Desalination and Water Treatment
www.deswater.com

12 (2009) 369–374

doi: 10.5004/dwt.2009.962

Effect of electrolyte components on electrochemical generation and disinfection efficiency of active chlorine

Husam Damen Al-Hamaiedeh

Civil and Environmental Engineering Department, Mu'tah University, P.O. Box 7, 61710 Karak, Jordan
Tel. +962 795515401; Fax +962 375540; email: husamh@mutah.edu.jo

Received 21 March 2009; Accepted in revised form 11 October 2009

ABSTRACT

Electrochemical generation of active chlorine (AC) from chloride bearing electrolytes of different constituents and different initial pH values has been studied in this paper. The research involved three stages. In the first stage, sodium chloride electrolytes were used, and the effect of electrolyte concentration and pH value on AC generation rate was studied. The second stage involved the combined effect of adding calcium chloride and sodium fluoride to the electrolyte on AC current efficiency. The disinfection efficiency of the generated AC from electrolytes of different constituents was investigated in the final stage. Use of electrolytes of low initial pH value and with low concentrations (less than 25 mg/L) decreased the generation rate of AC. Adding calcium chloride to the electrolyte in ratios up to 25% increased both disinfection and current efficiencies of AC. However, adding sodium fluoride to the electrolyte in concentrations up to 1 g/L did not affect AC current efficiency, which means that water disinfection and fluoridation of water can be conducted simultaneously. Because sodium and calcium chlorides are available as by products of potassium manufacturing in the Dead Sea area in Jordan, generation of AC from electrolytes containing both sodium and calcium chloride is highly feasible.

Keywords: Active chlorine; Electrolyzer; Current efficiency; Generation rate; Cathode

1. Introduction

Centralized manufacturing, packaging, transportation and distribution of dry disinfecting agents and liquid chlorine are expensive compared to onsite generation of these agents, and ecologically unsafe due to the possibility of accidental spillage and explosion during transportation and distribution [1,2]. It is acceptable practice; therefore, to electrochemically generate oxidizing agents used for water and wastewater treatment and disinfection on, or as close as possible to, their application sites [3–8]. Active chlorine (AC) which is a solution containing Cl_2. ClO^- and HClO is usually generated by the electrolysis of chloride bearing solution (electrolyte). The electrochemical generation of AC, using sodium chloride solution as chloride bearing electrolyte, has been studied by many researchers [5,7–11]. The results of these studies included the determination of the most effective methods of AC generation, and the exploration of the optimum electrolysis parameters, such as electrolyte concentration, flow rate, anodic current density and electrode materials. Result analysis of the above studies showed that the overall optimal operation conditions for AC generation were achieved by using electrolysis cell (electrolyzer) with a stainless steel cathode and titanium anode coated by cobalt oxide. The optimum anodic current density and electrolyte concentration was found to be 800–1000 a/m^2, 25–50 g/L as NaCl, respectively. The use of centralized manufactured dry chlorine compounds and liquid chlorine is still the most widely used disinfection method of water and wastewater in Jordan. In this research attempt was made to electrochemically generate AC using electrolytes containing a mixture of sodium and calcium chloride solutions. These solutions are accessible and abundant in Jordan as they are a by product of potash manufacturing in the Dead Sea area [10]. Sodium fluoride was added to the electrolyte for the purpose of evaluating the feasibility of combination of water fluoridation and disinfection. The main advantage of the on-site generation of disinfectants is to avoid the common problems of chlorination such as transport and storage of dangerous chlorine gas [1,2]. The objectives of the current research are to:

- Study the effect of electrolyte pH and concentration on the electrochemical generation rate of AC.
- Evaluate the possibility of combining both water fluoridation and disinfecting by adding sodium fluoride to the electrolyte before electrolysis.
- Study the effect of adding different ratios of $CaCl_2$ to NaCl electrolytes on AC disinfection and current efficiencies.

