International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March-2017
ISSN 2229-5518

Experimental Modelling of a Wide Working Range Electrochemical Water Disinfection Cell.

Joao Domingues Azevedo[1], Angeles López Agüera[1] , Pau Cervera Lloré [2].

Abstract— The experimental modelling of an electrochemical disinfection cell working on a wide range of natural waters is presented. The effective electric field intensity is parameterized as a product of independent functions from the electrolysis leading variables. The complete cell behaviour is described independently of the water characteristics either mineralization or electrical conductivity. A simple procedure to fix the optimal setting parameters has been performed. Model sensibility obtained is higher than 95%. The obtained results showed a promising feasibility for ensuring the commercial applications of the electrochemical water disinfection technique.

Index Terms— Electrical conductivities, Electric field parameterization, Electrochemical water disinfection, Natural water

Nomenclature

EWD – Electrochemical water disinfection
I - Current Intensity (A)
I_0 – Electric field intensity in standard conditions (A)
V – Cell potential (V)
G – Electrical conductivity (mS)
d – Inter electrode gap (mm)
T – Working Temperature (ºC)
T_0 – Initial Working Temperature (ºC)
t – Exposure time (s)
I_{eff} –Electric field effective intensity (A)
η_1 /η_2 - Constant obtained during parameterization
$a_{1...n}$ - Constants obtained during parameterization
α_{IV} - Correlation between cell potential and current intensity
α_{IG} - Correlation between electrical conductivity and current intensity
T_{amb} – Ambient temperature (ºC)
pH= Water pH

1 Introduction

Electrochemical water disinfection (EWD) is defined as the eradication of microorganisms by using an electric current passed through the water under treatment by means of suitable electrodes (electrolysis cell) [1]. Electrode potential, current intensity, current distribution, mass transport regime, cell design, electrolysis medium and electrode materials are the principal parameters determining electrolysis performance [2]. During the process, different disinfection agents (mainly oxidants) are generated and different physical chemical disinfection reactions take place at cell chamber [3], [4], [9], [13], [14].

Even there is assumed the potential of EWD for drinking water due to its simplicity, low maintenance and independence from external additives [1], [4], [5], [6], [11], the utilization of EWD cells still do not achieve the scalability expected from researchers in the last decade [5], [12]. In fact, few commercial solutions on EWD were developed for industrial and medium scale [6] but there is still a lack on the utilization of EWD in efficient, affordable and small-scale technologies [7], [8]. Some experiences on the utilization of EWD in tap and low chlorine water contents are resumed at [4].

The EWD cell setting parameters hardly depend on the electrolysis medium (water mineralization and electrical conductivity). Most of the developed solutions are optimised in a short range of waters salt contents. To expand the working range, particularly in natural low mineralization waters (including low chloride content), is considered the key factor for ensuring the massive use of this technique. Furthermore, to warrant sustainability, factors as reliable energy sources, accessibility to the materials used, spare parts and simple, efficient and performance control [10] of EWD cell should be taken into account.

The aim of the actual work is to design a EWD disinfection system for a wide water electrical conductivity operating limits. First of all, the full set of variables influencing the electrolysis process is studied independently in order to evaluate the importance in the whole process. Following, the effective electrical field intensity is parameterized in order to predict the cell behaviour for an extended range of water mineralization's. A simple procedure to define the optimal setting parameters independently on the water electrical conductivity is finally proposed. The full work has been developed using a dedicated experimental setup always visualising a sustainable frame.

- *1- Sustainable Energetic Applications Group, Department of Particle Physics & Galician Institute of High Energy Physics. Physics Faculty, Santiago of Compostela University, Spain. Phone/Fax number: 0034881813963, *e-mail:* **joao.francisco.domingues@gmail.com** a.lopez.aguera@gmail.com
- *2- Msc. collaborator,* cervera.pau@gmail.com

International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March -2017
ISSN 2229-5518

2 Experimental

2.1 Setup

The final aim is the design of a EWD prototype flexible enough to be extendedly used and preferably independent on water constraints. The experimental setup performed uses a non-commercial electrochemical cell as shown in Figure 1.

Fig. 1. Experimental setup used in laboratory tests.

