x 3.5 x 1 cm. The applied current intensities ranged from 50 mA to 500 mA; solution pH was adjusted to 3 the optimal value for electro-Fenton process and compressed air was bubbled continuously through a glass tube to maintain the solution saturated in O<sub>2</sub>. As usually samples were withdrawn regularly and analyzed by HPLC.

Figure 5.3 shows the effect of current intensity on the kinetic curves  $C = f(t)$  for the degradation of SMT when carbon sponge cathodes of different porosity were used. The cathodes were of five porosities; 30, 45, 60, 80 and 100 ppi (pores per linear inch. Clearly the slope of curves becomes steeper when  $I$  is increased as a result of Fenton's reagent generation in high quantities.

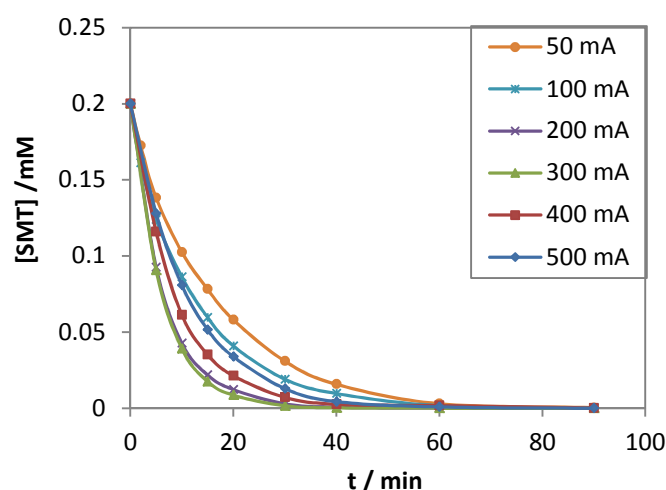




**Fig. 5.3.** Effect of current intensity on the degradation rate of SMT during electro-Fenton oxidation using carbon sponge (CS) of five different porosity: (a) Pt/CS30 ppi, b) Pt/CS45 ppi, c) Pt/CS60 ppi, d) Pt/CS80 ppi and e) Pt/CS100 ppi.  $V_s = 250$  mL,  $[SMT] = 0.2$  mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM, pH = 3.

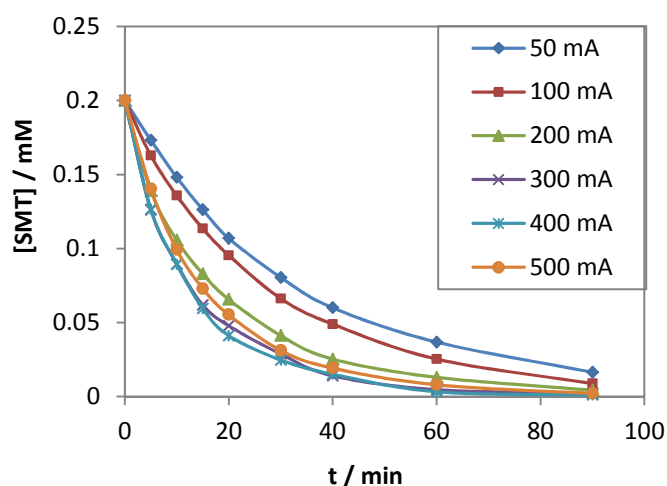
The shape of concentration decay curves indicates that there is always a pseudo first order kinetics that governs the degradation reaction. In fact, all cathodes exhibit excellent degradation efficiency, but no very significant difference is observed between them. The degradation rate is the lowest with the 30 ppi cathode, then it increases with 45 ppi which is even closer with 60 ppi and it decreases slightly for 80 and 100 ppi. An optimal current limit for the rate of degradation is attained at 300 mA revealing the intensification of parasitic reactions for higher currents. These are the common reactions of four electron oxygen reduction instead of two electron reduction for  $\text{H}_2\text{O}_2$  production at cathode, as well as hydrogen evolution at cathode and oxygen evolution at anode which compete with organics oxidation.

The effect of the current intensity on oxidation of SMT for the case of carbon felt cathode is presented in figure 5.4. The SMT degrades faster when current intensity increases from 50 mA to 200-300 mA where the limit of the rate of degradation is attained. This happens due to lower  $\text{H}_2\text{O}_2$  concentration in the solution at current intensities of 400 and 500 mA than for than of 200-300 mA. At high current intensities, the contribution of anodic oxidation becomes important and compensates the loss of efficiency at cathode due to the wasting reactions. Compared to other electro-Fenton cell 400 and 500 mA curves are very much slower than that obtained at 200 mA. As it has been shown in previous section, the hydrogen peroxide accumulation is the highest at 100 mA. That is why the rate of degradation at 50 and 100 mA is not very far from that at 400 and 500 mA.



**Fig. 5.4.** Effect of current intensity on the degradation rate of SMT in the Pt /Carbon felt cell.  $V_s = 250$  mL,  $[\text{SMT}] = 0.2$  mM,  $[\text{Fe}^{2+}] = 0.2$  mM,  $[\text{Na}_2\text{SO}_4] = 50$  mM, pH = 3.

