

## Electrochemical and Photo-electrochemical Treatment of Olive Oil Mills Wastewater in Western Region of Syria

Dr. Foiaad Saleh \*  
Dr. Mohammad ALshahneh \*\*  
Mosab Brakat Khalil \*\*\*

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### □ ABSTRACT □

Electrochemical and photo-electrochemical treatment of O.O.W.W was carried out to oxidize many of organic components presented in the water. The effect of anodic oxidation was determined by measuring the COD reduction for each case. The most considerable effect was reached by using anodes of CuO (65% reduction of COD) and 60% for anodes of Cu-metallic anodes, exceeding 50% for Pb-metallic anodes, compared to anodes of tin, Sn (about 25% COD reduction .)

Introducing UV-A radiations was of low effect, an additional reduction was obtained with CuO anodes of 4-5 % only, while no effect had been noticed for other metallic anodes .

Key Words:

Olive Oil Waste Water Treatment, Electrochemical Cells, Anodic Oxidation.

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\*Professor, Department of Chemistry, Faculty of Sciences, Tishreen University, Lattakia, Syria.

\*\*Professor, Department of Chemistry, Faculty of Sciences, Tishreen University, Lattakia, Syria.

\*\*\*Postgraduate Student, Department of Chemistry, Faculty of Sciences, Tishreen University, Lattakia, Syria.

## المعالجة الالكتروكيمياوية والالكتروكيمياوية الضوئية للمياه الملوثة لمعاصر زيت الزيتون في الساحل السوري

الدكتور فؤاد صالح\*

الدكتور محمد الشحنة\*\*

مصعب بركات خليل\*\*\*

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### □ الملخص □

تم استخدام المعالجة الالكتروكيمياوية ، والالكتروكيمياوية الضوئية لأكسدة العديد من الملوثات العضوية الموجودة في مياه معاصر الزيتون . تمت عمليات تحديد أثر الأكسدة الأنودية بواسطة خفض الدليل COD (الطلب الكيماوي للأكسجين ) لكل من الحالات المدروسة .  
حصلنا على أكبر قيمة لخفض الدليل COD باستخدام أنودات ( مصاعد ) من CuO بلغ خفض الدليل COD أكثر من 65% وإلى 60% في حال أنودات Cu ، ووصل هذا الخفض حتى أكثر من 50% في حال استخدام أنودات من الرصاص ، بينما حصلنا على خفض COD بحدود 25% في حال أنودات القصدير .  
أدى إدخال الأشعة UV-A إلى خفض إضافي بحدود 5-4% في حال أنودات CuO ، بينما لم تؤثر UV-A في حال بقية الأنودات .

كلمات مفتاحية :

معالجة مياه معاصر الزيتون، الخلايا الالكتروكيمياوية، الأكسدة الأنودية.

\* أستاذ - قسم الكيمياء - كلية العلوم - جامعة تشرين - اللاذقية - سورية.

\*\* أستاذ - قسم الكيمياء - كلية العلوم - جامعة تشرين - اللاذقية - سورية.

\*\*\* طالب ماجستير - قسم الكيمياء - كلية العلوم - جامعة تشرين - اللاذقية - سورية.

## Introduction:

Electrochemical oxidation technologies , including advanced oxidation , and using UV-A,B together beside electrochemical oxidation , have been rapidly developed in the last few years ,to destruct pollutants in waters, waste waters , coming from urban and from different industries. These processes have been widely spreaded in laboratory scales , as well as in fields in semi pilot and pilot plants , [ 1,2,3 ]

Olive oil was produced in the Syrian western coast thousands of year ago ,from the ancient times going back up to 2000 year B.C. Nowadays , Syria produce more than one million tons of olives , every year . Processing these quantities of olives , needs huge amount of water ; an about 800000 ton of water a year , to be used in short time ( about 3 months from October November up to the end of December every year). The problem of polluting the environment , around olive mills,the groundwaters basins etc.. , arises , and more sharply every year,[4,5,6,7]

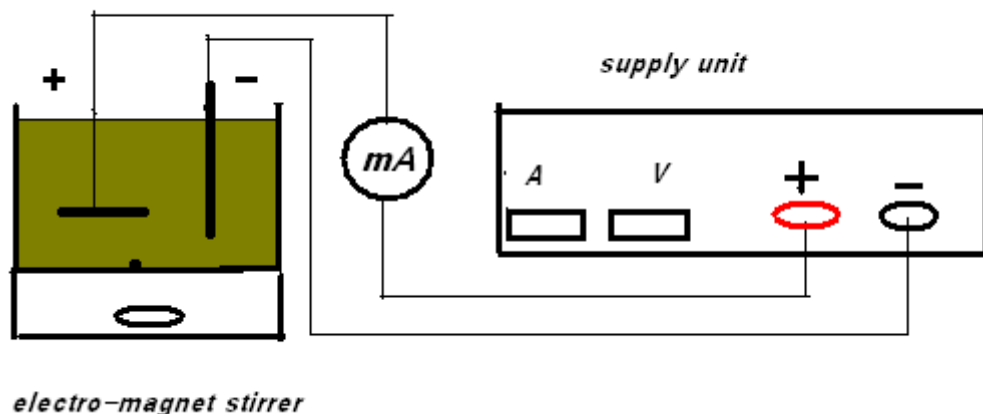
See Tab No (1) and No (2) for the General specificat and the content of pollutants presented in crude O.O.W.W .