It consists of two parallel holed plate electrodes screwed in two fixed connection bolts within a standard polypropylene water filter casing. The electrodes were separated with standard Teflon rings of 1 and 2 mm thickness. To ensure a low maintenance, anode and cathode material are stainless steel 304. The active surface of both electrodes was $280cm^2$. The distance between electrodes varies from 1 to 18mm during the experiments and the capacity of the casing vessel was 1 litter. Connection bolts are made of screwed steel M6 bars. Connection cables of 0,5m length and $S=2,5mm^2$ were used. Even if, the EWD prototype will be powered by PV energy, during laboratory tests the power was supplied using a VELPS 5005 power adjustable 0-48V $\pm$ 2mV; 0-5A $\pm$ 5mA. Voltage and current intensity were measured on the power supply witch was connected directly to the electrodes. A simple DAQ allows the control on the temperature and electrical conductivity using PCE-PHD1, 0-50ºC$\pm$0,01ºC and 0-2mS$\pm$0,001mS respectively. The pH meter used was TESTO 206-pH1, 0-14pH$\pm$0,02.

2.2 Measurements

Systematic studies were developed in laboratory under controlled conditions and the influence of EWD influencing parameters (electrode gap (d), applied potential (V), electric field intensity (I), exposure time (t), electrical conductivity (G), pH and temperature (T)) were analysed individually.

Table 1 resumes the different working ranges used for different parameter characterization during the experiments. Maximum electric field intensity used was 3A, due to the possible release of DBP (disinfection by products) from stainless steel over those currents [15]. Exposure times used during the experiments correspond to expected prototype flow rates of disinfection assuring 30 to 100litters/hour production. Voltages are fixed in the range of a PV power system. Turbidity was not considered as a variable.

Table 1. WORKING RANGES USED DURING LABORATORY EXPERIMENTS FOR PARAMETER CHARACTERIZATION.

Analysis Parameters	Working Ranges
Cell potential (V)	20 to 30
Inter electrode gap (mm)	1 to 18
Electrodes material Effective electrodes area (cm^2)	Stainless Steel 304 280
Current intensity (A)	0,5 to 3
Exposure time (s)	30 to 120
Electrical conductivities (mS)	0,028 to 0,646
Temperature (ºC)	10 to 50
pH	5.5 to 8.5

3 Results

In real fluids, the electric field intensity (I) should depend on potential applied (V), inter electrode gap (d), electrical conductivity (G) and working temperature (T) in a well-known way [17]. For natural water with variable salt content, with unknown composition and no homogenously distributed, the dependence became more complicated and an analytic development is far from being simple.

The dependence of the effective electric field intensity in a EWD cell performance in natural water is dominated by the fluid characteristic, in particular water salt types, molecular sizes and redox potentials. The salt content composition is a complex issue, not only for the uniqueness of each particular source but also because of the variations due to seasonality. The associated representative variables are the electrical conductivity and the pH factor.

To ensure a continuous optimal performance of a EWD cell, water electrical conductivity control is crucial. Water salt content composition (pH) will be desirable too. The easiest method to get this information is by a direct monitoring system able to update the cell working parameters during operation. This method is expensive, energy consuming and needing high levels of maintenance.

As alternative, a parameterization model based on experimental data is proposed. As first approximation, is considered that electric field intensity can be written as:

$$I = f_1 (G) \cdot f_2 (d) \cdot f_3 (V) \cdot f_4 (T) \cdot f_5 (pH) \qquad (1)$$

Where f_i (i=1…5) functions are considered full independent, as first approximation. For completeness, a dependence on the pH factor has been introduced.

International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March -2017
ISSN 2229-5518

In order to perform a global optimized working settle, adequate to a wide range of water characteristics, a dedicated study of leading parameters influencing the electric field effective intensity has been developed. Main results and discussion will be presented below.

3.1 Dependence of influencing variables in electric field effective intensity (I_{eff})

3.1.1 Electrical conductivity dependence

A set of measurements on four different natural water samples has been performed. During the full data taking, working cell potential, inter electrode gap distance and exposition time has been fixed.

