J. Mater. Environ. Sci. 6 (1) (2015) 138-145
ISSN : 2028-2508
CODEN: JMESCN

Investigation of the anodic oxidation of aryloxy propionic acid derivatives in acetonitrile

A. Zaouak[1*], F. Matoussi[2], M. Dachraoui[1]

[1] Laboratoire de Chimie Analytique et d'Electrochimie, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire, Université El Manar, 2092, Tunis-Tunisia
[2] Département de Génie Chimique et Biologique, Institut National des Sciences Appliquées et de Technologie, Université de Carthage, Centre Urbain Nord, BP 676, 1080 Tunis cedex-Tunisia

Received 02 April 2014; Revised 29 September 2014; Accepted 29 September 2014.
Corresponding Author. E-mail: amirazaouak@gmail.com . Tel (0021658430291)

Abstract

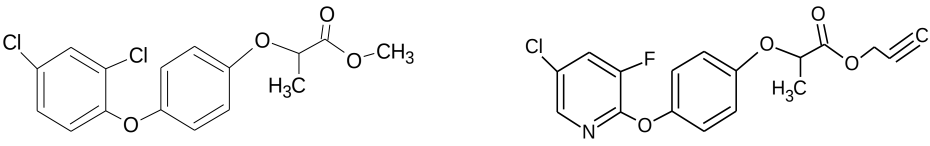
The electrochemical behavior of series aryloxypropionic acid derivatives used as herbicides was studied in acetonitrile using voltammetry and preparative electrolysis. The studied compounds were found electroactive both in oxidation and reduction. The stability of the corresponding cation radicals was shown to depends on the water content of the medium. A detailed voltametric study of the anodic oxidation of diclofop methyl (DM) led to the determination of the apparent rate constant of H_2O cation radical of DM. Determination of the oxidation products resulting from exhaustive electrolysis of DM at a constant potential showed a progressive degradation of the starting molecule. It was found that the early step of oxidation is the cleavage of the aryloxy-propionic ester bond with the formation of 4-(2,4-dichlorophenoxy) phenol (P1). The subsequent oxidation of P1 leads to several other phenolic intermediates. As a result, a mechanistic pathway was proposed for DM oxidation process" by "On the other hand, the exhaustive electrolysis of DM at a constant potential led to its fragmentation into several oxidation products that have been identified. Moreover, the GC/MS analysis of the course of the electrolysis showed that the first step of the degradation process is cleavage of the aromatic ether bond.

Key words: Aryloxy propionic acid, Arylether, Diclofop methyl, Electron transfer.

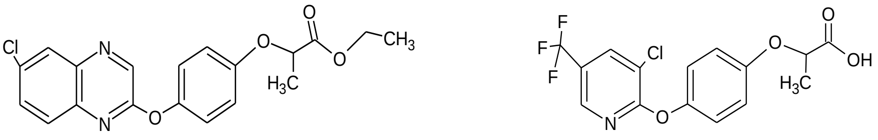
1. Introduction

Herbicides represent a largest proportion of pesticides. These herbicides are intended to protect crops from weeds and improve yields. However, these chemicals can remain in the soil and move into nearby aquatic systems, potentially threatening human health. The environmental fate of herbicides has been the subject of a number of studies investigating the degradation processes. Herbicides persistence in the soil expressed as half life of the original molecule is not absolute because it depends on the soil type, temperature, and concentration of the herbicide applied [1-8]. The persistence varies with the nature of a chemical and on soil and climatic conditions. Several phenomena may be involved in the degradation processes including biological breakdown by soil organisms and abiotic chemical and photochemical transformations [9-19]. Decomposition of herbicides by chemical processes in the soil is common for some herbicides. It may occur as the result of processes such as photolysis, hydrolysis and oxidation-reduction [20-26]. Photodecomposition is among the most general and important environmental reactions. It involves generally molecular oxygen occurring in diradical (triplet) forms. Hydrolysis is a process in which the herbicide molecules react with water. Usually, chemical bonds in the herbicide molecule are broken and one or more atoms or groups of atoms in the herbicide molecule are replaced by hydroxyl ions (OH^-) from water. Cleavage by hydrolysis is pH and temperature sensitive [4-6]. Oxidation-reduction reactions involve the transfer of electrons from one substrate to another. A variety of compounds exist within the organic matter matrixes that have the potential to receive electrons from or donate electrons to herbicide molecules. Typically phenoxy herbicides are likely oxidation and reduction in aqueous medium when activated by sunlight in air [27]. These reactions are not well understood but apparently occur in soil [28]. Therefore, information about the chemical properties of these compounds, in particular those concerning their electrochemical properties, are important. This allows, not only to predict their reactivity and fate in the environment but also to develop strategies to reduce their environmental impact. In a recent study we were interested in the characterization of electrochemical behavior of herbicides of the diphenyl ether group.