The experiments with the electrolytic system Pt/Stainless steel reveal another behavior (Fig. 5.5).



**Fig. 5.5.** Effect of current intensity on the electro-Fenton degradation rate of SMT in the Pt/Stainless steel cell.  $V_s = 250$  mL,  $[SMT] = 0.2$  mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM, pH = 3.

In this graph oxidation curves show a very slow degradation reaction. The concentration of SMT decays with the time according to pseudo first order reaction. The oxidation is relatively faster for higher current intensities up to 300 mA, and then for 400 and 500 mA one can observe that the oxidation is almost of the same efficacy. An important remark is that traces of SMT could be found even for the most effective currents.

To resume the performance of cathodes tested, a summarizing table of rate constants for the degradation of SMT obtained from semi-logarithmic plots  $\ln(C_0/C) = f(t)$  is given below.

According to the data given in the table rate constants increase with the current intensity until the optimal value of current is reached. The optimal current intensity for which highest rate constants are observed varies with different cathodes. It is attained at 300 – 400 mA for carbon sponge 30 – 60 ppi and at 200 – 300 mA for carbon sponge 80 – 100 ppi and carbon felt, 300 mA for stainless steel cathodes.

*Table 5.1. Apparent rate constants observed during degradation of SMT in an electrolytic cell constituted of different electrodes as a function of current intensity.*

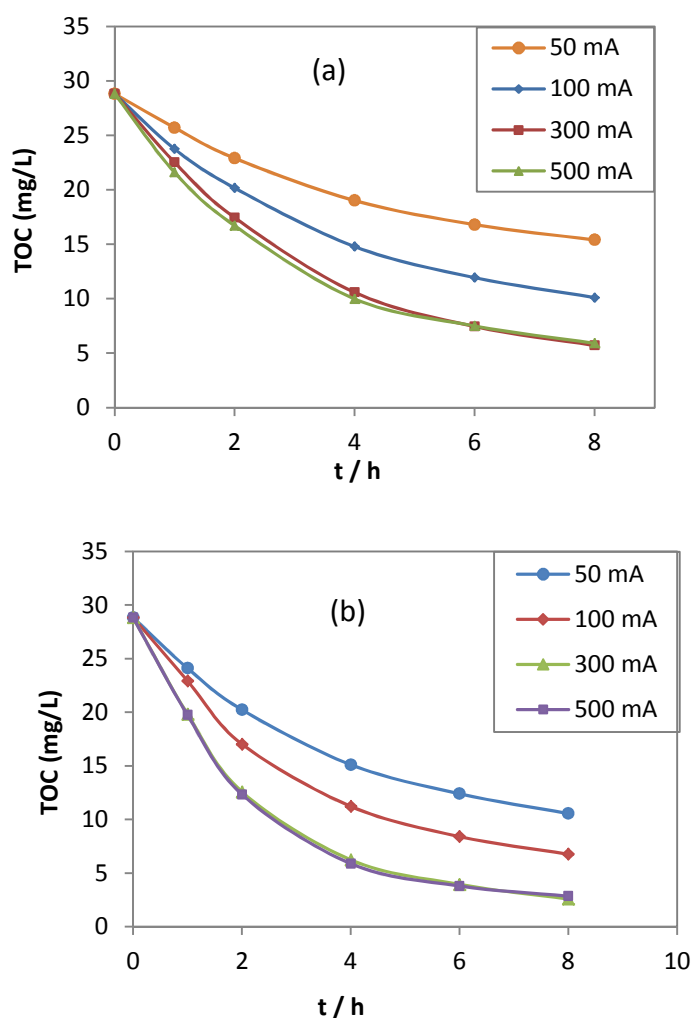
Cell	CS30 ppi	CS45 ppi	CS60 ppi	CS80 ppi	CS100 ppi	C F	S Steel
I (mA)	$k_{app}/\text{min}^{-1}$						
50	0.11	0.19	0.19	0.19	0.19	0.06	0.03
100	0.22	0.34	0.28	0.28	0.29	0.07	0.04
200	0.36	0.49	0.43	0.42	0.38	0.14	0.06
300	0.41	<b>0.60</b>	0.50	0.43	0.39	0.16	0.07
400	0.43	<b>0.61</b>	0.48	0.41	0.37	0.11	0.07
500	0.37	0.57	0.38	0.33	0.31	0.09	0.06

