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Full Length Research Paper

Electrochemical synthesis of disinfecting peroxocarbonate solutions and assessment of their antimicrobial effects

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ABSTRACT

Environmentally - friendly disinfecting peroxocarbonate solutions have been electrochemically synthesized by using a diluted alkaline carbonate solution and flow-through electrolytic modular elements FEM-3, which are the main constituent of the well-known STEL devices producing electrochemically activated (ECA) solutions. Peroxocarbonate solutions generated on a STEL-PEROX device with an anolyte capacity of 20 l/h demonstrated the following characteristics: $TDS_{an.} = 650 \pm 50$ mg/l, $TDS_{cath} = 620 \pm 40$ mg/l; oxidants concentration = 60 ± 5 mg/l; $ORP_{an.} = +800 \pm 50$ mV, $ORP_{cath.} = +160 \pm 20$ mV; $pH_{an.} = 6.6 \pm 0.2$, $pH_{cath.} = 9.5 \pm 0.5$. Low mineralization of anolyte PEROX provided a high stability of the molecular complexes, which were hydrated and transformed into electroneutral aquacomplexes, resulting in the increase of the stability of metastable anolyte PEROX solutions. The experimental data obtained showed that anolyte solutions produced on a STEL-PEROX device were an effective disinfectant against microorganisms: with an oxidant concentration of 60 mg/l and a bacterial suspension density of 10^8 CFU/ml anolyte PEROX completely killed *E.coli* after 5 min of exposition, while for *Salmonella – 10 min*.

Keywords: Electrochemical activation, anolyte, catholyte, metastability, disinfection.

INTRODUCTION

Solutions, which possess the highest biocidal activity among all known liquid chemical germicides at low toxicity for superior organisms, are those electrochemically activated (ECASOL) (Bakhir *et al.*, 2005). ECASOL generators have been commercialized and widely used internationally for more than 20 years (Chau *et al.* 2008a,b; Ha *et al.* 2008; Chau *et al.* 2012), where thousands of water purification systems and medical, agricultural and food processing devices are in operation now. These ECASOL generators have been developed by V. Bakhir Institute of Electrochemical Systems and Technologies (VBIECS&T) and produced under the name STEL. STEL-PEROX is a variation of initial STELs devices, wherein instead of a chloride salt a diluted sodium carbonate solution is used as a starting electrolyte. During electrolytic process in the chambers FEM-3 metastable hydrated substances are formed (Bakhir *et al.*, 2008). Hydrate shells surrounding the charged particles in the solution are in a close interaction with each other, and the degree of their mutual infiltration increases with the increase of electrolyte concentration (Bakhir, 2003). The concept of “structurized solution” implies in a relatively stable in time and space orderness of the disposition of mutually interacted soluble particles and water molecules regarding an arbitrarily selected particle. The famous L. Pauling’s postulate (Pauling, 1952) about the electroneutrality of hydrated ions says that the ion charge is redistributed on the hydrogen atoms of the water molecules surrounding ion. The main consequence from this conception is the possibility to represent the ion as a peculiar neutral particle.

Abbreviations

ECA - electrochemically activated;
ECASOL - solution electrochemically activated;
ORP - oxidation-reduction potential;
TDS - total dissolved solids;
VBIECS&T - V. Bakhir Institute of Electrochemical Systems and Technologies.

Redistribution of ion charge also exerted its influence on the water molecules in the region of the long-range hydration. Obviously, shifting of a partial electron density from the water molecules nearest to the ion of interest gives rise to its deficit on these molecules, which in turn will be compensated for by the displacement a partial electron density from the ensuing water molecules and so on. For anion particles shifting of of a partial electron density occurs in a reverse direction. The reason of these displacements is the striving to attain equilibrium state with minimal energy requirement. The Coordination of water molecules around a soluble particle as well as all the types of their interactions are the crucial factors for the solution structure (Bakhir, 1992).

Electrochemical synthesis of percarbonate solution in a STEL-PEROX generator was conducted by passing a diluted sodium carbonate (or hydrocarbonate) solution at concentrations of 0.4 - 1.0 g/l, so diluted as found at potable water, in a specially designed flow-through electrolytic modular element (FEM-3) (RF Patent N^{0}2329197).