The voltametric results have shown that the electroactive nature of this class of herbicides both in oxidation and reduction [29-30]. The present paper reports the electrochemical behavior, of a series of herbicides deriving from aryloxyphenoxypropionic acid: diclofop methyl (DM), clodinafop propargyl (CP), quizalofop ethyl (QZ) and halloxyfop (HX). The corresponding chemical structures and common names are given in Figure 1.



Diclofop-methyl (DM) Clodinafop-propargil (CP)



Quizalofop-ethyl (QZ) Halloxyfop (HX)

Figure 1: Chemical structures common names and abbreviations of the studied aryloxypropionic acid derivatives.

A detailed study of diclofop methyl oxidation using cyclic voltammetry and exhaustive electrolysis was carried out. The results allowed proposing a mechanistic scheme for the anodic oxidation. The rate constant of deactivation of the primary cation radical in wet acetonitrile could be determined.

2. Experimental

2.1. Electrochemical

The voltammetric study is performed with a Voltalab 80 analyser from Radiometer. The working electrode consisted of either platinum disk (2 mm diameter) plunged in acetonitrile containing NBu_4BF_4 (0.1 M) electrolyte or glassy carbon disk (3 mm diameter). The exhaustive electrolysis of DM was carried out under at a constant potential located on the first wave. They are performed with a PTJ 35-2 potentiostat and an IG5 integrator both from Tacussel. The separated cell is equipped with a platinum grid (4 cm^2) as the working electrode and a platinum wire as the auxiliary electrode. The reference is a saturated calomel electrode (SCE). The electrolysis solutions are evaporated then extracted with chloroform before chromatographic analysis.

2.2. GC/MS analysis

The extracts of DM electrolysis are analyzed by gas chromatography / mass spectrometry. The GC separation was performed with an Agilent (6890N) type chromatograph using a silica capillary column of 5% phenyl methyl siloxane (30 m X 0.25 mm in diameter, 0.2 µm film thickness). The temperature varies between 40 and 325°C at a rate of 6°C/mn. The mass spectrometric analysis is made with a 5957B type Agilent spectrometer. The mass spectrometer was operated with electron impact ionization at 70eV. The conditions of the analysis were as following: the temperature of the injector was 250°C, the ion source and the detector were held at 230°C and 280°C, respectively. The carrier gas was helium with flow rate at 1,2 mL/min.

2.3. Chemical

DM, CP, HX and QZ of analytical grade were purchased from Fluka. Tetrabutyl ammonium tetrafluoroborate (TBAF), used as supporting electrolyte, was purchased from Fluka and was purified by precipitation in methanol before use. Acetonitrile (HPLC grade) was from Panreac and used as received.

The characterisation of the electrolysis products of DM is achieved by mass spectrometry.

The corresponding spectra are given below:

- **P1**: m/z:{254 (100%), 256 (65%), 258 (11%): molecular cluster}, 184 (30%).
- **P2**: m/z: 104 (100%, molecular peak), 90(40%)
- **P3**: m/z: {162 (100%), 164 (66%), 166 (11%): molecular cluster}, 98 (26%), 64 (38%).
- **P4**: m/z: 110 (100%: molecular peak), 80 (30%), 54 (88%)
- **P5**: m/z: 108 (100%, molecular peak), 83 (38%), 54 (86%)

3 Results and discussion

3.1 Voltametric study

3.1.1. Cathodic reduction

The voltammetric study of the cathodic reduction of the different compounds was performed in acetonitrile on a glassy carbon electrode. The results show that the different species are electroactive except DM. The voltammograms obtained for compounds CP and HX give a single irreversible peak. However; QZ presents two cathodic peaks. The first is reversible and the second one is chemically irreversible (Figure 2).