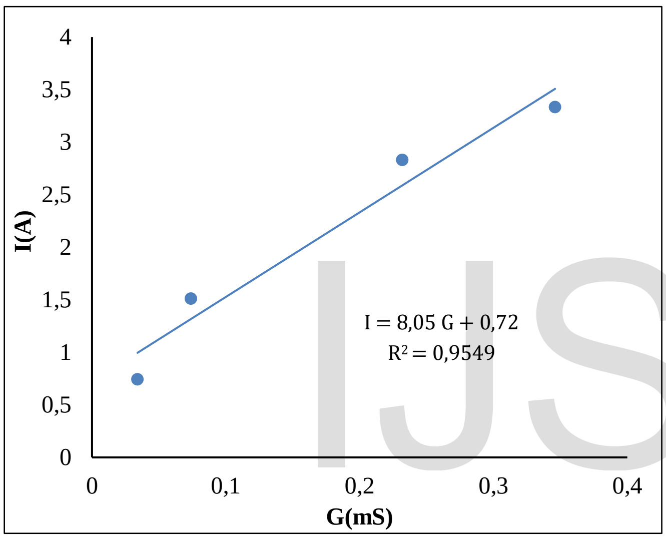

Fig. 2. Dependence of the effective electric field intensity I(A), with G(mS). Fixed conditions T=21ºC,V=24V, d=2mm, t=30s

The dependence on f_1 (G) (Fig. 2) is linear (within the experimental error) with a slope $\alpha_{IG} = 8{,}05 \pm 0{,}01$. Data taking has been repeated for other initial parameters with similar results.

$$f_1 (G) = \alpha_{IG}\, G + a_1 = 8{,}05G + 0{,}72 \quad (2)$$

3.1.2 Inter electrodes gap parameterization

The influence of inter electrode gap (d) is crucial for and adequate working settle. Because of the sensibility of this variable, seven different natural water samples have been probed. All tests were performed with non-previously electrolyzed water.

Figure 3 shows the obtained results. Even though the shape is similar for each water samples, a dependence on the water electrical conductivity is evident.

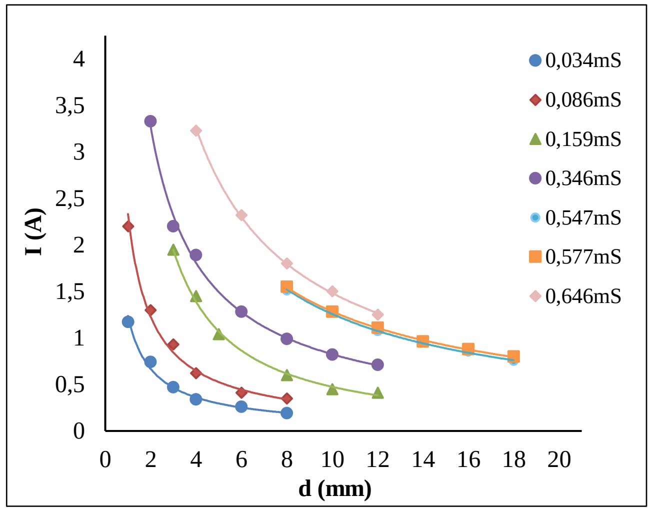

Fig. 3. Influence of different d(mm) on I(A) for 7 different G water samples; T=21ºC; V=24V; t=30s.

In these conditions, the hypothesis of a parameterization using independent functions is not valid anymore, at least in first approximation. The method applied take it into account in the use of the linear dependence obtained in 3.1.1, consequently, f_2 can be written as:

$$f_2 (d) = a_2\, \alpha_{IG}\, d^{-a_3} \quad (3)$$

Where a_2 and a_3 are constants obtained from the fitting, and α_{IG} includes the electrical conductivity dependence. The dependence of the electric field intensity with the inter electrode gap is slightly sharper than expected in a real fluid.

3.1.3 Voltage parameterization

As in previous cases a dedicated set of measurements has been performed, where in this case, temperature, exposition time and inter electrode gap has been fixed. The defined scan in working voltage (from 20 to 30V, step 1V) was selected considering the typical variation of a photovoltaic solar system when used as energy power supply.