In the process of electrochemical synthesis of peroxocarbonate a diluted sodium carbonate solution was injected into anode chamber of an electrolytic element FEM-3, while in cathode chamber fresh water flowed countercurrently. By using countercurrent flows alkaline cations could be removed more completely from the anolyte stream than the parallel version. The volume rate of water supply in the cathode chamber must exceed that of the carbonate flow in the anode space in order to set up the conditions in which electric current through the diaphragm of the electrolytic cell was provided exclusively by the transfer of cations from anode space to cathode one [RF Patent N^{0}2329335]. An additional factor allowing to prevent the penetration of hydroxide anions from cathode space into anode one was the pressure excess (0.1- 0.5kg/cm^2) in anode chamber. At pressure ≤ 0.1kg/cm^2 it was impossible to suppress the countercurrent flow of hydroxide ions from cathode space to anode one, and at pressures ≥ 0.5kg/cm^2, carbonate anions from anode chamber could also pass through the diaphram.

From the experimental data obtained in VBIECS&T, it was found that the low mineralization of the synthesized solution defined a high stability of the molecular complexes, whose components could be not only stable molecules but also ions, free radicals as well as excited molecules, named exciplexes, which in turn were hydrated and transformed into electroneutral aquacomplexes. Consequently, the smaller the concentration of ions in the solution, the greater the increase in the stability of aquacomplexes and the greater the decrease in the charge density of metastable compounds.

In a STEL-PEROX device (series STEL-P20-K60) there are 8 FEM-3 units hydraulically connected in series with anolyte and catholyte countercurrent flows. When water flow moves through the cathode chambers, the concentration of sodium hydroxide in the chambers increases due to the electromigration of sodium ions from anode to cathode chambers. In anode chambers at the beginning stage of the electrochemical process there took place reactions of formation of sodium mono- and di-percarbonate products:

$2Na_2CO_3 + 10H_2O \rightarrow 2HOC(O)OOC(O)ONa + 2NaOH + O_2 + 8H_2$;

$2Na_2CO_3 + 6H_2O \rightarrow 2HOC(O)OONa + 2NaOH + 4H_2 + CO_2$;

As carbonate solution moved along the connected in series anode chambers, the solution was depleted by sodium cations, causing decrease of the solution pH. Besides, in the last anode chambers the oxidation of water and electrochemical reactions products took place:

$2H_2O \rightarrow 4H^+ + 4e^- + O_2$; $2H_2O \rightarrow 2H^+ + 2e^- + H_2O_2$; $O_2 + H_2O \rightarrow O_3 + 2e^- + 2H^+$;

$3H_2O \rightarrow O_3 + 6e^- + 6H^+$; $H_2O_2 \rightarrow HO_2^{\bullet} + 1e^- + H^+$; $H_2O_2 \rightarrow {}^1O_2$ (singlet) $+ 2e^- + 2H^+$;

$H_2O \rightarrow 2H^+ + 2e^- + O^{\bullet}$; $H_2O \rightarrow H^+ + 1e^- + OH^{\bullet}$.

At the cathodes of the reactors chain the accompanying electrochemical reactions involving reduction of the products also occurred:

$O_2 + e \rightarrow O_2^-$; $O_2 + H_2O + 2e \rightarrow HO_2^- + OH^-$; $HO_2^- + H_2O + e \rightarrow HO^{\bullet} + 2OH^-$;

$e_{cathode} + H_2O \rightarrow e_{aq}$; $H_2O + e_{aq} \rightarrow H^{\bullet} + OH^-$; $CO_3^{2-} + 2H_2O + 2e \rightarrow HCO_2^- + 3OH^-$;

$2SO_4^{2-} + 5H_2O + 8e \rightarrow S_2O_3^{2-} + 10OH^-$; $SO_4^{2-} + 4H_2O + 2e \rightarrow SO_3^{2-} + 2OH^-$.

The catholyte solution containing these products offered an enhanced extra activity and high bioactivity owing to its low oxidation-reduction potential.

This study aimed to produce anolyte PEROX solutions by using the latest STEL type model STEL-P20-K60 and investigate their antimicrobial properties in comparison with well known disinfecting agents.

MATERIALS AND METHODS

The electrochemical synthesis of anolyte PEROX has been carried out on a STEL-P20-K60, the FEM-3 modules of which were acquired from VBIECS&T (Figure 1).

Sodium carbonate stock solution was prepared with a 12.0 g/l concentration. The water flows were adjusted in both anode and cathode chambers of the electrochemical chain in order to obtain approximately 20 l/h of anolyte and 60 l/h of catholyte respectively on the effluent and also to monitor total dissolved solids (TDS) concentration of anolyte flow to 650 - 700 mg/l.