The current efficiency of AC is the percentage of the current passing through the electrolyzer that accomplishes AC generation. Inefficiencies may arise from reactions other than the generation of AC, reaction taking place at the electrodes, or side reactions consuming the product. The current efficiency of AC was calculated as the ratio of the actually generated AC rate to the theoretically expected rate. The theoretical generation rate is calculated from the amount of electrical charge passed through the electrolyzer (Ah) and the theoretical production rate of active chlorine from chloride bearing electrolyte which equals 1.32 g/h per 1 Ah [12].

To achieve the stated objectives, experiments were carried out in three stages. First stage investigated the effect of electrolyte pH and concentration on AC generation rate. The influence upon AC current efficiency of the addition of sodium fluoride and calcium chloride in different proportions to the electrolyte were studied in the second stage. Finally the disinfection efficiency (inactivation of *E.coli* bacteria) of the generated AC was explored.

2. Materials and methods

A pressurized electrolyzer of concentric electrodes and up flow mode was used as a generator of AC. The electrolyzer has a cylindrical form; it consists of a tubular stainless steel cathode that is 60 mm in diameter and 80 mm high. A stainless steel bar with diameter of 20 mm was used also as a central cathode which passes inside the tubular titanium anode of 40 mm diameter. The anode was surface-coated with cobalt oxide, and the distance between the electrodes was 10 mm. The electrolyte from the container was pumped through the electrolyzer by

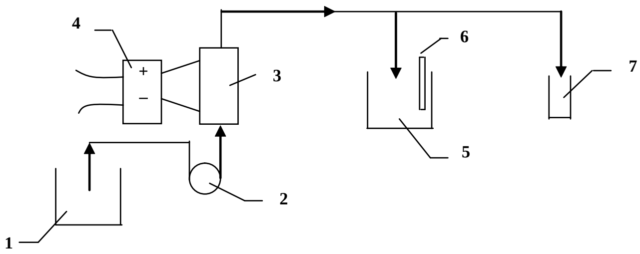

Fig. 1. Laboratory setup. 1 – electrolyte vessel; 2 – peristaltic pump; 3 – electrolyzer; 4 – rectifier; 5 – AC solution vessel; 6 – thermometer; 7 – sampling glass.

peristaltic pump at a flow rate of 6–8 L/h (Fig. 1). Flow rate was monitored with a Teflon flow rate meter. The differential potential between electrodes was applied with a Franell AP (100 V – 90 A), and the anode current density of 1000 a/m^2 was adjusted. AC solution was collected in a container, where the temperature was continuously monitored by a thermometer.

The measurements of AC and chloride concentrations were carried out according to the standard methods [13]. All experiments were duplicated, and the results were presented as mean values with deviations of less than 5%. Electrolysis of sodium chloride solutions of different concentrations and different pH values were carried out to determine the effect of electrolyte pH on the generation rate of AC. The electrolyte pH value was adjusted by adding H_2SO_4 and NaOH to the electrolyte.

Calcium chloride was added to the electrolyte in different proportions to study the effect of its addition on AC current efficiency. Three chloride bearing electrolytes of different concentrations (6.07, 15.17, and 30.33 g/L as Cl^-) were prepared by mixing of $CaCl_2$ and NaCl in different ratios, keeping the chloride ion concentration constant in each electrolyte. An increase of $CaCl_2$ ratio in each electrolyte required a decrease in NaCl ratio. The above electrolytes concentrations are equivalent to 10, 25 and 50 g/L as NaCl, respectively. The ratio between $CaCl_2$ and NaCl concentrations in the electrolytes was expressed as the ratio between Ca^{2+} and Na^+ concentrations. Sodium fluoride was added to the electrolyte in different concentrations up to 1 g/L in order to study the feasibility of combination of water disinfection and fluoridation.