International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March -2017
ISSN 2229-5518

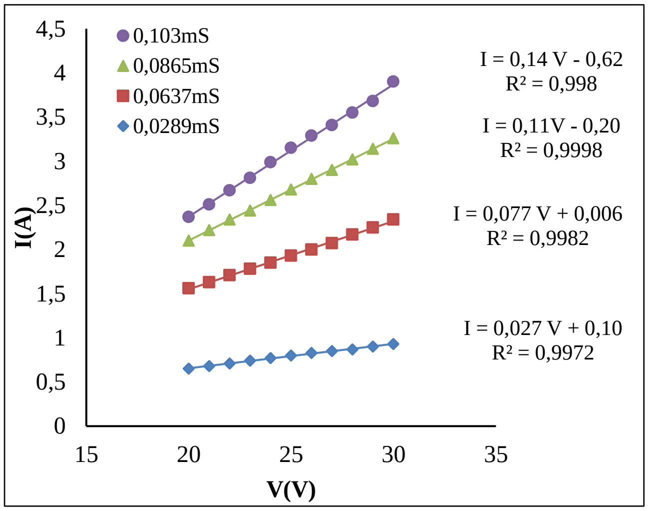

Fig. 4. Influence of different V (ΔV=10 V) in 4 water conductivities; T=21ºC; d=2mm; t=15s

Figure 4 show how, as in an ideal fluid, the dependence on V, f_3, is lineal. Even though the parameterization slope α_{IV} looks hardly dependent on the electrical conductivity. Once more, this dependence will be taken into account using the 3.1.1 linear fit.

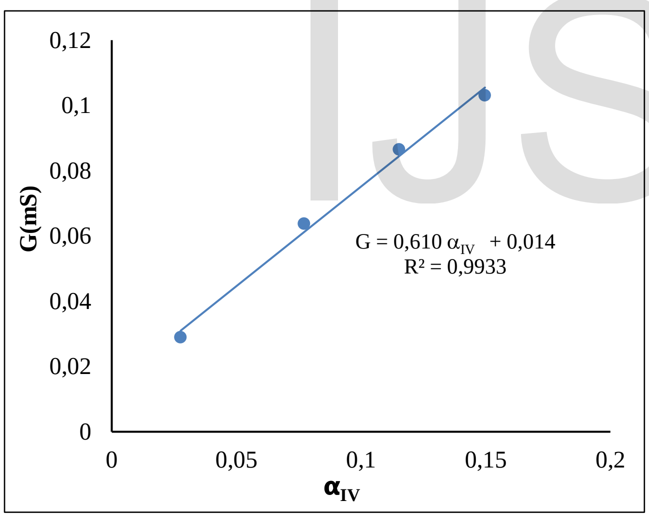

Fig. 5. Influence of different G in α_{IV}; T=21ºC; d=2mm; t=30s.

Figure 5 shows a lineal dependence of α_{IV} slope with the water electrical conductivity (Eq. 4).

$$f_3(V) = a_3\,\alpha_{IV}\,V + a_4 \quad (4)$$

Where a_3 and a_4 are fitting constants and α_{IV} include the electrical conductivity dependence. This parameterization is valid for the full water range.

3.1.4 Temperature and meteorological conditions

The behaviour of an EWD based prototype depends on working temperatures. Temperature variations can occur due to external climatological conditions or internal process effect. Both effects should be evaluated separately.

In principle, the EWD disinfection cell should be adapted to any emplacement worldwide, independently on climatological conditions. To evaluate the associated influence, a dedicated test has been provide under fixed test conditions and controlled temperature variations from 10º to 40ºC. Two different natural waters with extreme electrical conductivities have been selected.