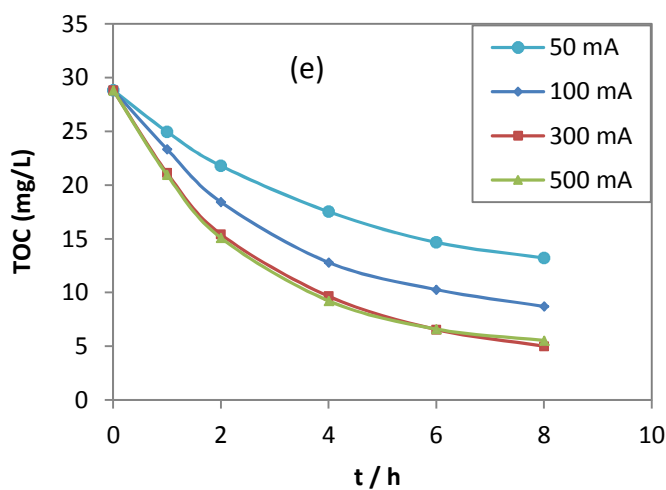
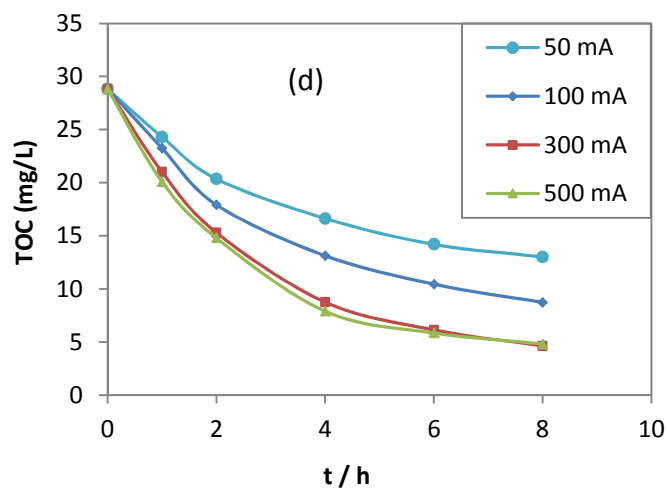
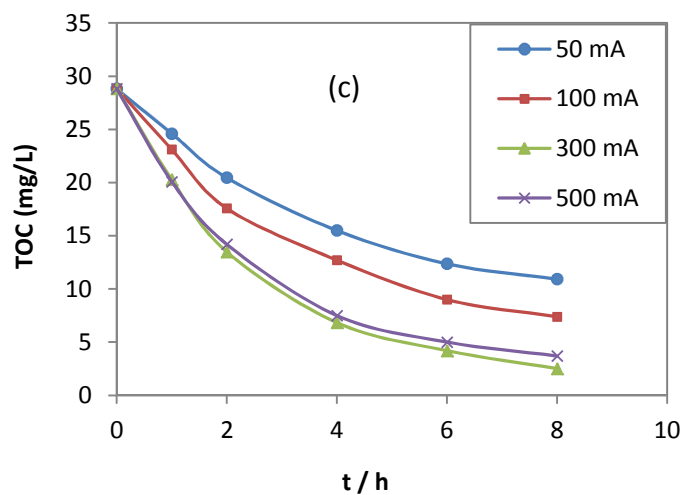
The best cathode for SMT degradation was found to be carbon sponge 45 ppi, exhibiting excellent removal rates. The lowest rate constants were obtained with carbon sponge 30 and 100 ppi porosity. In the other side all carbon sponge cathodes were much more performing than carbon felt and stainless steel. The poorest degradation could be achieved with stainless steel cathode, even with the better current intensity no complete oxidation of SMT occurred after 90 min. of electrolysis. This is because of small specific surface which gives no significant quantity of hydrogen peroxide. In contrast carbon based cathodes are three dimensional and have large surface areas which support hydrogen peroxide production at higher quantities.

However a big difference between carbon sponge and carbon felt is also evident. This can be explained by considering the hydrodynamic conditions in the bulk of cathodes. Carbon felt is a very porous material with a large surface area even more porous than carbon sponge so that we could expect better performance from it; in fact experiments demonstrate the contrary. Carbon felt physical structure being very porous and dens hamper the mass transfer in its bulk. Similarly can be explained the difference on degradation rate constants between carbon sponge cathodes; starting with 30 ppi the rate constant increases for 45 ppi then owing to the increase in the surface area, and then it decreases for 60 ppi and mostly for 80 and 100 ppi because of unfavorable mass transport conditions.

### 5.3. The effect of current intensity on the mineralization of SMT

Mineralization experiments were also achieved to estimate of oxidizing power of the electro-Fenton systems with different cathodes. Experiments have been done under the same conditions as degradation experiments. Current intensities of 50, 100, 300, and 500 mA were applied. Higher current intensities like 700 and 1000 mA were not applied as when testing anodes during mineralization, because the cathodes of small surfaces could not resist to high current intensities. The high electric resistances (ohmic drop  $I \times R$ ) led to heating the solution and the collapse of the system. The results obtained for five carbon sponge cathodes are given in the figure 5.6.

