UDC 544.65+661.43

O. Shmychkova [a], I. Borovik [b], D. Girenko [a], P. Davydenko [b], A. Velichenko [a]

THE EFFECT OF IMPURITIES ON THE STABILITY OF LOW CONCENTRATED ECO-FRIENDLY SOLUTIONS OF NaOCl

[a] Ukrainian State University of Chemical Technology, Dnipro, Ukraine
[b] Dnipro State Agrarian and Economic University, Dnipro, Ukraine

The synthesis of hypochlorous acid from low concentrated chloride-containing electrolytes has been studied on various oxide materials at the anode current density of 50 mA cm^{-2}. Boron doped diamond, platinized titanium, metallic titanium doped with platinum and palladium and materials based on lead (IV) oxide modified with fluorine and surfactants turned out to be promising for the synthesis of hypochlorous acid by electrolysis. Whereas, given the stability of oxidant synthesis during cumulative electrolysis, titanium modified with platinum and palladium as well as pre-treated lead (IV) oxide containing surfactants (sodium laureth sulfate) was the best. One should additionally take into account the possibility of combined use of electrocatalysts for the synthesis of strong oxidants in the reverse current mode in flow systems, when the implementation of the gas cathode leads to the formation of hydrogen peroxide and hypochlorous acid is formed at the anode. In fact, only a metal electrocatalyst, such as titanium modified with platinum and palladium, can be a suitable material. The kinetics of hypochlorite conversion is primarily determined by the pH value of freshly prepared solutions, temperature and storage conditions. The presence of different organic and inorganic micro-impurities in the solution also affects the kinetics of the hypochlorite salt decomposition. The following micro-impurities show the most negative impact on the stability of sodium hypochlorite solutions: Co(II), Cu(II), Mg(II), Al(III), and $K_3[Fe(CN)_6]$; Ni(II), Fe(III), and $K_4[Fe(CN)_6]$ influence the stability to a lesser extent. The effect of chlorate on the inhibition of sodium hypochlorite activity as a disinfectant has been investigated. The presence of chlorate in the disinfectant solution involved results in the absence of bactericidal activity against S. aureus and P. aeuruginosa. The growth of pseudomonas colonies becomes more abundant with increasing chlorate content in the disinfectant.

Keywords: doped platinized titanium; disinfectant; sodium hypochlorite; test culture; chlorate; micro-impurities.

Introduction

Extensive positive experience has been gained with the use of sodium hypochlorite solutions, the scope of application is expanding, and new treatments are being developed in recent years [1]. According to the pharmacological action, sodium hypochlorite solutions have disinfectant, antiseptic, antimicrobial, detoxifying properties [2]. In addition, the immunostimulatory and regenerative effects of these solutions are noted [3]. They are practically non-toxic, do not cause allergic reactions, and their components do not accumulate in humans and animals, so the development of new medical and veterinary pharmaceuticals based on sodium hypochlorite is of considerable interest.

Sodium hypochlorite is known mainly as an effective and harmless agent for disinfection of premises in livestock farms [3]. Recently, sodium hypochlorite has been widely used in medicine: at renal and hepatic dysfunction, sepsis, peritonitis, food poisoning, gastric ulcer, pneumonia, diabetic coma, mushroom poisoning (toadstool) [4]. Sodium hypochlorite is a donor of active oxygen and stimulates the body's oxidation of exogenous and endogenous toxic substances: tissue breakdown products, toxins of microorganisms, drugs. Sodium

hypochlorite is produced by macrophages in phagocytosis, it shows the ability to improve hematological parameters and immune status [5].

The main focus of researchers is on the development of promising anode materials for electrolysis of low concentrated NaCl solutions, where IrO_2 and PbO_2 are used as electrocatalysts [6], as well as on the study of the effect of current density on the current efficiency of the target product. IrO_2-based materials were shown to be quite promising for electrolysis, but their high cost, imperfect sol-gel anode fabrication technology, and increasing chlorate content in the target product with increasing current density are significant barriers to their implementation. Much attention is paid to direct electrochemical or secondary chemical treatment of toxic effluents using NaOCl [7]. The used wastewater treatment methods should be divided into several groups: reagents for the addition of hydrogen peroxide and/or other oxidants, such as ozone, sodium hypochlorite together with catalysts; photocatalytic and electrocatalytic [8]. It was noted that peroxene systems are promising for practical application, a hydroxyl radical formed from the primary oxidant by its catalytic decomposition being an effective oxidant [9]. It was shown that the use of peroxene systems of different types is the most effective for the treatment of biological contaminants. The presence of oxygen-containing radicals in such systems can completely destroy both bacteria (including genes that cause their resistance to modern drugs) and viruses [10]. Particular attention should be paid to the synthesis of hypochlorous acid, as the latter is widely known as antimicrobial, antiviral and antifungal agent [5], the effectiveness has been proven even to the coronavirus COVID-19 [9]. The synthesis of such an oxidant in the process of electrolysis is also interesting in the context of disinfection of hospital effluents.