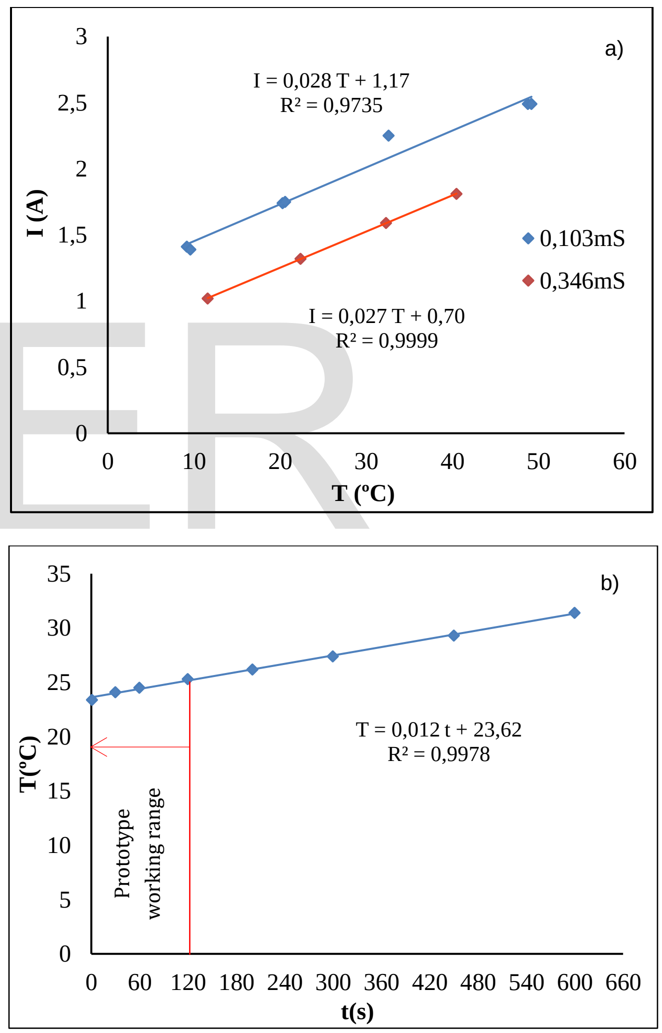

Fig. 6. a) Influence of temperature variation (ΔT = 30ºC) on current intensity (I) for two different natural waters; V=24V; d(0,346mS)=8mm, d(0,103mS)=2mm; t=30s. b) Influence of exposure time (t) on temperature (T) on uninterrupted functioning; T_{amb}=24ºC, d=3mm, I=2,8A,V=24V, G=0,346mS.

Figure 6a) show a lineal dependence that can be expressed as in Equation 5. As main remark the slope β looks independent on mineralization.

International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March -2017
ISSN 2229-5518

$$f_4(T) = I_0^T + \beta\,(T - T_0), \qquad \beta = 0.027 \pm 0{,}0006\ (A/^{0}C) \quad (5)$$

Where I_0^T correspond to the electric field intensity in standard conditions (T_0=25⁰C) and depends on water electrical conductivity.

Internal process effect is correlated to the exposition time. That is the time in which the electrolytic process is continuously working. The exposition time is inversely proportional to the expected production water rates (see table 2 for details). To study how this factor affects the working temperature a dedicated test has been performed at fixed experimental conditions. The electrolytic cell prototype has been forced to work uninterrupted for a period of 600 seconds without water interchange.

Table 2. CORRESPONDENCE OF EXPOSITION TIME (S) AND EXPECTED WATER FLOW RATE.

Expected Water flow Rate (liters/hour)	Exposition time (s)
120	30
60	60
30	120
15	240
7,5	480
6	600

Figure 6b) show the obtained results. The maximum variation of temperature achieved was 8ºC for Δt = 600s. An increase of 0.77±0,01ºC/min was measured. As presented in [16], exposure periods over 120s do not increase the generation of disinfection agents but increase the overall energy consumption. For exposure time of 120s a maximum increase of 0,041±0,001A on current intensity is observed (ΔT=1,5⁰C).

Equation 1 resumes the parameterization of the electric field effective intensity on temperature dependence, where only ambiance temperature needs to be considered. The electrolytic process does not influence significantly on water temperature.

3.1.5– pH

pH is other intrinsic characteristic of natural waters. Its variability can be associated to the presence of different dissolved substances (salts, metals and non metals) and physicochemical reactions during disinfection processes. In the case of EWD processes, two different scenarios have to be considered for pH effect evaluation; the influence of natural pH variations on current intensity (I) and the influence of EWD cell on pH variation. Both effects should be evaluated separately.

The EWD cell should be adapted to work on a wide range of pH water values. To evaluate the influence of pH variations on current intensity (I) a dedicated test has been performed, in which pH modifications were artificially induced using controlled amounts of Sodium hydroxyl (NaOH) and acetic acid ($C_2H_4O_2$). The tests were repeated for 2 extreme natural waters electrical conductivity.