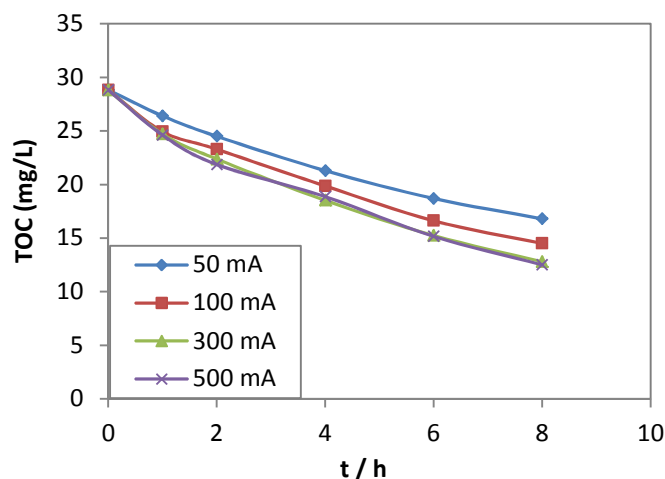




**Fig. 5.6.** Effect of current intensity on the mineralization of SMT in the Pt/Carbon sponge cell. a) 30 ppi, b) 45 ppi, c) 60 ppi, d) 80 ppi, e) 100 ppi,  $V_s = 250$  mL,  $[SMT] = 0.2$  mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM, pH = 3.

The TOC decay is exponential with time and varies with current intensity being steeper for higher values. Here again the efficiency of abatement follows a similar order as for oxidation experiments. The TOC removal is the lowest for 30 ppi carbon sponge cathode, it increases for 45 ppi being almost identical with 60 ppi and decreasing for 80 and 100 ppi porosities. The TOC removal for 45 ppi cathode at the optimal current was 91.1%. The optimal current for TOC abatement for all five cathodes was 300 mA whereas 500 mA was showed almost identical results.

Lower percentages of mineralization of organic matter were obtained with the carbon felt cathode (Fig. 5.7). 55.7% of initial TOC was the maximal value that could be removed from the solution at 300 mA. It can be noticed that curves are closer each other than for carbon sponge cathodes. This is because for lower current intensities applied here 50 mA and 100 mA more hydrogen peroxide can be produced where by higher electro-Fenton action. At 300 mA the anodic oxidation is more intensive and compensates the loss of efficiency of cathode for higher currents, and hydrogen peroxide loss at anode. So increasing current intensity favors anodic oxidations but reduce the effect of electro-Fenton that is why curves are not very different.

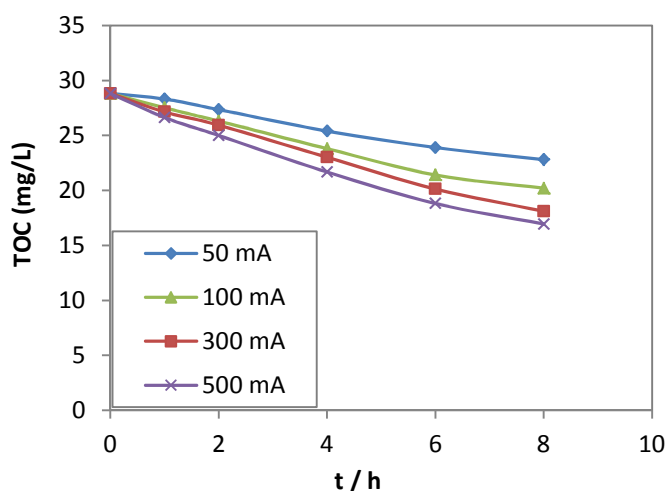


**Fig. 5.7.** Effect of current intensity on the mineralization of SMT in the Pt/Carbon felt cell.  $V_s = 250$  mL,  $[SMT] = 0.2$  mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM, pH = 3.

The poorest mineralization extent was observed for Pt/Stainless steel cell. Results obtained with Stainless steel cathode are given in the figure. 5.8. As it can be seen the curves are almost those characteristic for anodic oxidation with Pt which exhibits lower



mineralization efficiency seen in chapter 3. Only 37.1% of the initial TOC could be removed from the solution with this cell at 300 mA, which is the lowest value obtained than all others.



**Fig. 5.8.** Effect of current intensity on the mineralization of SMT in the Pt/Stainless steel cell.  $V_s = 250$  mL, [SMT] = 0.2 mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM, pH = 3.

A resuming table representing TOC removal in percentages at 8 h electrolysis for all the cathodes tested is given below.

*Table 5.2. TOC percentage removal from different electrolytic cells as a function of current intensity.*