In this paper , we have been using a laboratory scale electrochemical cell , low in cost ,and simple in construction aiming to the reduction of non –biodegradable COD of olive oil waste water , produced by different mills in the area near city lattakia, Syria.[8,9,10,11]

The Cells:

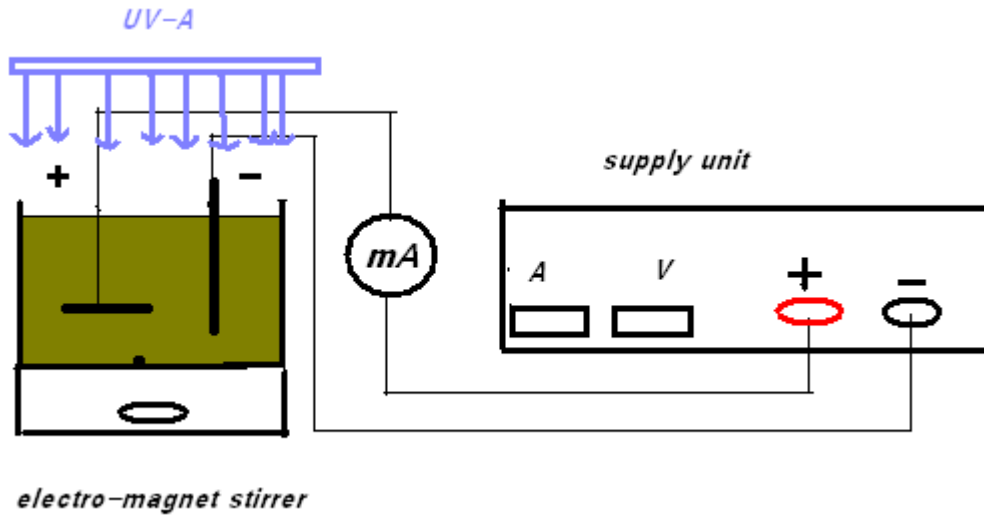
Fig -1-

(a)



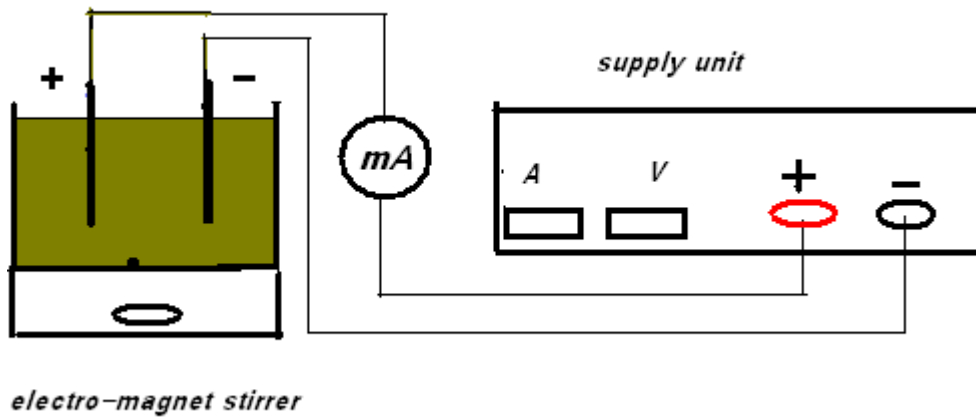
(The cell, electrochemical treatment)

(b)

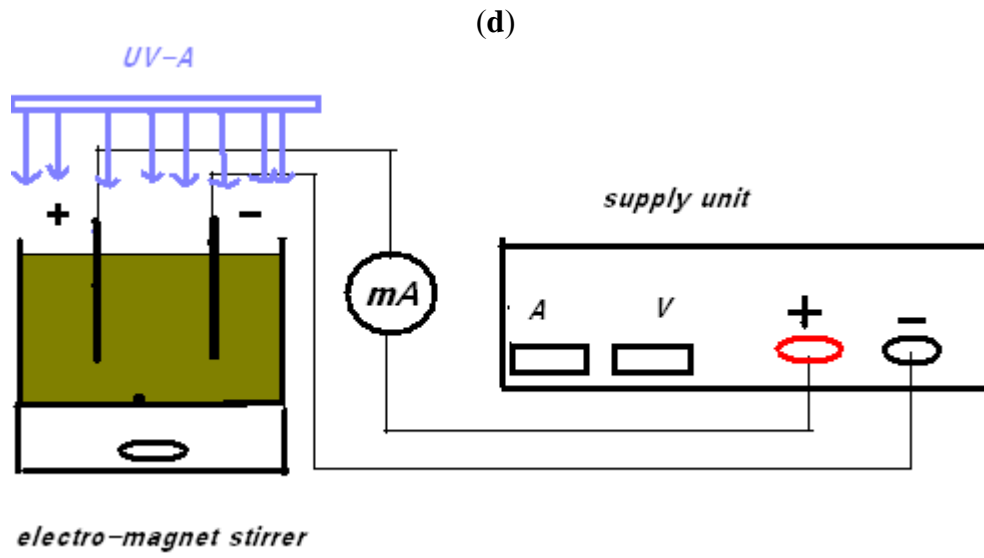


(The cell, electrochemical Treatment + UV-A , Horizontal anode position.)