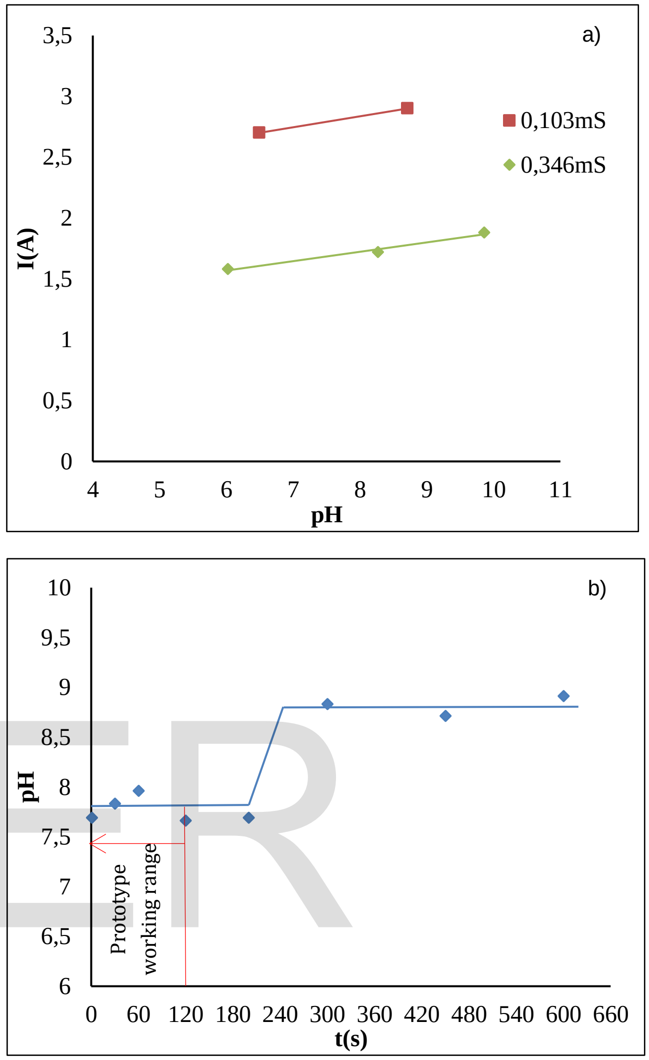

Fig. 7. a) Influence of pH variation on current intensity (I) for two different natural waters; V=24V; d (0,346mS)=6mm, d(0,103mS)=3mm; t=30s. b) Influence of electrolytic cell uninterrupted functioning on pH variation; T_{amb}=22ºC, d=2mm, I=2,8A,V=24V, G= 0,346mS, t_{max}=600s.

Figure 7a) show that a slight lineal variation on current intensity occur in both water samples, the maximum variation of current intensity achieved was 0,3A for ΔpH=4, never expected to occur in natural waters. Water pH variations do not influence significantly current intensity (I).

EWD cell can induce pH variations during continuous operation. To study how this factor affects the pH a dedicated test has been performed at fixed experimental conditions without water interchange. Figure 7b) show the main results. For exposure period of 120s a maximum ΔpH=0.3 was achieved, which does not influence significantly initial water pH. For larger exposition times a step, probably associated to some ferric salt ionization is observed.

International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March -2017
ISSN 2229-5518

Even for extreme variations of water pH, electric field effective intensity is not significantly influenced, as well as cell operation do not induce relevant water pH variations in prototype maximum expected exposure periods. The dependence can be expressed as:

$$f_5\,(pH) = I_0^{pH} \qquad (6)$$

Where I_0^{pH} correspond to a corrective factor associated to the water pH.

3.2 – Effective Electric field Intensity Parameterization.

From the obtained functions dependences (eq. 1, 2, 3, 4, 5 and 6) and managing the full sample of previous results the equation of the effective electric field intensity can be written as:

$$I_{eff} = f_1\,(G) \cdot f_2\,(d) \cdot f_3\,(V) \cdot f_4\,(T) \cdot f_5\,(pH) = \eta_1\, I_0^T\, I_0^{pH} \cdot \alpha_{IV} \cdot d^{-\eta_2} \qquad (7)$$

Where η_1 and η_2 compile all constraints obtained during the parameterization of data, and I_0^T and I_0^{pH} are constants experimentally measured for each implemented EWD system.

The main advantage of the proposed method is the independence of the system, allowing the optimization of EWD system current intensity functioning for any natural water without the need of previous electrical conductivities measurement.