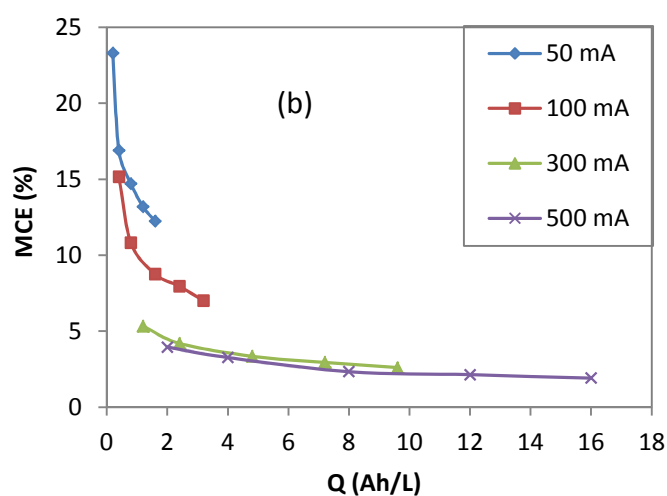
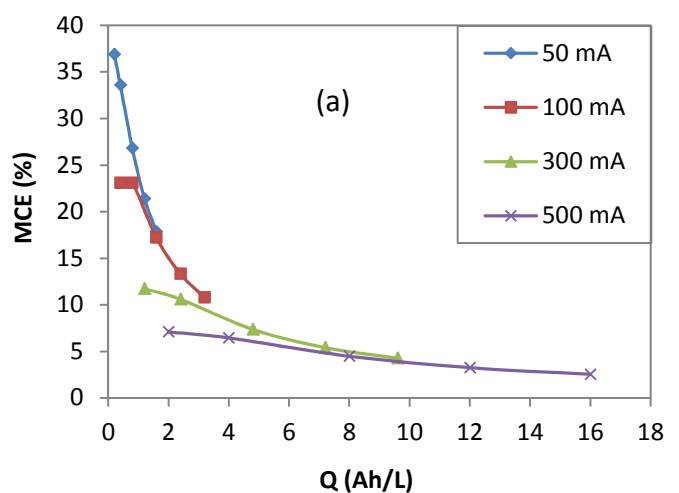
Cell	CP30 ppi	CP45 ppi	CP60 ppi	CP80 ppi	CP100 ppi	C F	S Steel
I (mA)	% TOC removal 8h						
50	46.5	63.4	62.1	54.8	54.1	43.4	20.9
100	67.7	76.6	74.3	69.7	69.7	49.7	29.9
300	80.2	<b>91.1</b>	91.2	83.9	82.6	55.6	37.2
500	79.5	<b>90.1</b>	83.6	83.3	80.7	56.6	41.2

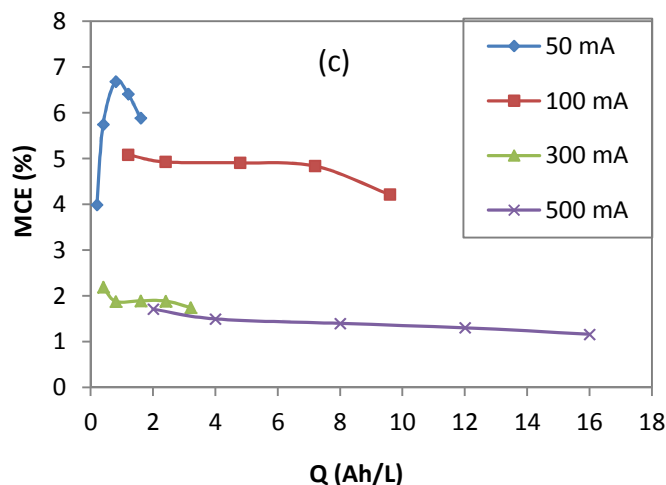
The tabled data reveal that the most effective cathode for the TOC abatement is the carbon sponge of porosity of 45 ppi and 60 ppi. Carbon sponge of 80 and 100 ppi porosities have very similar performance. All carbon sponge cathodes could remarkably better support electro-Fenton process than two others. TOC abatement with stainless steel was the lowest whereas carbon felt exhibited mediate TOC removal extent.

High surface area, the rigid and porous structure of carbon sponge provided very good mass transport conditions leading to higher amounts of  $\text{H}_2\text{O}_2$  production and faster catalyst  $\text{Fe}^{2+}$  regeneration, responsible for high mineralization efficiencies. Stainless steel did not provide interesting mineralization percentages because of its small surface area and poor  $\text{H}_2\text{O}_2$  production ability.

#### 5.4. Mineralization current efficiency

To have an idea of energy consumption when a cathode was used for electro-Fenton treatment, mineralization current efficiency was calculated for each cathode and current applied. The data obtained are plotted versus specific charge consumed during electrolysis in the Fig. 5.9.





**Fig. 5.9.** Mineralization current efficiency of electro-Fenton process during mineralization of SMT aqueous solutions using Pt anode and different cathode material: (a) Carbon sponge 45 ppi, (b) Carbon felt and (c) Stainless steel.  $V_s = 250$  ml,  $[SMT] = 0.2$  mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM, pH = 3.