The effect of $CaCl_2$ addition to electrolytes on the disinfection efficiency of the generated AC was studied. AC which generated from electrolytes concentration of 15.17 g/L as Cl^-containing $CaCl_2$ in different ratios (0%, 15%, 25%, 50% and 75%) was used. Dosages of 1 and 2 mg/L of AC generated from each electrolyte were added to bacterial model water samples, the number of *E. coli* bacteria in the samples was determined before disinfection and after contact periods of 1, 2, 5, 30 min and 24 h. The procedures used in this study for the preparation and enumeration of *E. coli* were similar to those used by

[14]. *E. coli* strain, ATCC 8739, was used throughout the experiments. *E. coli* was inoculated in tryptic soy broth in a 50 ml or 200 ml flask and grown for 18 h at 37°C. The bacteria were harvested by centrifugation in a 50 ml conical tube at 1000 g for 10 min and washed twice with 50 ml phosphate buffered saline (PBS, pH 7.0). Stock solutions of *E. coli* were prepared by re-suspending the final pellets in 50 ml of PBS. The initial populations of *E. coli* were obtained by diluting the stock solution. *E. coli* was enumerated by the spread plate method, in which the colony-forming units (CFUs) are counted after overnight incubation of the plates at 37°C. 1 ml of the solution treated with AC was withdrawn at each sampling time and then diluted 1:1, 1:10, and 1:100. Then 0.1 ml samples of both the undiluted and the diluted solutions were inoculated onto three replicate plates in order to count the number of *E. coli*.

3. Results and discussion

The results presented in Fig. 2 show that AC generation rate increased with increasing the electrolyte concentration. This occurred due to the increase in electrical conductivity which caused the increase in energy efficiency — where energy efficiency is defined as the ratio of electrical energy actually consumed for AC generation. The effect of the initial pH value of the electrolytes on the AC generation rate varies depending on the electrolyte concentration. Three solutions of different concentrations: 10, 25, 75 g/L, were used. For low concentration of 10 g/L, the increase in the initial pH value (up to 4) resulted in an increase in the generation rate of AC. This trend is due to the fact that in acidic solution (low pH), a high proportion of AC exists in the form of Cl_2 gas, which is released to the atmosphere causing a decrease in the AC generation rate. However, the increase in the initial pH value beyond 4 resulted in a decrease in the AC generation rate. This occurred due to additional consumption of energy for formation of byproduct gases resulting in a decrease of energy efficiency. For high concentrations (≥ 25 g/L), the increase in the initial pH value resulted in an increase in the AC generation rate. This is due to the fact that, first, AC in the form of Cl_2 decreases as the pH value increases, second, high concentrated electrolytes have higher electrical conductivity, which compensates for the loss of energy consumed for gas formation resulting in a continuous increase of the AC generation rate. In addition, the increase in the pH value of AC solution increased energy efficiency as AC compounds in alkaline electrolytes exist in the form of ClO^- ions, preventing the decrease of AC concentration by release of chlorine gas Cl_2 to the atmosphere [12]. The generation rate of AC from electrolytes of concentrations more than 25 g/L and of high initial pH (11–12) was increased about 12–14 % compared to the generation rate from the same electrolytes of a low initial pH (2–4) (Fig. 2). The results illustrated in Fig. 3 show the combined effect of electrolyte concentration and initial pH value on the pH value of the generated AC solution. For electrolytes of lower initial pH values (1.8) and with concentrations 10 g/L, there was no noticeable increase in the pH value of the produced AC solution indicating that the high proportion of the produced AC exists in the form of Cl_2 gas, while for electrolytes of the same initial pH values and of higher concentrations there was a significant increase in the pH value of the produced AC solution. On the other hand,