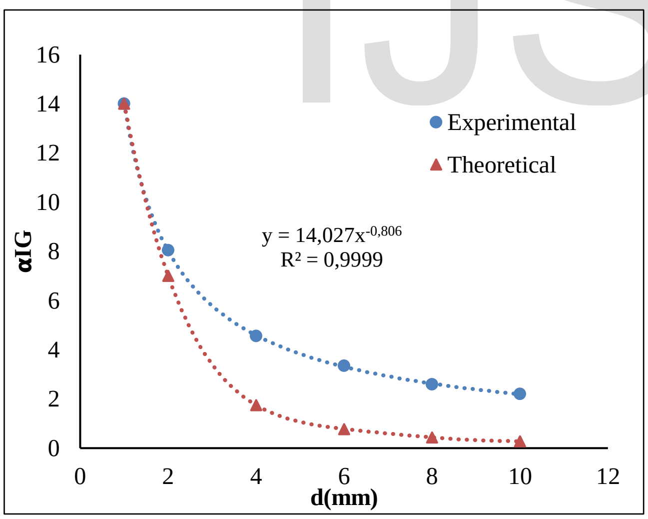

Fig. 8. Electric field shape between experimental and theoretical analysis normalized to d=1mm.

Finally, the complete parameterization of the electric field effective intensity (Fig. 8), shows the dependence of effective electric field intensity with the inter gap distance. α_{IG} is plotted for simplicity, and electric field shape for experimental and theoretical analysis is presented.

3.2.1 Setting parameters performance and sensibility

The actual model allows the control of the electric field effective intensity in EWD systems independent on the internal characteristics of raw waters. The reduction to minimum control parameters was obtained with the establishment of correlations between main influencing parameters as presented above. The next step is to try to perform a simple method, based on a few number of direct measurements able to fix the optimal working parameters for an extended range of natural waters.

Any water sample is characterized through the parameterization functions (α_{IV} and α_{IG} respectively), where α_{IG} is obtained from previous experimental data of a wide set of natural waters laboratory analysis and α_{IV} is calculated for the actual water sample in study across a I-V scan, in controlled conditions.

First, with pre fixed inter electrode gap (d), an I-V scan (from 20 to 30V) on water sample is made, and α_{IV} is measured. From the value of α_{IV}, f(G) can be obtained. Using the effective electrical field parameterization (Eq. 2), and pre calculated α_{IV} and α_{IG} a simple dependence of effective electric field with f(d) is obtained. It allows the optimization of cell setup depending on desired current intensity (adapting d) as well as evaluated initial values of G and possible variations on it during cell functioning.

In order to check the setting procedure of optimal working parameters, a set of "blind" tests on four non-characterized natural water samples is performed. The procedure used was equal for all experiments and water samples.

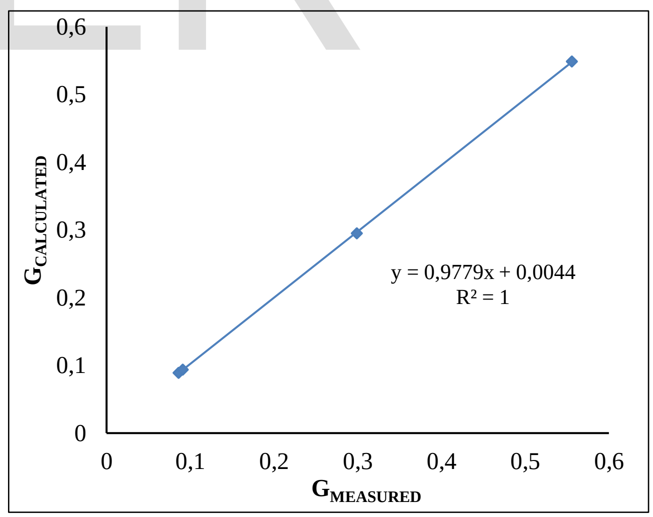

Fig. 9. Model verification of theoretically calculated and laboratory measurements of G in 4 different blind samples.

Figure 9 shows the comparative results obtained from theoretical calculated values of G from model and direct laboratory measurements of G for same water samples. The sensibility of this "blind method" is better than 95%, especially for medium/high natural water mineralization's.
All parameters analysed in the experiment show certain influence on the variation of electric field effective intensity (I_{eff}) and

International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March -2017
ISSN 2229-5518

correspondent mass transport regime as shown in Equation 7.