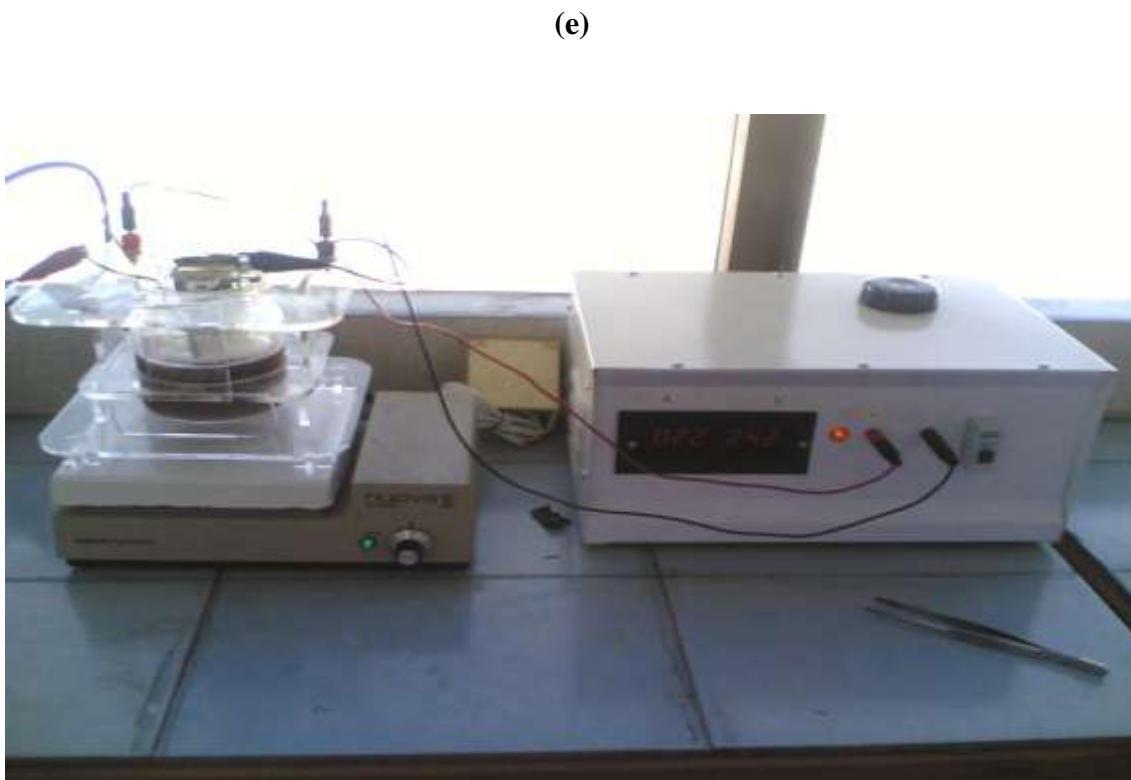
(C)



(The cell, electrochemical oxidation , vertical anode position )

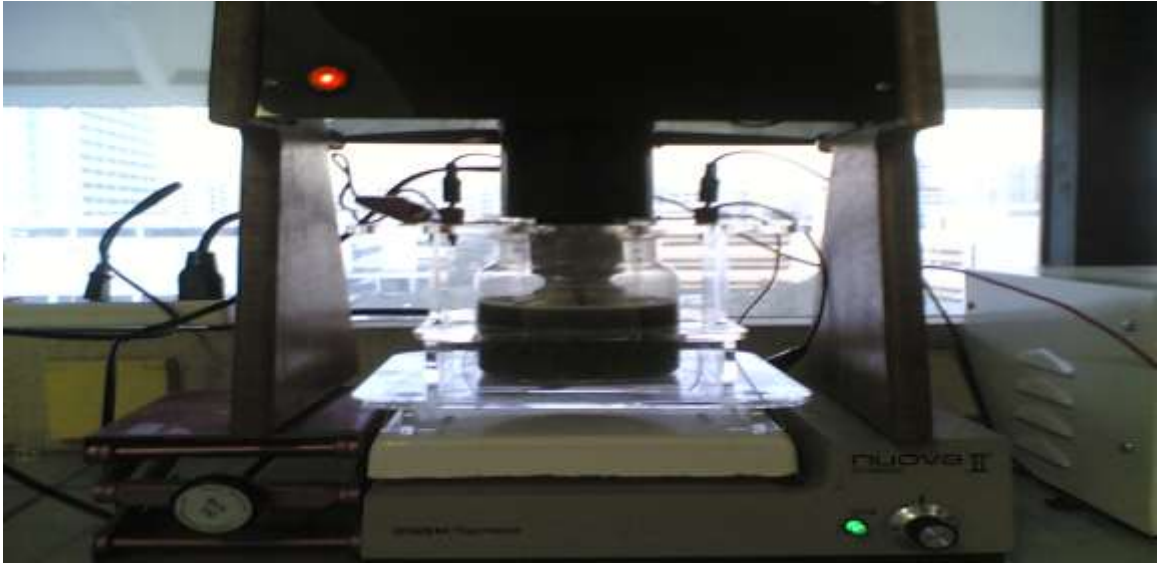


(The cell, electrochemical oxidation +UV-A , vertical anode position )



(Electrochemical cell connected to the supply unit)

(f)



(The cell,electrochimecal treatmeant + UV-A .)