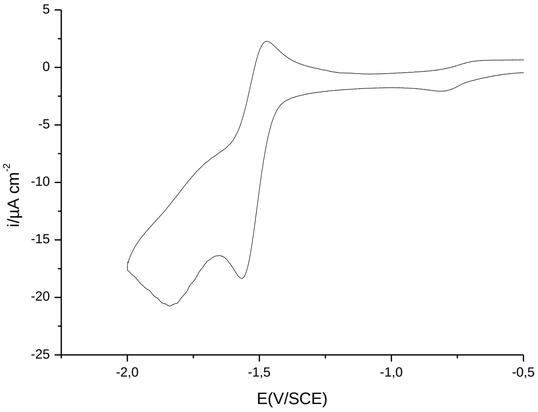


Figure 2: Reduction of QZ at Glassy carbon disk (ϕ = 3mm), in acetonitrile (TBAF 0.1M), C = 1 mM, v = 100 mV/s.

The irreversible peak potentials are given in Table 1. A shift towards more negative potential values is observed when considering successively QZ, HX and CP compounds. The results are correlated with the electron receiving site that is located at the heterocyclic moiety of the reacting molecule".

3.1.2. Anodic oxidation

A shift towards more negative potential values is observed when considering successively QZ, HX and CP compounds. The results are correlated with the electron receiving site that is located at the heterocyclic moiety of the reacting molecule". The first one is irreversible, and the second is two times more intense and shows some reversibility

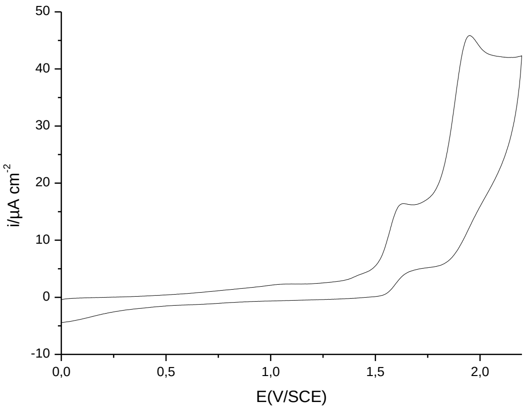


Figure 3: Oxidation voltammogram of diclofop methyl in acetonitrile, (TBAF 0.1M), C = 1mM, v = 100 mVs−1, Pt (ϕ = 2 mm), reference: SCE.

The reversibility of the first peak is evidenced when the potential sweep is reversed before the second anodic peak as shown in Figure 4 obtained with compound DM.

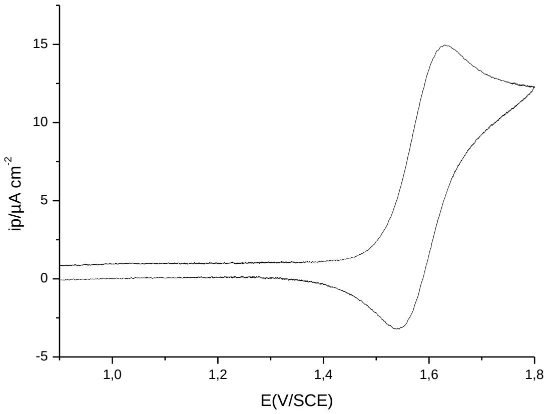


Figure 4: Oxidation voltammogram of diclofop methyl in CH_3CN, (TBAF 0.1M), C = 1mM, v = 100 mVs−1, Pt (ϕ = 2 mm), reference: SCE**.**

The first peak potentials given in Table 1 are close enough in contrast reduction’s observation. The oxidation site is very probably located on the aromatic ring bearing the propionic acid group. The number of electrons involved in the first anodic peak is estimated by comparing the peak current with that obtained from ferrocene. The values are approximately 1 except for QZ which gives a number close to 1.5.

Table 1: Peak potentials in CH_3CN. Reference ECS, *v* = 100 mV/s.

Compounds	E_{pc1}(V)	E_{pc2}(V)	E_{pa1}(V)	E_{pa2}(V)	n_e
DM	-	-	1.63	1.94	1
CP	-2.09	-	1.73	-	1
HX	-1.74	-	1.69	2.08	1.5
QZ	-1.61^{*}	-1.83	1.78	*	1

n_e : number of electrons on the first anodic peak, - no peak is observed,* peak reversible
E_{pc1} : peak potential of the first cathodic
E_{pc2} : peak potential of the second cathodic
E_{pa1} : peak potential of the first anodic
E_{pa2} : peak potential of the second ano*dic*
ne : number of electrons on the first anodic peak
*****The peak is reversible

3.1.3. Effect of the presence of water

The presence of water in the medium affects significantly the voltammetric behavior of compounds DM, CP and QZ. The addition of 1% water suppresses the reversibility of the first anodic peak of DM and substantially increases its intensity indicating a change in the oxidation mechanism (Figure 5).