After the devise reached the optimal operating conditions an anolyte solution was collected for physico-chemical and microbiological analyses. TDS, oxidation-reduction potential (ORP) and pH of the ECA solutions were measured on a multifunctional analyzer HACH SenSion-

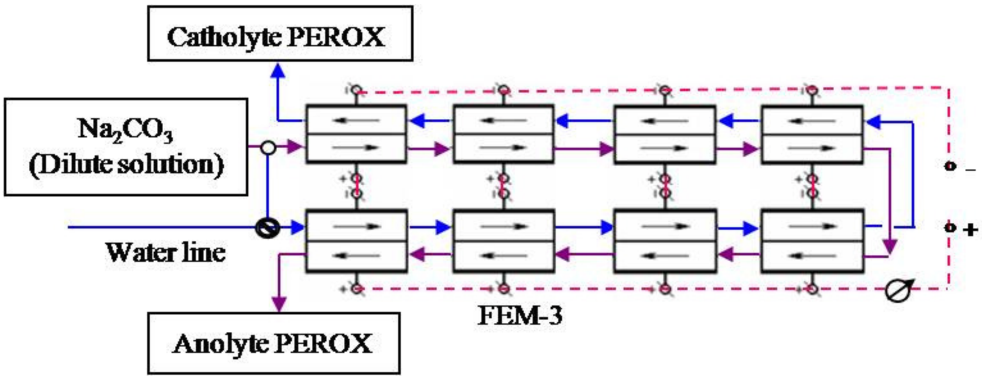


Figure 1: *The schematic layout of electric and hydraulic connections of electrolytic units FEM-3 in STEL-P20-K60*

Table 1. Technological indices of STEL-P20-K60 and physico-chemical parameters of its ECA solutions

ECA solution	[Na_2CO_3], g/l (initial content)	El. Current (A)	El. Voltage (V)	Capacity (l/h)	TDS (mg/l)	pH	ORP (mV)	[Oxidants] (mg/l)
Anolyte	12			20 ± 1	650 ± 50	6.6 ± 0.2	+800 ± 50	60 ± 5
Catholyte		20 ± 1	40 ± 1	60 ± 2	620 ± 40	9.5 ± 0.5	+160 ± 20	-

156. The total concentration of oxidants in ECA solution was determined by iodometric titration method (Alpha, 1998).

Microbial cultural media:

- Pepton for preparation of physiological solutions;
- Chromocult and SS_agar as media for *E.coli* and *Salmonella* isolation respectively;
- PCA medium for quantitative analysis of microbes.

All the cultural media were acquired from company MERCK through their representative office in Vietnam: LABOTECH. JSC, 13-1B Trung Yen ward 7, Trung Hoa str., Dist. Cau Giay, Ha Noi city.

Study of bactericidal effect of anolyte PEROX

E.coli and *Salmonella* used for appraising microbicidal activity of the anolyte PEROX solutions were separated from a waste water source and multiplied to obtain a bacterial density of 10^8 CFU/ml. Microbiological samples were collected from fishery water, a surface of working tools as well as a carcass of fishery products.

9 ml of an anolyte PEROX solution with a 60 mg/l concentration was placed in a sterilized test-tube (at this rather low oxidants concentration the osmotic pressure of microbial cells remained unchanged). Then 1ml of *E.coli* or *Salmonella* suspension of certain microbial concentration was added. After 5, 10 and 15 min exposition to the anolyte PEROX the number of survived microorganisms were determined by measuring the turbidity at 600 nm using UV-VIS spectrophotometer. For the control anolyte PEROX solution was substituted by pure water.

RESULTS AND DISCUSSION

Physico-chemical parameters of anolyte PEROX

The working parameters of an ECA devise STEL-P20-K60 and physico-chemical indices of its ECA solutions presented in Table 1 showed that at a low mineralization (not more than 650 mg/l of total dissolved solid) anolyte PEROX attained a high ORP, up to +800 mV, proving its high oxidation ability.

The experimental result obtained for the changes in physico-chemical parameters of anolyte PEROX while being stored for 9 days in closed polypropylene can at room temperature and in a dark place (Figure 2) indicated that concentration of the oxidants and ORP of the ECA solution decreased rather slowly during this storing time (ORP decreased by 10% and oxidants – by 25%). This result confirmed the high storing stability of anolyte PEROX solutions in comparison with that of the anolyte solutions produced on STEL-ANK devices, of which the metastability of generated oxidants degraded completely after 3 – 4 days of storing ((Bakhir, 2003; Bakhir, 2008).