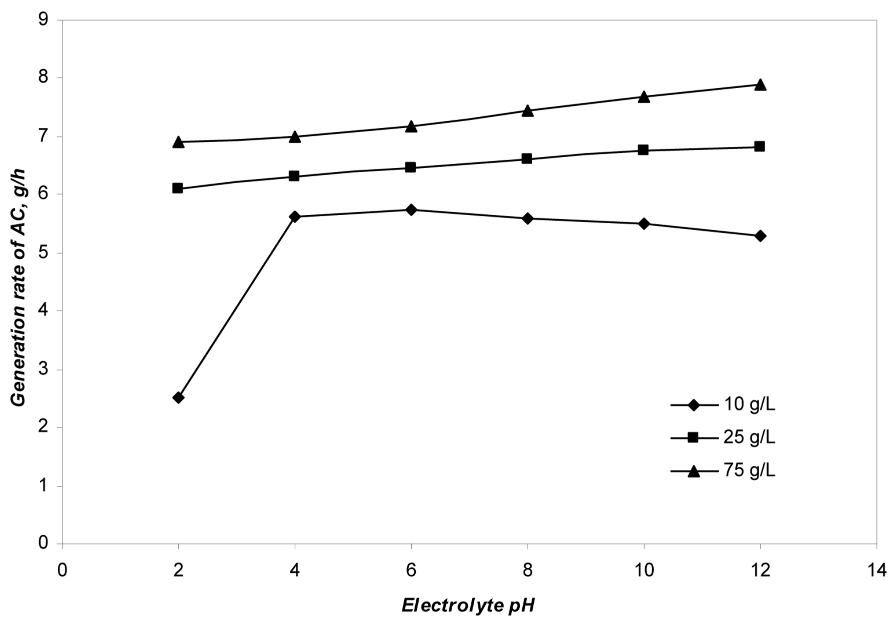

Fig. 2. Effect of electrolyte concentration and initial pH value on AC generation rate.

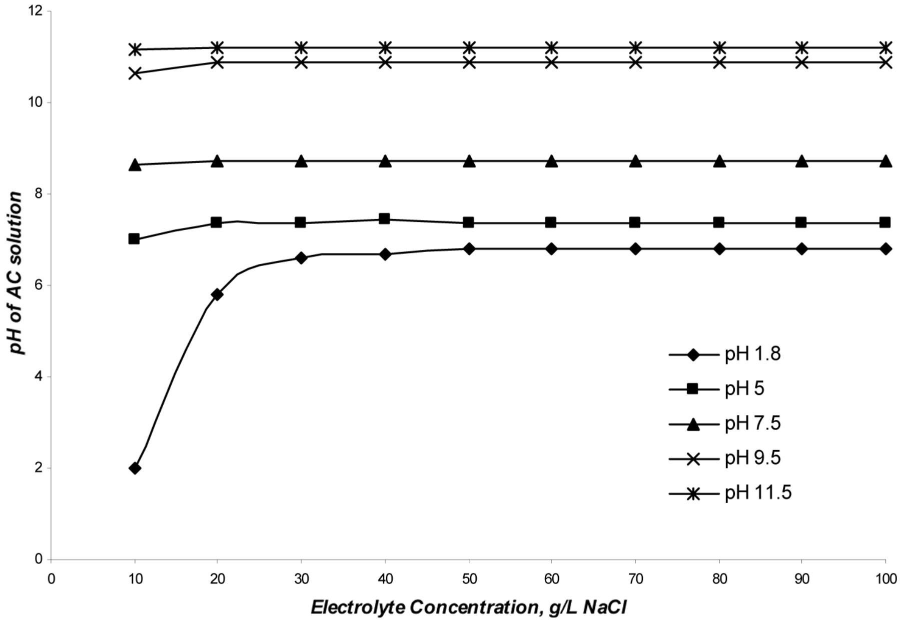

Fig. 3. The effect of the initial electrolyte pH and concentration on the pH value of AC solution.

for electrolytes of higher initial pH values up to 10, and regardless of the concentrations, there was a significant increase in the pH value of the generated AC solution.