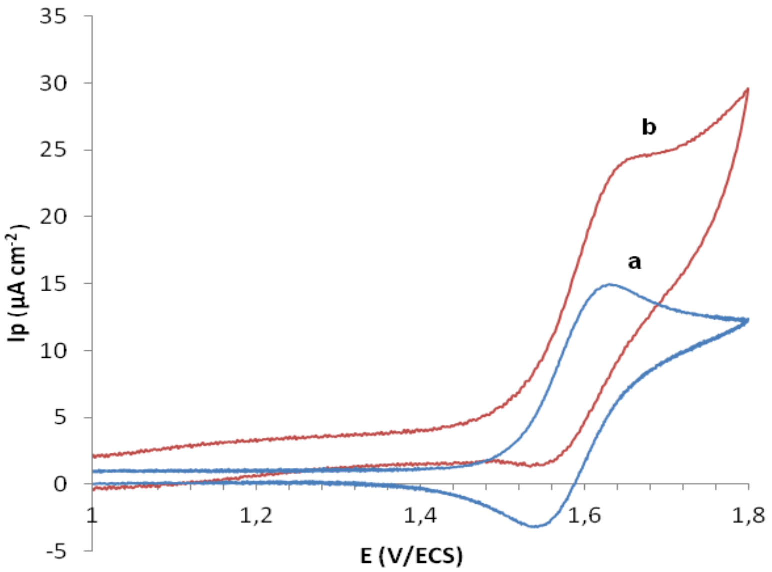


Figure 5: Oxidation voltammogram of DM, *C* = 10^{-3} M, TBAF (0.1M). (a) Anhydrous acetonitrile, (b) acetonitrile + 1% H_2O, *C* = 1 mM, *v* = 100 mV/s, Pt (ϕ = 2 mm), reference: SCE.

The disappearance of reversibility and the increase in current are indicative of the transition to an ECE mechanism. This is confirmed by the decrease of the ratio ip/√v with increasing scan rate as shown in Figure 6 which is typical of the transition from a mechanism with two electrons (type ECE) to a mechanism with a single transfer of electron. Such behavior obtained with Compound DM is suitable for a precise kinetic study.

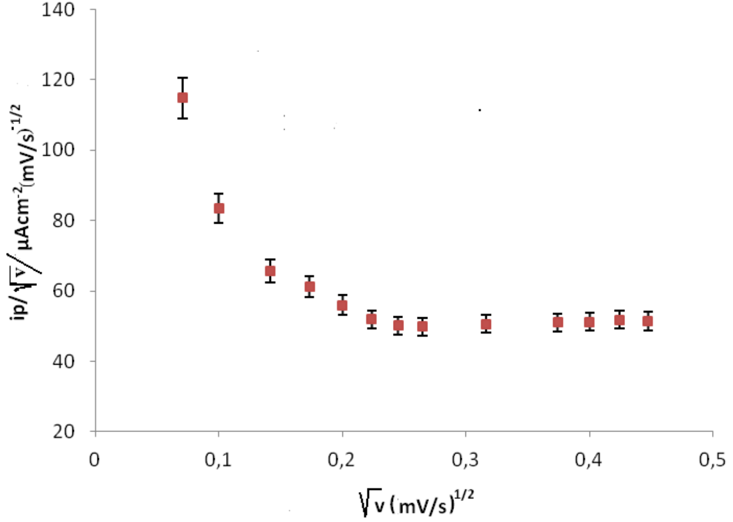


Figure 6: Variation of ip/√v ratio with the scan rate, DM: C = 1 mM, in acetonitrile 1% H_2O.

The evolution of the ip/√v depending on the scan rate of DM in acetonitrile with 1% water.

The cation radical species which is derived from the first electron transfer, most likely undergoes an attack by water leading to a species easily oxidizable than the starting compound. The proposed successive steps of the anodic oxidation of DM in presence of a low amount of water are the following:

$$DM \longrightarrow DM^{\cdot+} + 1e \quad (I)$$

$$DM^{\cdot+} + H_2O \longrightarrow X \quad (II)$$

$$X \longrightarrow P + 1e \quad (III)$$

It is possible to access to the rate constant of the chemical reaction (II) by plotting the variation of the peak potential versus the logarithm of the scan rate. Figure 7 shows two line segments. The first one obtained for low scan rates relative to the ECE process has a slope about 30 mV indicating a first order rate determining step. The second segment obtained for higher scan rates is related to the monoelectronic reversible process.