(g)



(COD determination , Digester)

**Tab -1-**

General specifications of o.o.w.w	
Colour	Black -Brown
Sedimentation / rate	~ 25% V/V after 48 H
Suspensions ratio	~ 5.4 %
COD	80 - 100 gr/ lit
Fats	1.8 - 2 gr/ lit

**Tab-2-**

Parameters of O.O.O.W.W	Technology	
	Centrifuging Forces	Pressing Forces
PH	4.55 - 5.89	4.73 - 5.73
Dry matter ( g/l )	9.5 - 161.2	15.5 - 266
Specific Weight	1.007 - 1.046	1.02 - 1.09
Oil ( g/l )	0.41 - 29.8	0.12 - 11.5
Reducing sugars ( g/l )	1.6 - 34.7	9.7 - 67.1
Total polyphenols ( g/l )	0.4 - 7.1	1.4 - 14.3
O - diphenols ( g/l )	0.3 - 6	0.9 - 13.3
Hydroxytyrosol ( mg/l )	43 - 426	71 - 937
Ash ( g/l )	0.4 - 12.5	4 - 42.6
COD ( g O <sub>2</sub> /l )	15.2 - 199.2	42.1 - 339.5
Organic nitrogen ( mg/l )	140 - 966	154 - 1106
Total phosphorus ( mg/l )	42 - 495	157 - 915
Sodium ( mg/l )	18 - 124	38 - 285
Potassium ( mg/l )	630 - 2500	1500 - 5000
Calcium ( mg/l )	47 - 200	58 - 408
Magnesium ( mg/l )	60 - 180	90 - 337
Iron ( mg/l )	8.8 - 31.5	16.4 - 86.4
Copper ( mg/l )	1.16 - 3.42	1.10 - 4.75
Zinc ( mg/l )	1.42 - 4.48	1.60 - 6.50
Manganese ( mg/l )	0.87 - 5.20	2.16 - 8.90
Ni ckel ( mg/l )	0.29 - 1.44	0.44 - 1.58
Cobalt ( mg/l )	0.12 - 48	0.18 - 0.96
Lead ( mg/l )	0.35 - 0.72	0.40 - 1.85

Ref : ( International Council for olive oil , Madrid , SPAIN )

## The Method :

Different designs of electrochemical cells have been used, as figure -1- shows.

Direct current DC densities from a supply unit were used to maintain electrochemical oxidation of materials existing in O.O.W.W which was diluted to 10% of original O.O.W.W.

The DC voltage was fixed to the values between 2.5-3.5 volts, with current densities beginning from 37 mA/cm<sup>2</sup> of anode area.

The procedure of the whole processes was as in fig -2-

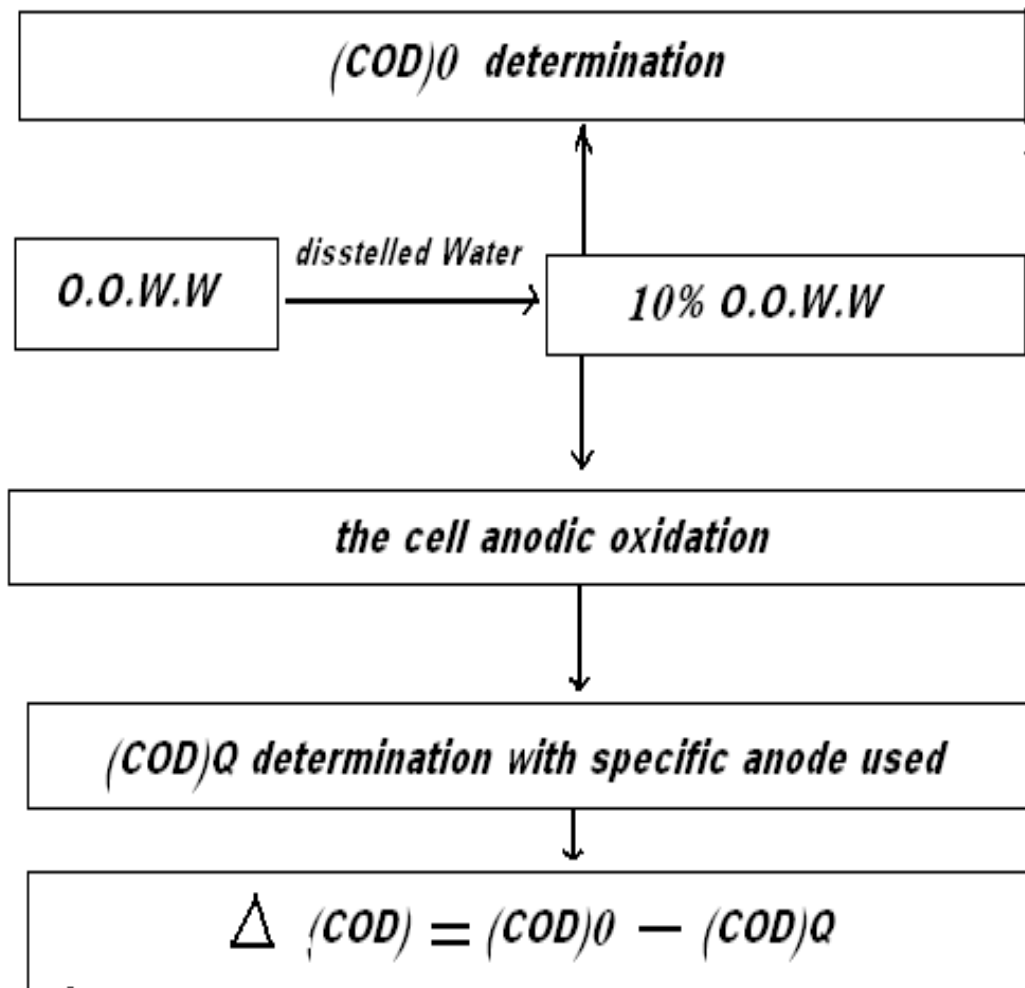


fig -2-

where Q indicate to the proper conditions: nature of anode, anode oxide, UV-A,B used, electrical charge used.