Adding sodium fluoride to the electrolyte up to 1 g/L did not affect the AC generation rate demonstrating the possibility of simultaneous water disinfection and fluoridation. In AC solution with concentration of 3 g/L, the fluoride concentration was found 0.9 g/L, when electrolyte containing 1 g/L sodium fluoride was used for AC generation. AC dosage of 5 mg/L was found to contain 1.5 mg/L of fluoride. The control of fluoride concentration in the AC solution can be done by changing sodium fluoride concentration in the electrolyte or by changing the electrolyte flow rate through the electrolyzer. The results presented in Fig. 4 show the effect of adding different proportions of $CaCl_2$ to electrolytes of different concentrations (as Cl^-) on AC current efficiency. Despite of the electrolyte concentration, the current efficiency increased gradually with the increase of $CaCl_2$ ratio in the electrolyte reaching its maximum value when $CaCl_2$ ratio reached 25%. However, a noticeable decrease in current efficiency occurred when the ratio of $CaCl_2$ in the electrolyte increased beyond 25% returning to its initial value when $CaCl_2$ reached 60%. The addition of small proportions of $CaCl_2$ up to 25% to the electrolyte caused a formation of a thin film of calcium hydroxide

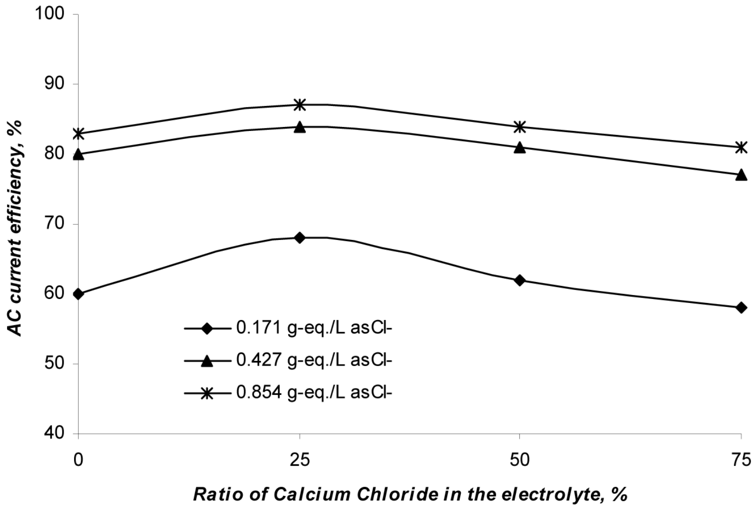

Fig. 4. The effect of calcium chloride addition to the electrolyte on AC current efficiency.

deposits on the cathode surface. The formation of the thin film at the cathode inhibited or reduced the reduction of hypochlorite ions at the cathode causing an increase in AC current efficiency. However, as the ratio of $CaCl_2$ in the electrolyte increased beyond 25% a decrease in AC current efficiency took place due to accumulation of calcium hydroxide deposits at the cathode which caused a decrease in the energy efficiency and raised the electrolyte temperature. The increase of electrolyte temperature decreased the AC current efficiency; high temperature stimulated the oxidation of AC compounds to produce unfavorable compounds, namely ClO_3 and ClO_4. The above results show that formation of the thin film of deposits on the cathode surface increased the AC current efficiency, while excessive growth of this film decreased the AC current efficiency.

The effect of adding $CaCl_2$ in different proportions to electrolytes of different concentrations on the pH values of both electrolytes and the generated AC solutions are presented in Table 1. The results show that a small change in the pH values of the electrolyte and AC solutions occurred despite of electrolyte concentration and Ca^{2+} ratio. Such change had no effect on AC current efficiency proving that the increase in energy consumption and reduction of AC current efficiency occurred as a result of deposits accumulation at the cathode.

The disinfection efficiency (inactivation of *E.coli*) of AC generated from electrolytes containing $CaCl_2$ in different ratios is presented in Table 2 and Fig. 5. Adding $CaCl_2$ to the electrolytes up to 25% increased the disinfection efficiency of the generated AC. A dosage of 1 mg/L of AC generated from electrolytes containing 25% Ca^{2+} was sufficient to inactivate *E.coli* concentration of (4000–4800)/100 ml, while a dosage of 2 mg/L of AC produced from electrolytes containing 0% Ca^{2+} (pure NaCl electrolyte) was required to inactivate the same concentration of *E. coli* bacteria. More increase in Ca^{2+} ratio in the electrolyte beyond 25% did not increase the disinfection efficiency of the generated AC, such results complies with the results obtained in previous studies [15].