Figure 3 demonstrated the influence of electric current on ORP and the mineralization degree of ECA solutions (anolyte PEROX and catholyte PEROX). It was interesting to note that, with the increasing of electric current, in the anolyte mineralization decreased while

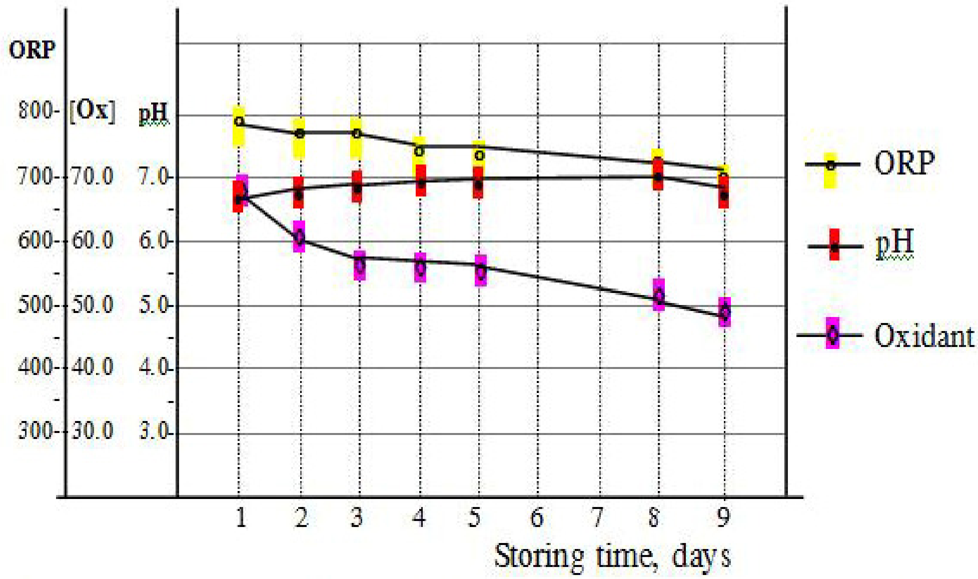
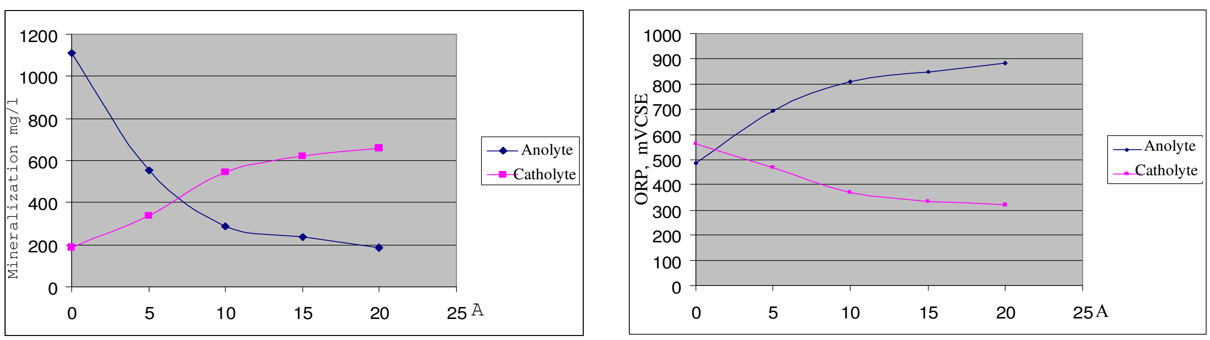


Figure 2. The storage time- dependence of Physico-chemical characteristics of anolyte PEROX solution, stored in a dark place in a closed polypropylene can



a b

Figure 3. Effects of mineralization degree (a) and ORP (b) of the anolyte PEROX and catholyte PEROX solutions upon an electric current of the electrochemical process

Table 2. Antibacterial activity of anolyte PEROX ([Oxidants] = 60 mg/l) against Salmonella and E.coli under different microbial density and contact time Salmonella (CFU/ml) (initial bacterial concentration 10^8 CFU/ml)

Sample	**Dilution degree of**					
	10^0	10^1	10^2	10^3	10^4	10^5
	Concentration of oxidants = 60mg/l					
Control (without anolyte)	*	*	*	>>	284	28
Exposition 5 min	>>	>>	>>	~ 1700		
Exposition 10 min	0	0	0	0		

(* Uncountable)

ORP increased, and for the catholyte, in contrast – mineralization increased while ORP decreased. Evidently, with the increasing of electric current the through-membrane transport of sodium ions from anode space to cathode one became more intense, resulting in mineral depletion in anolyte and enrichment in catholyte, and consequently ORP increased in anolyte and decreased in catholyte (Bakhir *et al.*, 2005) .

It was shown that the decomposition of percarbonate ions, hence loss of antimicrobial activity of anolyte PEROX occurred rather slowly: after 30 days of storage antimicrobial activity decreased not more than 20%. This was caused by an extremely diluted anolyte solution and a structural rigidity of ion-hydrate shells, which formed in the high intensity electrostatic field near the electric double layer.