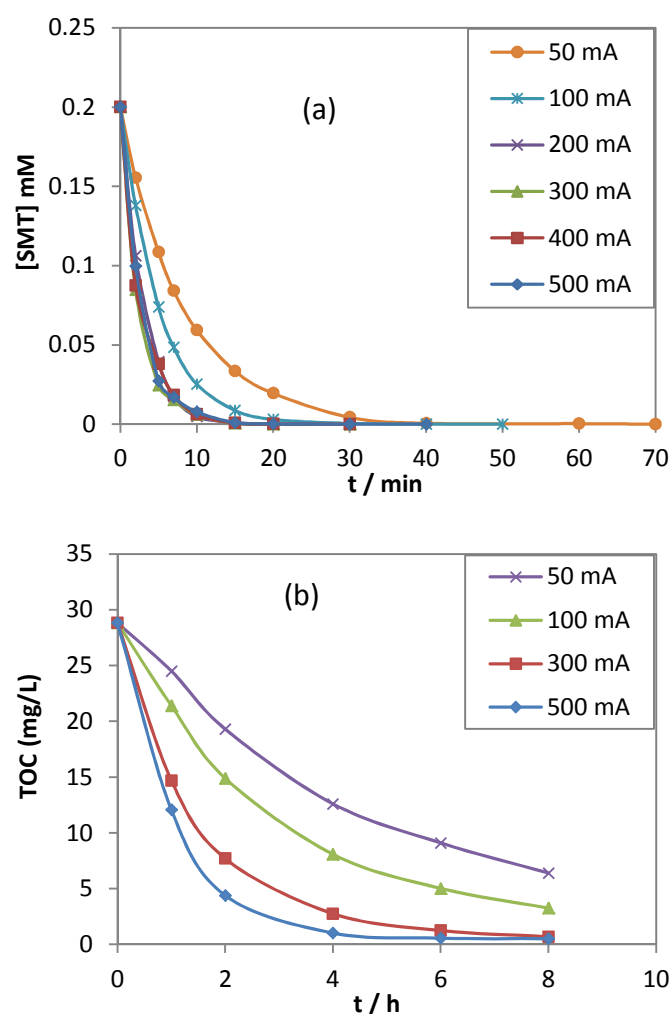
As the anode was always platinum and considering the contribution of Pt(OH) is similar for each cell, the difference in MCE changes are only a result of cathode employed. The differences between three cathodes are obvious, where carbon sponge 45 ppi is distinguished for its better MCE value. The initial mineralization current efficiency for carbon sponge 45 ppi is 36.8% when 50 mA is applied, and then it decreases steeply with the specific charge passed. MCE decays because of the decrease of organic species in the solution, which means that less organic matter is available to be degraded for the same charge passed (as current intensity is constant). The production of more persistent at as the formation of carboxylic acids along the electrolysis which additionally can form complexes with iron ions is another inhibiting factor which reduces the efficiency. The MCE is lower when current intensity increases, as already explained at high currents parasitic reactions like oxygen evolution on anode and hydrogen evolution on cathode becomes more and more intensive. These reactions lower the contribution of anode on SMT oxidation and the production of Fenton's reagent on cathode.

MCE is neatly smaller for the case of carbon felt cathode and it is very low for the stainless steel. For 50 mA the initial MCE value for carbon felt is 23.3% whereas it is only 3.9% for stainless steel cathode. It can be noticed that MCE increases with the specific charge, (Fig. 5.9c), at the beginning of electrolysis and then it decreases steeply. This increase

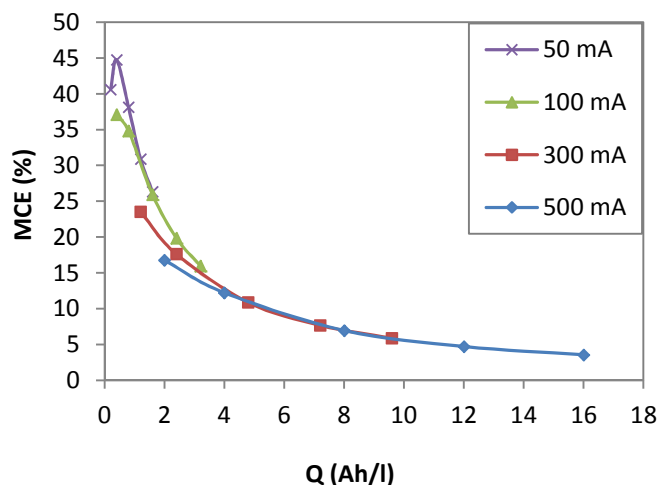
is because the mineralization of SMT (Fig. 5.8) is slower at the beginning then it accelerates slightly between 1 and 4 h.

### 5.5 Choosing the best electrode material for electro-Fenton process

In the previous chapters it resulted that BDD was the most efficient anode for the electro-Fenton process. Then, different cathodes were tested using platinum as anode. We used the platinum as anode in order to see better the effect of cathode, because as already demonstrated BDD anode can hide to some extent the electro-Fenton process because of hampering catalyst regeneration and the additional hydroxyl radicals created on its surface. After determining the best anode and cathode (BDD/Carbon sponge 45 ppi) degradation and mineralization experiments were realized with this best couple chosen.



**Fig. 5.10.** Effect of current intensity on the oxidation of SMT (a) and mineralization of its aqueous solution (b) in the BDD/Carbon sponge 45 ppi cell.  $V_s = 250$  mL,  $[SMT] = 0.2$  mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM, pH = 3.



**Fig. 5.11.** Mineralization current efficiency during electro-Fenton oxidation of SMT using BDD/Carbon sponge 45 ppi cell.  $V_s = 250$  mL,  $[SMT] = 0.2$  mM,  $[Fe^{2+}] = 0.2$  mM,  $[Na_2SO_4] = 50$  mM, pH = 3.