4 Conclusion

A simple EWD cell based prototype, has been modelled, developed and tested under controlled laboratory conditions. The system has been designed to work in an extended range of water mineralization (0,028-0,346mS) in optimal conditions.

A simple experimental setup, attending to future sustainability request has been developed in the laboratory. As main characteristics, low consuming renewable energy based system and accessible worldwide materials were used.

The electric field intensity has been described as a product of three independent functions of the electrolysis leading variables: cell voltage, electrodes gap and water electrical conductivity. The functions shapes have been obtained by parameterization using a wide range of mineralization waters. No dependence on other working characteristic as temperature or water pH is observed.

A simple procedure to define the optimal setting parameters, based on current-voltage (I-V) scan and independent of the water electrical conductivity has been performed. A blind cross-checking probe has been carrying out. More than 95% of efficiency has been obtained.

References

[1] Djamel Ghernaout, Mohamed Wahib Naceur, Ali Aouabed. “On the dependence of chlorine by-products generated species formation of the electrode material and applied charge during electrochemical water treatment”. Desalination 270 (2011) 9–22

[2] D. Pletcher, F.C. Walsh, *“Industrial Electrochemistry,”* Chapman and Hall, London, 1982

[3] L. Mezule, M. Reimanis, V. Krumplevska, J. Ozolins and T. Juhna, “Comparing electrochemical disinfection with chlorination for inactivation of bacterial spores in drinking water”, Water Science & Technology: Water Supply (2014) (158-159)

[4] Carlos A. Martínez-Huitle* and Enric Brillas, “Electrochemical Alternatives for Drinking Water Disinfection”. Electrochemical Water Purification, minireviews (2008)

[5] Erik Sogaard (Auth.)-“Chemistry of Advanced Environmental Purification Processes of Water”. Fundamentals and Applications. Aalborg University Esbjerg (2014),123

[6] Alexander Kraft, “Electrochemical Water Disinfection: A Short Review “, Platinum Metals Rev., 2008, 52, (3), 177–185

[7] W.T. Mook , M.K. Aroua G. Issabayeva , “Prospective applications of renewable energy based electrochemical systems in wastewater treatment: a review”. Renewable and Sustainable Energy Reviews 38 (2014) 36–46

[8] Ghernaout, D., Ghernaout, B., 2010. “From chemical disinfection to electro- disinfection: the obligatory itinerary?” Desalin. Water Treat. 16, 156–175.

[9] Joonseon Jeonga, Choonsoo Kimb, Jeyong Yoonb,* “The effect of electrode material on the generation of oxidants and microbial inactivation in the electrochemical disinfection processes”. Water research 43 (2009) 895–901

[10] John N. Myersa, William H. Steineckera, Zechariah D. Sandlinb, James A. Cox, Gilbert Gordon, Gilbert E. Pacey, “Development of an automated online electrochemical chlorite ion sensor”. Talanta 94 (2012) 227–231

[11] Hongna Li, Xiuping Zhu, Jinren Ni, “Comparison of electrochemical method with ozonation, chlorination and monochloramination in drinking water disinfection”. Electrochimica Acta 56 (2011) 9789–9796

[12] M.I. Kerwick, S.M. Reddy, A.H.L. Chamberlain, D.M. Holt. “Electrochemical disinfection, an environmentally acceptable method of drinking water disinfection?”, Electrochimica Acta 50 (2005) 5270–5277

[13] Henry Bergmann, A. Tansu Koparal, A. Savas Koparal, Fred Ehrig. “The influence of products and by-products obtained by drinking water electrolysis on microorganisms”. Microchemical Journal 89 (2008) 98–107

[14] C. Comninellis and G. Chen, “Electrochemistry for the Environment, - Springer New York (2010)”. Chapter 7

[15] Cervera Lloré, Pau, “PV based Water disinfection unit by electrolisis”.. Physics faculty, University of Santiago de Compostela. (2014). (Master thesis)

[16] Domingues, J., Cervera, P., and Lopéz, A. “Optimization of an electrochemical water disinfection cell PV power supply depending on the installation climatic zone” ,2015. (Unpublished)

[17] Serway, R. Electricity and Magnetisme. McGrawhill 6th Edition1996. (Book)