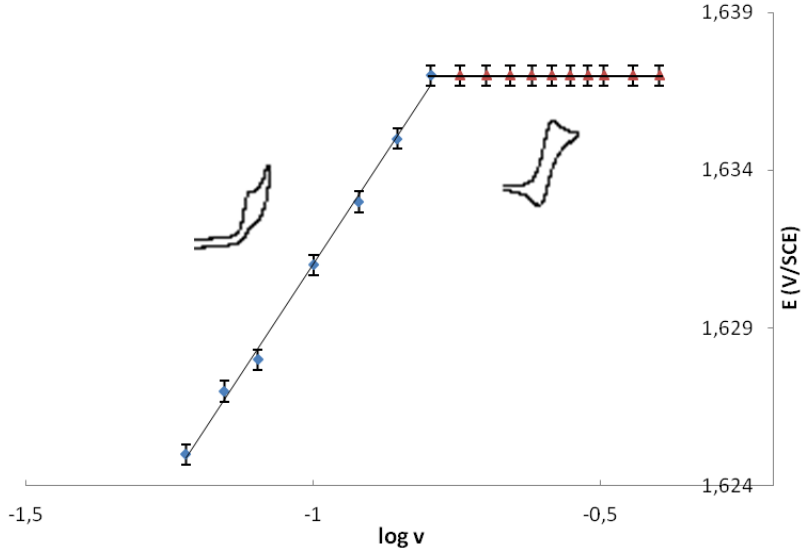


Figure 7: DM potential peak variation with scan rate (C = 1mM) in acetonitrile with 1% water.

This configuration allows the access to thermodynamic and kinetic characteristics of the system. The horizontal segment allows the determination of the standard potential of the couple E_{01} $DM^{\cdot+}$ / DM:

$$\mathbf{E_{01}} = 1{,}608 \text{ V/SCE} \pm 0{,}02 \text{ V}$$

The pseudo first order rate constant of reaction (II) can be obtained using the following relation [31].

$$Ep = E0 + 0{,}780\ (RT/nF) - (RT/2nF) \log (k/v\ (RT/nF))$$

The value obtained is:

$$k_{app} = 0{,}223\ s^{-1}$$

3.1.4. Preparative electrolysis of DM

Preparative electrolyses of DM in acetonitrile were conducted at a constant potential located on the first anodic peak. The analysis of the final solution by gas chromatography-mass spectrometry showed the formation of five main products. Based on mass spectrometric identification the chemical structures given in Figure 8 were attributed to each product.

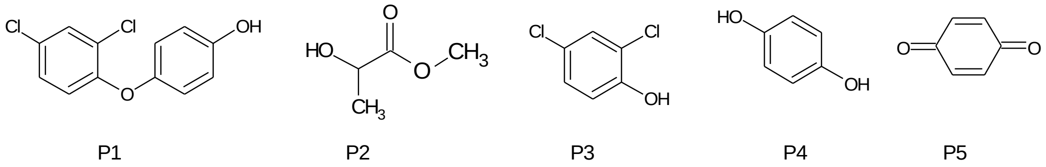


Figure 8: Products of anodic oxidation of D

Monitoring the changes in the composition of the solution during electrolysis showed that intermediate 4-(2,4 dichlorophenoxy) phenol (P1) is predominant at the beginning of electrolysis and then it decreases gradually in favour of 2,4 dichlorophenol (P3), 1,4 hydroquinone (P4) and quinone (P5). These results suggest that the electrochemical decomposition of the starting molecule proceeds via an early breaking of the aryloxy-propionic ester bond leading to P1 and P2. This step requires the exchange of two electrons per molecule of the starting compound. The subsequent oxidation of P1 leads to P3 and P4 by cleavage of the phenoxy phenol bond. Finally product P4 oxidized to P5. The proposed reaction sequence is illustrated in figure 9.