In the part (a) of the figure 5.10 are shown the kinetic curves for SMT oxidative degradation. The optimal current intensity is attained at 300 mA. The slope of the curves is slightly lower compared to those obtained in same conditions with Pt, because of the already mentioned effect of BDD on the active form of catalyst. In contrast the TOC abatement is much higher in the BDD/Carbon sponge 45 ppi cell owing to the action of both very intensive  $\cdot OH$  production in the solution bulk and those formed on the BDD surface,  $M(\cdot OH)$ . So, complete disappearance of SMT was reached at 60 min. for the lowest current intensity of 50 mA, and at 15 min under currents of 200-500 mA. On the other hand the TOC removal (mineralization) is almost complete (95% of TOC removal) at 4 h electrolysis at 500 mA (Fig. 5.10b).

*Table. 5.3. Apparent rate constants and TOC percentage removal observed during electro-Fenton treatment of SMT aqueous solution with BDD/Carbon sponge 45 pp. cell.*

I (mA)	$k_{app}/min^{-1}$	TOC removal at 6h / %
50	0.12	77.7
100	0.21	82.6
200	0.35	-----
<b>300</b>	<b>0.38</b>	<b>95</b>
400	0.36	-----
<b>500</b>	<b>0.35</b>	<b>98</b>

Apparent rate constants and TOC removal percentages are given in the Table 5.3 SMT has almost completely mineralized at 6 h electrolysis. An effective TOC removal means good mineralization efficiency, as shown in figure 5.11. MCE percentages are higher than for the same experiments when platinum was used as anode in the same conditions. In fact, from 36.8 % initial MCE for Pt/Carbon sponge 45 ppi it increased at 44.7 % for BDD/Carbon sponge 45 ppi when 50 mA were applied. The initial MCE values were 11.7 % for Pt/Carbon sponge 45 ppi whereas it increased up to 23.5 % in case of BDD/Carbon sponge 45 ppi.

## 5.6 Conclusions

Degradation and mineralization experiments were realized to evaluate the performance of different cathodes. Hydrogen peroxide which is obtained during the electrochemical reduction was dosed for all electrolytic cells. Finally the best couple anode-cathode was selected by performing degradation and mineralization experiments. Between cathode materials tested, carbon sponge exhibited the best results. From carbon sponge cathodes the most interesting results were obtained with the cathode of porosity 45 ppi. Then the comparison with carbon felt and stainless steel gave the following performance order: carbon sponge > carbon felt > stainless steel. These results were confirmed by hydrogen peroxide dosage experiments where the same rang in its production were found. The better performance of carbon sponge 45 ppi can be attributed to its very appropriate mass transport conditions. Its high surface is due to high porosity and also hard constitution which is stable and allows very god circulation of the solution through it. So molecular oxygen can easily reach to its bulk surface, and hydrogen peroxide generated can move freely towards the bulk of the solution where it reacts with  $\text{Fe}^{2+}$  to give hydroxyl radicals. The transport of  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  is hampered in carbon felt because of its more dense structure leading to lower Fenton's reactive generation. Stainless steel has a very small surface compared to carbon sponge and carbon felt whereby its very low efficiency for Fenton's reagent production.

So after the determination of the best cathode, it was coupled to the best anode, the BDD, determined in the previous experiments for the electro-Fenton processl. The results obtained clearly revealed it as the best couple anode cathode to be applied in electro-Fenton technology for water remediation.

## GENERAL CONCLUSIONS

This study has been realised in the frame of treatment of polluted water technologies, with the aim of estimating the influence of different electrode (anode and cathode) materials on efficiency of the electrochemical advanced oxidation process "electro-Fenton". This is a technique based on the in situ production of hydroxyl radicals  $\cdot\text{OH}$  through the electrochemically assisted Fenton's reaction. To test the efficiency of organic pollutants abatement with several electrodes, two model pollutants, namely sulfamethazine SMT and amoxicillin AMX has been selected. These two compounds are belonging to antibiotic family and are very frequently found in waters and represent disturbing properties for the aquatic life (as explained in the introduction).

A systematic study on the anodic oxidation of AMX and mineralization of its aqueous solution with anodes Pt, DSA, BDD,  $\text{PbO}_2$ , Graphite, Carbon felt and Carbon fibre showed a strong dependence of oxidation efficiency on the anode material. The most efficient anode for the anodic oxidation of AMX was BDD due to its high capacity to generate the highly oxidizing agent BDD( $\cdot\text{OH}$ ) from water water oxidation but also the electrogeneretad oxidants like  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  that undergo mediated oxidation in the solution. The generation of such oxidants on the BDD surface is due to its high oxygen evolution overpotential, which is not the case of the DSA anode. This last anode shows a low efficiency for the degradation and mineralization of AMX. DSA presents a low oxygen evolution overpotential, therefore generates less quantities of hydroxyl radicals and exhibits lover oxidation power compared to BDD anode. In addition, the intensive  $\text{O}_2$  evolution hampers the production of possible other oxidants from electrolyte anions ( $\text{SO}_4^{2-}$ ). Pt,  $\text{PbO}_2$ , Graphite and Carbon fibre represented medium efficiencies inAMX abatement. Carbon based anodes showed a ~~more~~-characteristic behavior, they could perform the degradation of AMX at lover current intensities, and he only graphite could perform the mineralization for currents of 150 mA and lower. The rate of AMX oxidative degradation was remarkable with carbon felt, it was even better than that with BDD at the beginning of electrolysis but then it slowed down by the end of treatment. This was because of the destruction of anode under the effect of electric potential, that led to the complete failure in the case of the mineralization of AMX.