Determination of COD for each case was performed using laboratory grade of  $H_2SO_4$ ,  $K_2Cr_2O_7$ ,  $Ag_2SO_4$ ,  $Hg_2SO_4$ , and distilled water.

Digestion samples have been performed using COD reactor, and Hanna, type 839800. Dichromate is consumed in the oxidation of organic material during digestion which prolonged up to (3) hours for each case. COD was determined by titrating the remaining dichromate after digestion, because titrating method has greater accuracy and sensitivity when compared to other methods.

## Results and Discussion :

### 1- Effect of anode nature on COD reduction :

Table -3 and Fig -3- show the dependence of  $\Delta COD$  to the quantity of electrical power passed through the cell , measured in ( a.h). A mixing magnetic bar was used to sustain continuous stirring to the solution during anodic oxidation of organics contained in the solution. In all cases, we can find that  $\Delta COD$  is nearly proportional to the amount of (a.h) passed through the anodes, while it is un-markable for graphite anodes



( and Sn- anodes), it is of high influence when Cu –anodes and Pb-anodes were used, especially for high values of ( Q). In the last cases , $\Delta\text{COD}= 108 \text{ mg}$ , that is equivalent to 1080 mg, when considering the raw waste water from olive oil mills .Table - 4 and fig -4- shows the percentage of COD reduction, rising with the electrical power consumed in the electro- chemical cell. Again we can find very low effect in the case of Sn–anodes and stainless steel –anodes, while it reaches up to 60% in the case of Pb-, Cu-anodes in the same conditions.

## 2- Effect of additional irradiation with UV-A :

A source of UV-A radiation was located or posited above the electro-chemical cell, (high as 15Cm), using a Philips Tl 29 D16/ 09N (15 W) lamp with accessories ( $\lambda=350\text{-}380 \text{ nm}$ ) in such a way that a part of the UV-A beam laminates the opening of the (E.C.C) the anod section, while the rest of the lamp was covered by black carton, so not to affect the eyes of the working personnel in the aria. As seen in Table (5-6) and fig -5- and -6- a high effect of COD reduction was noticed in the case of Cu- , Pb- anodes too, but not exceeding the values of  $\Delta(\text{COD})$  when using these anodes without UV-A in this process, although it can be assumed that the UV-A power is too low (much less than UV-A found in solar radiation in the area of Syrian coast, approximately equal to  $7\text{-}10 \text{ w / m}^2$  ),for activating the anodic reaction in the (E.C.C), beside low photonic efficiency of the whole process.

### Notes:

1-Caculation of  $\Delta(\text{COD})$ , when Q (ah) was consumed ,was as per formula:

$$\Delta(\text{COD}) = (\text{COD})_{Q=0} - (\text{COD})_Q \quad ; \quad Q = I (\text{a}) \times t (\text{h})$$

2-During the period (  $t=0$  ;  $Q= 0.1 \text{ (ah)}$  )the system was in changing state from  $Q=0$  to the Q of power passed it .

3- The strait lines were noticed, only after the value of  $Q =0.1 \text{ (ah)}$  .

**Table -3- shows the dependence of  $\Delta\text{COD}$  to the quantity of electrical power passed through the cell , measured in( a.h) .**

$\Delta \text{COD} \cdot 10^3 \text{ (mg/l)}$						Q(a.h)
Kind of anodes						
S.S- anode	C - anode	Zn - anode	Sn - anode	Cu - anode	Pb - anode	
9.79	6.6	5.88	22.08	29.02	12.36	0.1
23.52	8.3	18.61	28.32	63.03	55.12	0.2
45.08	8.8	47.73	32.78	77.44	78.96	0.3
54.4	10.92	62.73	36.22	87.24	87.24	0.4
67.74	11.26	77.44	38.06	102.25	100.72	0.5
71.07	12.61	82.34	39.23	114.15	108.07	0.6