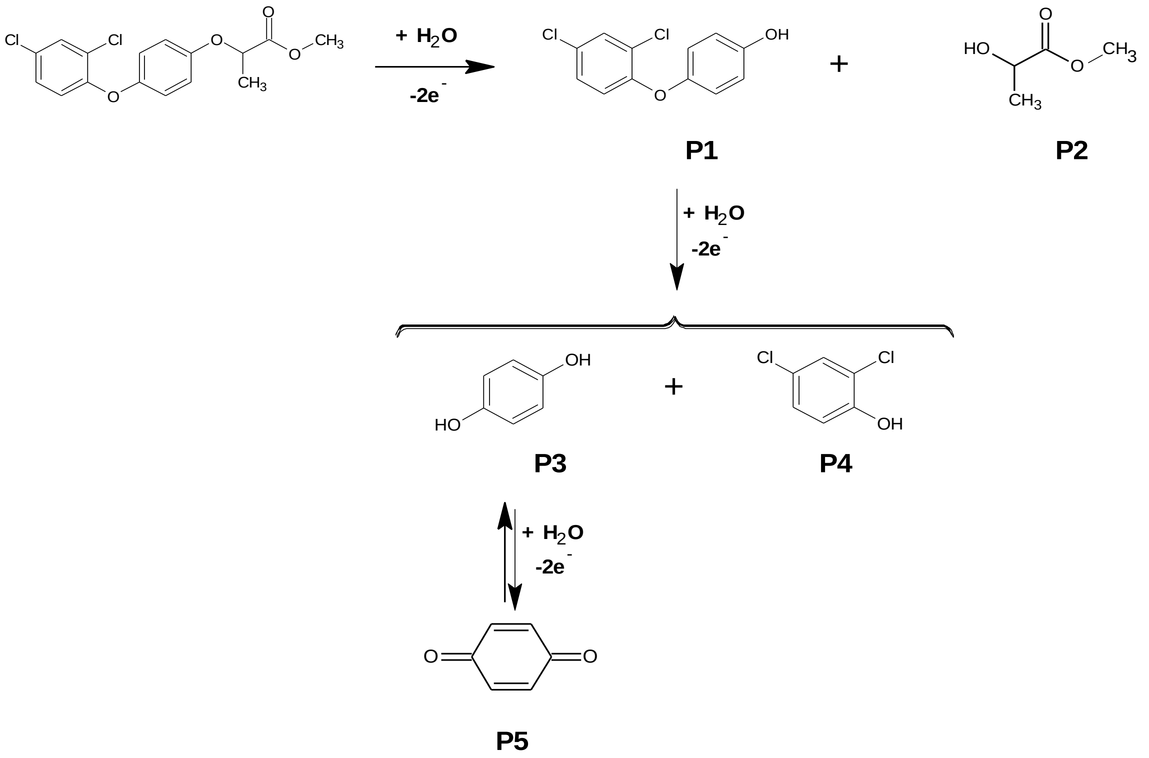


Figure 9: Mechanistic scheme for anodic oxidation of DM.

This mechanistic scheme could account also for the voltammetric behavior described above. Thus, the first anodic peak observed in the voltammogram of Figure 3 is probably the result of an incomplete conversion of DM into P1. The subsequent oxidation of P1 leading to P3 and P4 could not be accomplished at the time scale of cyclic voltammetry.

Conclusion

The electrochemical behavior of four aryloxyphenoxy propioniate herbicides was studied in acetonitrile. The electroactive nature of these compounds was evidenced in both oxidation than reduction. In anhydrous medium the oxidation of various compounds studied leads to a stable cation radical in the scale of cyclic voltammetry. But in the presence of low amounts of water, the radical cation undergoes deactivation by water leading to an ECE mechanism. A detailed voltametric study of the anodic oxidation of DM led to the determination of the apparent rate constant of the deactivation by water of corresponding cation radical. Determination of the oxidation products resulting from exhaustive electrolysis of DM at a constant potential showed a progressive degradation of the starting molecule into products of lower molecular weight. As a result a mechanistic scheme is proposed for DM anodic oxidation process in which the key steps correspond to the primary breakdown of aromatic ether links.

Acknowledgments-This work has been achieved with the financial support of the Ministère de l'Enseignement Supérieur et de la Recherche Scientifique (Tunisia).