In terms of energy consumption, mineralization current efficiencies MCE (in percentage) were calculated from experimental data for each anode. MCE as a function of specific charge showed that the highest mineralization efficiencies were reached with the BDD anode with lower current intensities (11.0%, 7.2%, and 4.7% for 300, 500 and 1000 mA



respectively) followed by  $\text{PbO}_2 > \text{Pt} > \text{DSA}$ . It should be remarked that better efficiencies were reached with Graphite (7.0 and 14.9% for 50 and 150 mA respectively) than with Pt and DSA anodes (Pt/3.0%, 3.2% and 2.0% for 300, 500 and 1000 mA respectively, and DSA/0.1%, 0.3% and 0.5% for 300, 500 and 1000 mA respectively). This leads to the conclusion that graphite is a material of interest because it is cheap and can be very useful in coupled techniques of water treatment (it does not offer high mineralization degrees when used as anode, but the level of mineralization attained may be sufficient for a biological post-treatment).

Afterwards, a comparative study was realised with four anodes: Pt, DSA, BDD and Carbon felt to assess their influence on electro-Fenton process. The SMT degradation experiments revealed that apparent rate constants were almost similar for Pt, DSA and BDD although the oxidation capacities of these anodes are very different (as shown by the anodic oxidation curves). Taking in consideration the fact that electro-Fenton degradation of SMT was remarkably faster than anodic oxidation only, one can explain why the rate of degradation is not very different for the different anodes. As the surface of cathode was always the same, the same amount of hydroxyl radicals was generated in the solution and this is the main oxidizing agent that degrades SMT. As most of SMT molecules are oxidized by  $\cdot\text{OH}$  radicals generated in the bulk of solution (where they are formed) the prevailing effect of electro-Fenton is only observed. At the contrary, much higher rates of degradation are observed with carbon felt than with Pt, DSA and BDD due to much larger surface area of the carbon felt electrode.

The kinetic analysis realised by the method of competition kinetics taking p-hydroxybenzoic acid as standard competitor revealed that the reaction of SMT with  $\cdot\text{OH}$  is a very fast reaction of order  $10^9 \text{ mol}^{-1} \text{ L s}^{-1}$ .

The mineralization experiments showed a completely different behaviour of these anodes. Carbon felt that could perform very well oxidation of SMT could only give medium TOC removal for current intensity lower than 100 mA as it was damaged for higher current values. The best TOC removal percentages were attained with BDD where the TOC abatement of organic content could be improved until 1000 mA. Platinum was less performing than BDD but better than DSA. Unlike BDD, Pt and DSA represented an optimal limit of current intensity for TOC abatement which was 500 mA.

The mineralization of SMT was accompanied by oxidation reaction intermediates which disappeared during electrolysis after reaching a maximum concentration, nevertheless some short chain carboxylic acids and probably some short aliphatic compounds remained at the end of treatment in trace concentration level. The ionic chromatography analysis revealed the almost quantitative release of heteroatoms in form of inorganic ions such as  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  which fits with the mineralization degree for each anode.

After determining BDD as the most efficient anode in electro-Fenton technology, some cathodes were also tested for their ability to perform Fenton's reagent production. Carbon sponge of porosities 30, 45, 60, 80 and 100 ppi, Carbon felt and Stainless steel were comparatively studied by performing degradation and mineralization experiments of SMT as model pollutant. Carbon sponge of 45 ppi porosity was the most performing in both degradation and TOC abatement trials. However, the difference of efficiency with other carbon sponges and particularly the 60 ppi was not significant. On the other side carbon sponge was neatly more efficient than carbon felt and stainless steel which could barely lead to SMT mineralization. The dosage of  $\text{H}_2\text{O}_2$  as one of the two component of Fenton's reagent corresponded to the previous experiments of SMT abatement. The concentration of  $\text{H}_2\text{O}_2$  attained in the electrolytic cells was in the same order as the degradation and TOC removal efficiencies: Pt/Carbon sponge > Pt/Carbon felt > Pt/Stainless steel. Therefore, as expected, the highest MCE per unit specific charge was obtained with Carbon sponge 45 ppi cathode.

Finally the best anode BDD and the best cathode Carbon sponge 45 ppi were connected in the electrolytic cell to see their performance in the electro-Fenton process. Comparing BDD and Pt as anodes, the rate of degradation of SMT was slightly lower with BDD but the TOC removal was significantly improved. This led to better MCE per unit specific charge; from 36.8% initial MCE for Pt/Carbon sponge 45 ppi it increased to 44.7% for BDD/Carbon sponge 45 ppi when 50 mA were applied. The MCE decreased with the current, but at every current intensity, it was higher than with other anode tested.

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