Table 2 contiues. *E.coli* (CFU/ml) (initial bacterial concentration 10^8 CFU/ml)

Sample	Dilution degree					
	10^0	10^1	10^2	10^3	10^4	10^5
	Concentration of oxidants = 60mg/l					
Control (without anolyte)	*	*	*	>>	>>	10^2
Exposition 5 min	0	0	0	0	0	
Exposition 10 min	0	0	0	0	0	
Exposition 15 min	0	0	0	0	0	

(*Uncountable)

Table 3. Antibacterial activity of anolyte PEROX ([Oxidants] = 60 mg/l) in the treatment of marine squid products

Samples	***TPC* (CFU/ml)**	***E.coli* (CFU/ml)**	***Coliforms* (CFU/ml)**	***Salmonella***
Control (immersing in tap water)	$7,8 \times 10^5$	36	$2,7 \times 10^2$	+
Immersing in anolyte PEROX 15 min	$4,5 \times 10^5$	14	$1,7 \times 10^2$	-
Immersing in anolyte PEROX 30 min	$8,5 \times 10^4$	14	$1,4 \times 10^2$	-

("**+**" – present; "**-**" – absent)

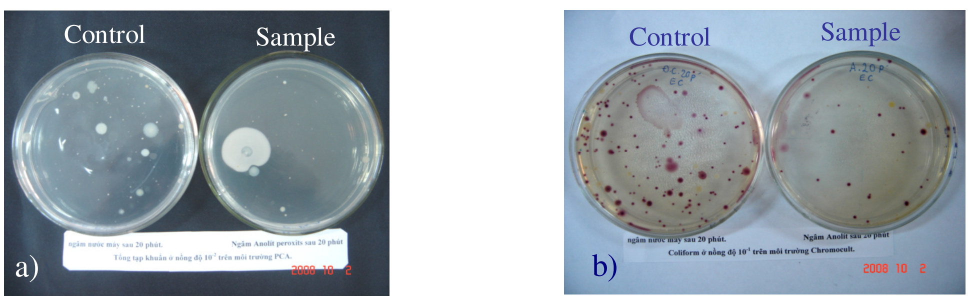


Figure 4. Inactivation of bacteria in squid's flesh after immersing the marine product into anolyte PEROX of 60 mg/l concentration for 20 min: a) TPC, dilution degree 10^2, cultivated in PCA medium; b) Coliforms, dilution degree 10^1, cultivated in Chromocult medium;

STEL-P20-K60 devices have been shown to be capable of producing not only non-toxic solutions but also highly effective disinfectants, that effectively destroy microorganisms such as *Salmonella* and *E.coli*.

The produced anolyte PEROX solutions have been used for studying its antimicrobial activity with respect to some pathogenic bacteria encountered in fishery processing enterprises. Bactericidal activity of anolyte PEROX towards *Salmonella* and *E.coli* presented in Table 2 showed that after 5 min exposition of bacterial suspensions to an anolyte PEROX of 60 mg/l concentration all *E.coli* were killed, meanwhile *Salmonella spp*. were completely killed after 10 min exposition, even at undiluted bacterial suspension (10^8 CFU/ml).

Table 3 demonstrated the antibacterial activity of anolyte PEROX during the processing of squid products in Vietnam. The data showed that microbial density in squid's flesh diminished after half an hour immersing the product into anolyte PEROX solution of 60 mg/l concentration: *TPC* decreased by 9 times, *E.coli* and *Coliforms* – almost by twice, while *Salmonella* were completely inactivated.

Figure 4a,b presented the results of microbiological determination of the antibacterial strength of anolyte PEROX against TPC (total plate count) and *Coliforms* commonly encountered in marine fishery products.

CONCLUSION

The low mineralization of anolyte PEROX provides a high stability of the molecular complexes, which in turn were hydrated and transformed into electroneutral aquacomplexes. Consequently, the lower the concentration of ions in solution, the greater the decrease of the charge density of metastable particles, hence, the greater the stability of the metastable anolyte PEROX solutions.

Metastable low-mineralized percarbonate solutions, generated on STEL-P20-K60 device, were as effective as chlorine-oxygen containing anolyte ANK against microbes. The experimental data showed that anolyte PEROX solutions with prolonged metastable state were highly effective disinfectants against microorganisms: with an oxidant concentration of 60 mg/l and bacterial suspension of 10^8 CFU/ml anolyte PEROX completely killed *E.coli* after 5 min of exposition, while for *Salmonella – 10 min*.

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