References

1. Kumar K., Goh K. M Crop Residues and Management Practices: Effects on Soil Quality, Soil Nitrogen Dynamics, Crop Yield, and Nitrogen Recovery; Adv. Agron (1999).
2. Radosevich S. R. Action and fate of herbicides. Weed ecology: implications for management, 2nd Edition; S.R. Radosevich J. Holte, C. Ghersa, Eds., John Wiley and Sons:New York , (1997) .
3. Haygarth P. M., Jarvis S. C. pesticides and persistent organic pollutants. Agriculture, hydrology, and water quality; Haygarth P. M., Jarvis S. C., Eds., CABI publishing: New York (2002).
4. Navaro S., Vela N., Giménez M. J., Navaro G. *Chemosphere*, 57 (2004) 51.
5. Singh S. B., Kulshrestha G. *Pestic. Res. J.* 12 (2000) 235.
6. Ratasuk N., Boonsaner M., Hawker D. W. *J. Environ. Sci. Health. Part A.* 47 (2012) 1687.
7. Lalah J. O., Kaigwara P. N., Getenga Z., Mghenyi J. M., Wandiga S.O., *Toxicol. Environ. Chem.* 81 (2001)161.
8. Taha M. E. M., El-Zorgani G. A., El-Hassan A. M., Salghi *R., J. Mater. Environ. Sci*. 4 (5) (2013) 621.

9. Holtze M.S., Sorensena S.R., Sorensena J. A. *Environ. Pollut.* 154 (2008) 155.
10. Grenni P., Caracciolo M. B., Rodriguez-Cruz M. J., Sanchez- Martin M. *J.Appl. Soil Ecol.* 41(2009) 2.
11. Tixeier C., Sancelme Ait- Aissa M. S., Widehem P., Bonnemoy F., Cuer A., Truffaut N., Veschambre H. *Chemosphere*, 46 (2002) 519.
12. Ramezani M., Olivier D. P., Kookana R. S., Grill G., Preston. Ch. *J. Environ. Sci. Health*., *Part B*. 43 (2008) 105.
13. Klopffer W. *Sci. Total. Environ*. 123 (1992) 145.
14. Aziz S., Dumas S., El Azzouzi M., Sarakha M., Chovelon J. M. *J. Photochem. Photobiol. A,* 209 (2010) 210.
15. Benitez J. F., Real F. J., .Acero J. L, Garcia C. *J. Hazard. Mater*. 138 (2006) 278.
16. Espana P. S., Moran B. S., Calvo L., Miranda M. M., Prados J. L. A. *Microchem. J.* 106 (2013) 212.
17. Paul R., Singh R. P. *J. Environ. Sci. Health. Part B*. 43(2008) 506.
18. Elazzouzi M., Mekkaoui M., Zaza S., El Madani M., Zrineh A., Chovelon J. M. *J. Environ. Sci. Health., Part B.* 37 (2002) 445.
19. Printz H., Burauel P., Fuhr F. *J. Environ. Sci. Health., Part B*. 30 (1995) 435.
20. Boschin G., D’Agostina A., Antoninoni C., Locati D., Arnoldi A. *Chemosphere* 68 (2007) 1312.
21. Ying G. G., Williams B. *J. Environ. Sci. Health., Part B.* 34(1999) 549.
22. Halladja S., Khodja A. A., Halle A., Boulkamh A., Richard C. *Chemosphere* 69 (2007) 1647.
23. Wei L., Zhu H., Mao X., Gan F. *Sep. Purif. Technol.* 77 (2011) 18.
24. Sabali D., Ellington J., Lekevicius R. Int. *J. Environ. Anal. Chem.* 64 (1996) 123.
25. Xuan R., Arisi L., Wang Q., Yates S. R., Biswas K. C. *J. Environ. Sci. Health., Part B*. 45 (2009) 73.
26. Zaouak A., Matoussi F., Dachraoui M. *Desalin. Water. Treat.* 52 (2014) 1662.
27. El Yadini A., Marouane B., Ahmido A., Dunlop P., Byrne J. A., El Azzouzi M., EL Hajjaji S. *J. Mater. Environ. Sci*. 4 (6) (2013) 973.
28. Crosby D. G., Wong A. S. *J. Agric. Food Chem*. 21 (1973) 1052.
29. Moilanen K. W., Crosby D. G., Soderquist C. J., Wong A. S. *Environ. Sci. Res*. 6 (1975) 45.
30. Zaouak A., Matoussi F., Dachraoui M. *Inter. J. Electrochem.* (2011) Article ID 904570.
31. Bard A. J., Faulkner L. R. Electrochemical Methods, Student Solutions Manual: Fundamentals and Applications. 2nd edition, C.G. Zoski, A.J. Bard, J. Leddy, L.R. Faulkner, wiley (2002).

(2015); http://www.jmaterenvironsci.com