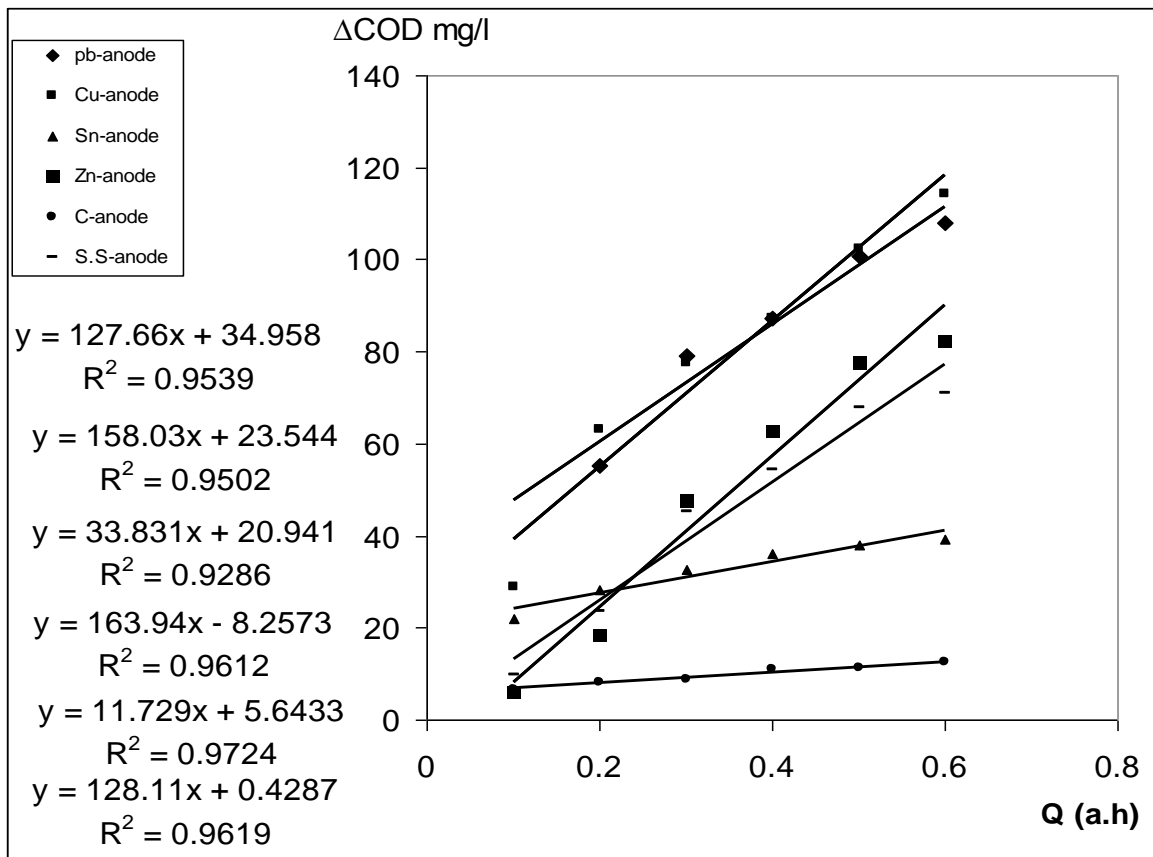


Fig -3- shows the dependence of  $\Delta$ COD to the quantity of electrical power passed through the cell , measured in( a.h) .

Table -4- shows the percentage of COD reduction, rising with the electrical power consumed in the electro-chemical cell.

$\Delta$ COD %						Q(ah)
Kind of anodes						
S.S- anode	C - anode	Zn - anode	Sn - anode	Cu - anode	Pb - anode	
4.89	3.3	2.94	11.04	14.51	6.18	0.1
11.76	4.15	9.30	14.16	31.51	27.56	0.2
22.54	4.4	23.8	16.39	38.72	39.48	0.3
27.2	5.46	31.36	18.11	43.62	43.62	0.4
33.82	5.63	38.72	19.03	51.12	50.36	0.5
35.53	6.30	41.17	19.61	57.1	54.03	0.6

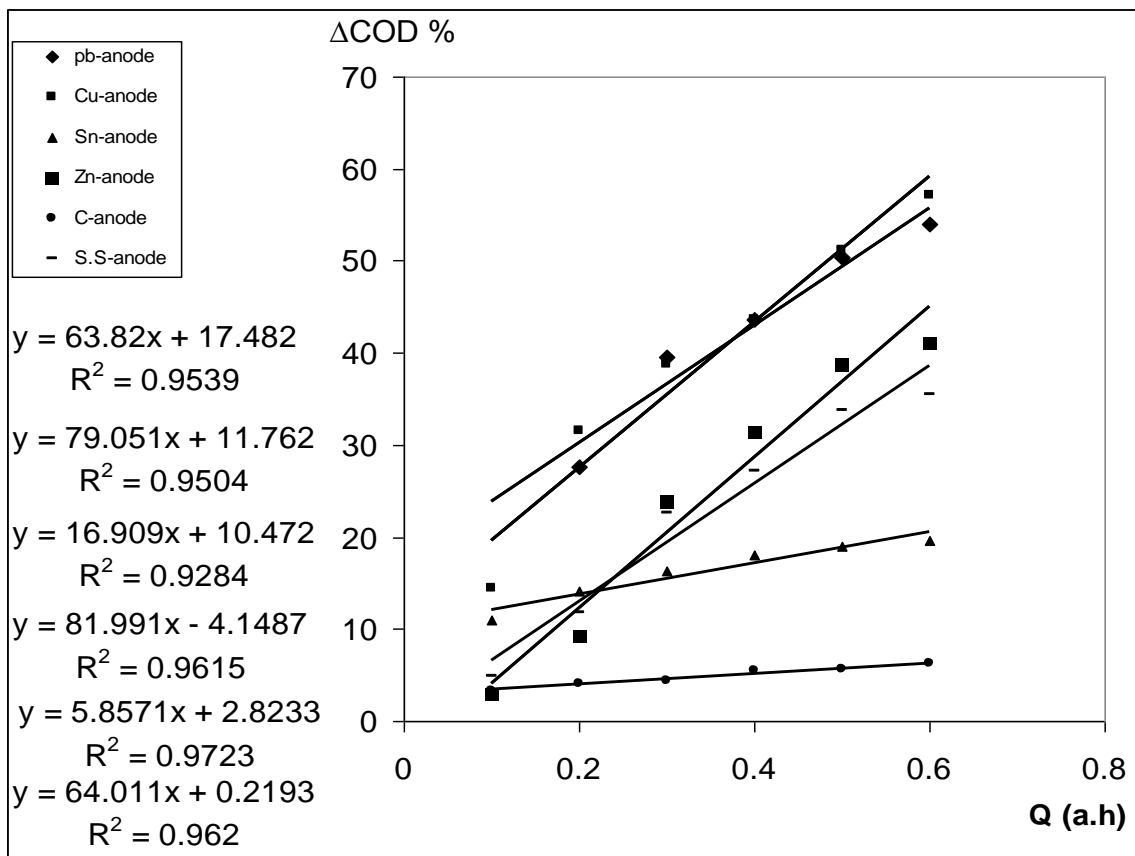


fig -4- shows the percentage of COD reduction, rising with the electrical power consumed in the electro- chemical cell .