Table 1
The effect of $CaCl_2$ addition to the electrolytes on the pH value of the electrolytes before and after electrolysis

$CaCl_2$ ratio,%	pH			
	Electrolyte concentration 6.07 g/L as Cl^-		Electrolyte concentration 15.17 g/L as Cl^-	
	Before electrolysis	After electrolysis	Before electrolysis	After electrolysis
0	7.44	8.06	7.27	8.46
10	7.84	7.95	7.26	8.23
25	7.26	7.80	7.21	7.94
50	7.21	7.52	7.20	7.71
75	7.18	7.29	7.11	7.36
100	7.18	7.11	7.11	7.21

Table 2
Evaluation of the disinfection efficiency of the generated AC from NaCl electrolytes containing different ratios of $CaCl_2$

$CaCl_2$ ratio,%	Salt concentration in the electrolyte		AC dosage, mg/L	*E. coli*/100 ml after						*E. coli*/100 ml
	NaCl g/L as Cl^-	$CaCl_2$ g/L as Cl^-		1 min	2 min	5 min	10 min	30 min	24 h	
0	0.427	0	1	2464	2434	2296	2212	2164	—	4672
			2	8	2	0	0	0	0	4128
15	0.363	0.064	1	752	512	384	280	10	2	4228
			2	0	0	0	0	0	0	4132
25	0.3202	0.1068	1	0	1	0	0	0	0	4512
			2	0	0	0	0	0	0	4782
50	0.2135	0.2135	1	6	1	1	0	0	0	4512
			2	0	0	0	0	0	0	4732
75	0.1068	0.3202	1	1440	1024	608	544	19	10	4232
			2	0	0	0	0	0	0	4320

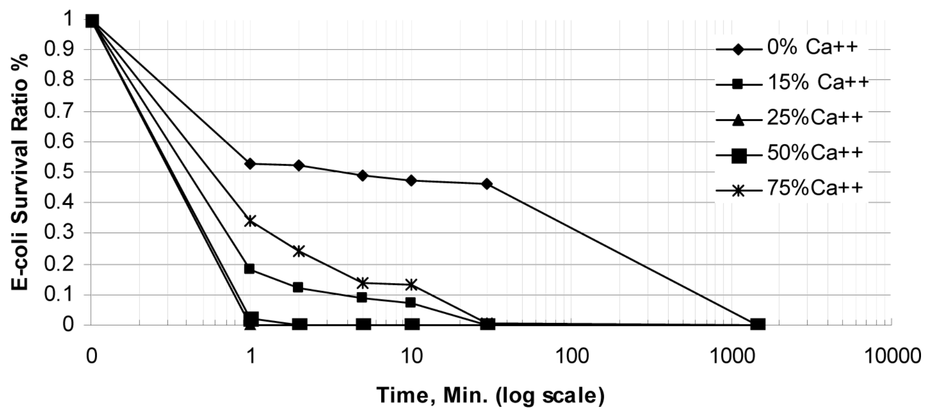

Fig. 5. Change in *E. coli* survival ratio with time due to adding AC generated from electrolytes containing different proportions of $CaCl_2$, dosage of 1 mg/L.

4. Conclusion

This study reports that the effect of electrolyte initial pH on AC generation rate varies depending on electrolyte concentration. Increasing the initial pH value of electrolyte of low concentration (10 g/L) from 2 up to 4 resulted in an increase in the generation rate of AC. However, the increase in the initial pH value beyond 4 resulted in a decrease in the AC generation rate. For electrolytes of high concentrations (≥ 25 g/L), the increase in the initial pH value resulted in a continuous increase in the AC generation rate. Adding sodium fluoride to the electrolyte up to 1 g/L did not affect the AC generation rate demonstrating the possibility of combining both water disinfection and fluoridation. The AC current efficiency increased gradually with the increase of $CaCl_2$ ratio in the electrolyte reaching its maximum value when $CaCl_2$ ratio reaches 25%. However, a noticeable decrease in current efficiency occurred when the ratio of $CaCl_2$ in the electrolyte increased beyond 25% returning to its initial value when $CaCl_2$ reached 60%. Adding $CaCl_2$ to the electrolytes up to 25% significantly increased the disinfection efficiency of the generated AC.