Table -5- Effect of additional irradiation with UV-A

Δ COD.10 <sup>3</sup> (mg/l)						Q(ah)
Kind of anodes						
S.S- anode	C - anode	Zn - anode	Sn - anode	Cu - anode	Pb - anode	
13.22	6.99	14.22	23.33	43.42	15.15	0.1
30.87	9.03	30.61	30.32	67.94	59.91	0.2
48.03	10.71	53.09	33.78	82.45	84.93	0.3
61.58	10.99	66.54	36.89	89.95	92.12	0.4
67.64	12.61	78.44	38.26	104.7	105.72	0.5
73.52	13.35	83.68	40.28	116.96	113.58	0.6

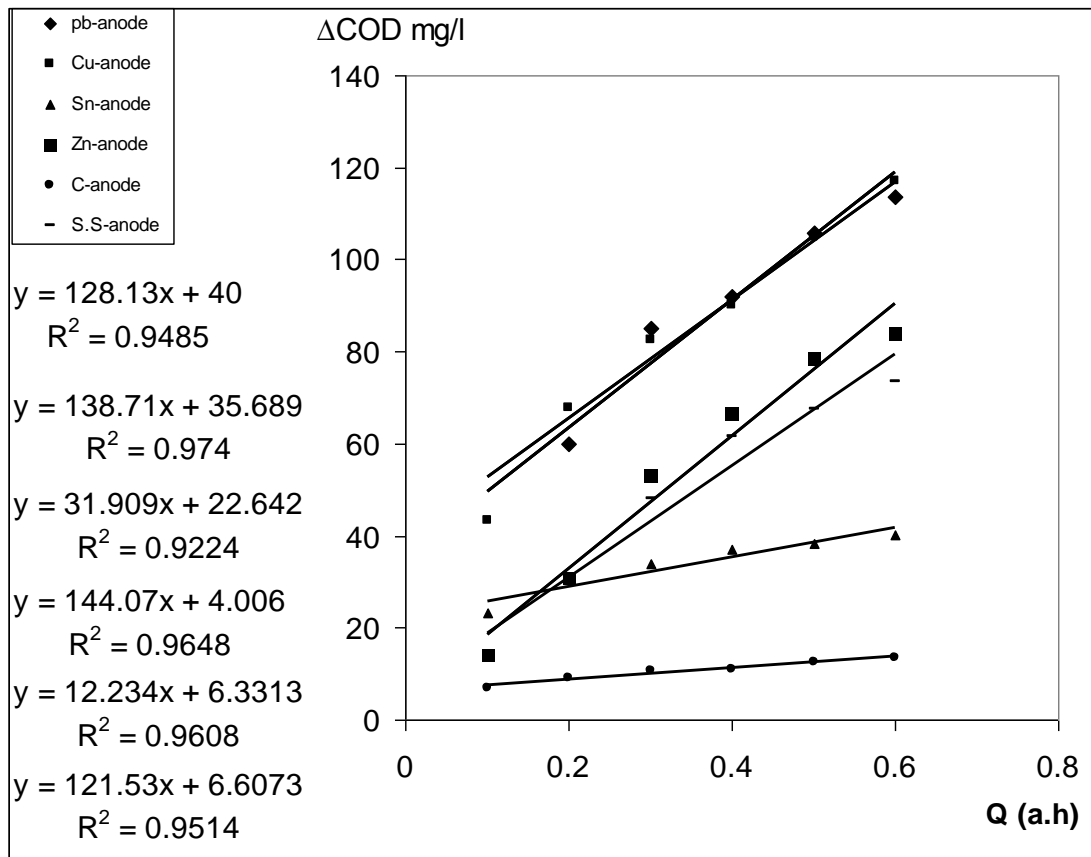


Fig -5- Effect of additional irradiation with UV-A

Table -6- - Effect of additional irradiation with UV-A

Δ COD %						Q(ah)
Kind of anodes						
S.S-anode	C - anode	Zn - anode	Sn - anode	Cu - anode	Pb - anode	
6.61	3.49	7.11	11.66	21.71	7.57	0.1
15.43	4.51	15.30	15.61	33.97	29.95	0.2
24.01	5.35	26.54	16.89	41.22	42.46	0.3
30.79	5.49	33.27	18.44	44.97	46.06	0.4
33.82	6.30	39.22	19.13	52	52.86	0.5
36.72	6.67	41.84	20.14	58.48	56.03	0.6