References

[1] K. Rajeshwar and J.G. Ibanez, Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement. Academic Press, San Diego, USA, 1997.

[2] A. Kraft, M. Stadelmann, M. Blaschke, D. Kreysig, B. Sandt, F. Schroder and J. Rennau, Electrochemical water disinfection. Part I: Hypochlorite production from very dilute chloride solutions, J. Appl. Electrochem., 29 (1999) 859–866.

[3] K. Shimada and K. Shimahara, Responsibility of hydrogen peroxide for the lethality of resting *Escherichia coli* B cells exposed to alternating current in phosphate buffer solution. Agric. Biol. Chem., 46 (1982) 1329–1337.

[4] G.E. Stoner, G.L. Cahen, M. Sachyani, Jr. and E. Gileadi, The mechanism of low frequency a.c. electrochemical disinfection, J. Electroanal. Chem., 141 (1982) 229–243.

[5] L.V. Venczel, M. Arrowood, M. Hurd and M.D. Sobsey, Inactivation of *Cryptosporidium parvum Ocysts* and *Clostridium perfringens* spores by a mixed-oxidant disinfectant and free chlorine, Appl. Environ. Microbiol., 63 (1997) 1598–1601.

[6] G. Gordon, W.J. Cooper, R.G. Rice and G.E. Pacey, Disinfectant Residual Measurement Methods, AWWA Research Report American Water Works Research Foundation, Denver, Colorado, 1987.

[7] K.R. Venkitanarayanan, G.O. Ezeike, Y.C. Hung and M.P. Coyle, Efficacy of electrolyzed oxidizing water for inactivating *Escherichia coli* O157:H7, *Salmonella enteritidis*, and *Listeria monocytogenes*, Appl. Environ. Microbiol., 65 (1999) 4276–4279.

[8] P. Drogui, S. Elmaleh, M. Rumeau, C. Bernard and A. Rambaud, Oxidising and disinfecting by hydrogen peroxide produced in a two-electrode cell, Water Res., 35 (2001) 3235–3241.

[9] L.A. Kulsky, B.D. Grebnyuk and O.S. Savluk, eds., Electrochemistry in Water Purification, Technika, Keiv, 1987.

[10] H.D. Al-Hamaiedh, Advanced treatment of domestic wastewater in rural areas. PhD thesis, Saint Petersburg State University of Architecture and Civil Engineering, Saint Petersburg, 1993.

[11] H.D. Al-Hamaiedh and I.G. Krasnoborodko, Investigation of the electrochemical process of hypochlorite production from the Dead Sea brine, 51, Proc. Conf. Saint Petersburg State University of Architecture and Civil Engineering, Saint Petersburg, 1–3 February 1994, pp. 66–71.

[12] H.D. Al-Hamaiedeh, Combination between Coagulation and disinfection in water treatment, Dirasat, Engineering Sciences, University of Jordan, vol. 31, No. 2, October 2004.

[13] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 19th ed., Washington, DC, 1995.

[14] M. Cho, Y.H. Lee, H. Chung and J. Yoon, Inactivation of *E. coli* by photochemical reaction of ferrioxalate at slightly acidic and near-neutral pHs, Appl. Environ. Microbiol., 70 (2004) 1129–1134.

[15] L.N. Kusminski, J.H. Zeng and C.C. Zin, Effect of calcium bicarbonate on disinfection by halogens, Sanitary Eng. Proc. Amer. Soc. Civ. Eng., vol. 98, no. 1, 1972.