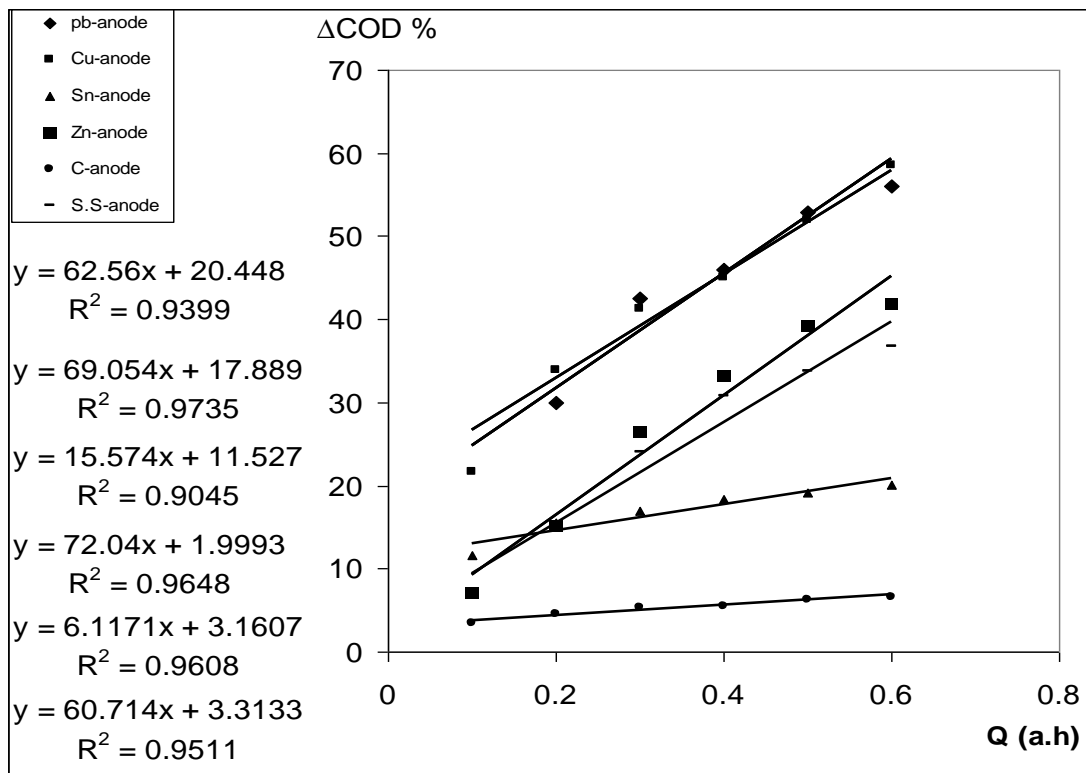


Fig -6- - Effect of additional irradiation with UV-A

### Conclusion :

In summary, we can find that these results are quite promising with respect to the overall conditions of this anodic oxidation of pollutants in the O.O.W.W coming directly from these mills in the area. These preliminary results prove the feasibility of the concept, but require further investigation. It is advisable to run these tests in direct sun light (which we plan to do in near future ) using suitable photo catalyst, deposited on the anode surfaces,[12].

## References :

- 1-RODRIGO , etal, *BDD electrode for Oxidation of 4- Chloropenols* J.Electrochemical Soc. 148 , D-60 –D64 , 2001 .
- 2- SALTMIRAZ ,D.A. ; LEMLEY A.T . *Atrazine degradation by Anodic Fenton treatment.* Ashland Inc .Dublin ,OH 43017 ,USA water Res. , 2002 , 36 (20)
- 3-QIQUNAN WANG etal . *Kinetic Effect of Humic Acid , by Anodic Fenton oxidation . J . Environmental Qual. Madison , WI, 53771, USA .2004 , 33. 2343 -2352 .*
- 4-GILORY ,D.; STRADON - CAMPPELL , D.A . *Treatment of Concentrated Toxic Waste by Electrochemical Oxidation . EA Technology Ltd. Cape Hurst, Chester, United Kingdom. « www.eatl.Co.Uk» Des.2000*
- 5- FREUDEN HAMMER , H. ; SALEH, F. etal . *Water Sciences &Technology , Vol 35 , N<sup>o</sup>4 , UK 1997 , PP, 149-156*
- 6- PEREZ ,J. ; DELA RUBIA ,T. ; MORENO , J. et-al . *-Phenolic Content and anti bacterial Activity of Olive Oil Waste Water, Environmental Toxicology and Chemistry, 11. 1992, 489-495*
- 7- BEKBOLT ,M, et al, *Photocatalyticdetoxification with the Thin-film Fixed Reactor (TFFBR):clan-up of Highypolluted Landfill Effluents Using a Novel TiO<sub>2</sub> - Photocatalyst . Solar Energy . vol 56 ,N<sup>o</sup>5, ,May 1996, pp.455-469(15)*
- 8- LIGRINI ,O. etal . *Photochemical Processes for Water Treatment . Chem . Rev .93, 1993, 671-897.*
- 9- MILLS ,A. ; DAVIES, R. ; WORSLEY, D. *Water Purification by Semiconductor Photocatalysis . Chem . Soc . Rev .22, 417 , 1993 .*
- 10- FEITZ,A,J. ; BOYDEN, B.H. ; WAITE T.D. *Evaluation of Two Solar Pilot Scale Fixed-bed Photo Catalytic Reactors. Water Res . 34 , 16, 2000.*
- 11- POULIOS,I. et-al , *Photo Catalytic Treatment of Olive Milling Waste Water . Global Nest . the Int .J . Vol. 1, N<sup>o</sup> 1. 1999 .*
- 12- ANTONY BYRNE , etal . *The Effect of Hole Acceptors on the Photo Current , of Particulate TiO<sub>2</sub> Anodes, Analyst , 1998 , 123 ,2007 -2012.*