The main obstacle to the use of sodium hypochlorite solutions in medicine and veterinary medicine is the lack of the necessary electrocatalysts that allow developing the optimal design of the flow electrochemical cell to obtain solutions of the required purity.

The features of the anodic and cathode processes, the creation of an anode with a highly selective electrocatalytic coating, on the one hand, and the presence of micro-impurities in solutions, on the other hand, are recognized to be determined. In the presence of micro-impurities, the anode surface can be modified, irreversibly or reversibly. By adsorbing on the electrode surface, impurities can change the energy of surface particles, block the

surface, and so on.

The presence of micro-impurities can affect not only the selectivity and electrocatalytic activity of the anode, but also the further stability of the resulting solutions. It is quite a difficult task to study the effect of certain impurities both in terms of analytical chemistry and in terms of possible complex regularities of action of impurities from the bulk.

Having in mind that the kinetics of NaOCl decomposition is influenced by the presence in the solution of micro-impurities of organic and inorganic nature, the effect of metal impurities in the form of simple or complex ions on the stability, as well as the chlorate influence on the bacteriostatic effect of the solutions involved was investigated in the present work.

Considering results discussed herein, we envisage that the low concentrated eco-friendly NaOCl has interesting, prospective application as disinfectant agent against multi-resistant strains of microorganisms.

Materials and methods

All chemicals were reagent grade. Several types of oxide and metal catalysts were used in the work. The current collectors were a Ti plate with the required surface area. The surface of the titanium substrate was pre-machined, degreased at room temperature in 5 M NaOH solution and then the surface was etched at 80^0C in 6 M HCl for 20 min.

Platinum was deposited from nitrite electrolyte at the temperature of 80^0C [11]. Under these conditions, the current efficiency of platinum was about 30%. The content of deposited platinum was monitored gravimetrically. The surface platinum content was $1-4$ mg cm^{-2}. Palladation was performed at 60^0C from phosphate electrolyte. The current efficiency was 90%.

An equimolar solution of $SnCl_4$ in n-C_4H_9OH based on SnO_2 was used as a basic coating solution to obtain coatings by pyrolytic method. For its preparation, 5 cm^3 of $SnCl_4$ was dissolved at cooling in 15 cm^3 of n-butanol. To apply a modified coating in 1 cm^3 of this basic solution, additives were introduced in appropriate amounts in the form of $RuCl_3$, $H_2PtCl_6·6H_2O$, $PdCl_2$, and $IrCl_3·3H_2O$, pre-dissolved in a small amount of concentrated hydrochloric acid. The layers were applied with a brush, followed by drying at the temperature of $80-90^0C$ for 10 minutes. After drying, the surface became brownish-brown. Next, the anode was heat-treated in a muffle furnace at 450^0C for 5 min. After application of 10 layers, the heat treatment was performed at 500^0C for 60 minutes.

For the preparation of anodes with an active

coating based on lead (IV) oxide, a basic electrolyte with the following composition was used: 0.1 M CH_3SO_3H/HNO_3 and 0.1 M $(CH_3SO_3)_2Pb/Pb(NO_3)_2$. Some modifying additives were added to the deposition electrolyte by a portion or an appropriate aliquot to achieve the desired concentration of the additive in the solution. Surfactants were introduced into the electrolyte in the form of aqueous solutions of known concentration. The thickness of the studied coatings was $20-50$ μm. Platinized titanium was used as a collector for PbO_2-based anodes.

The concentration of $NaClO$ and $NaClO_3$ in solutions was determined by iodometric titration [12]. The standard deviation in determining the concentration does not exceed ± 3 mg L^{-1} and ± 2 mg L^{-1} for sodium hypochlorite and sodium chlorate, respectively. Standard deviations for current efficiencies are $\pm 1.0\%$ and $\pm 0.5\%$ for hypochlorite and chlorate, respectively.

The determination of bactericidal activity and control of the absence of bacteriostatic effect of solutions involved were determined against seven cryogenic strains (E. coli, S. aureus, S. tiphymurium, P. aeruginosa, L. monocytogenes, L. ivanovi, and L. innocua) according to the following method. Washings from beveled solid nutrient medium of test cultures of strains involved were obtained with sterile saline under aseptic conditions. Further, suspensions of these test cultures were made according to the McFarland optical turbidity standard, which

corresponds to $2.0 \cdot 10^9$ colony forming units/cm^{-3}; then we used them for testing to determine the bactericidal activity and control the absence of bacteriostatic effect of experimental disinfectants. The tests were performed by the suspension method using 3 sterile tubes (three repeats of the tests) of each working dilution of the experimental disinfectant, spilled on 4.5 cm^3. In all tubes with working dilutions of disinfectant, 0.5 cm^3 of the prepared appropriate suspension of test cultures of microorganisms were taken, mixed thoroughly and kept in a working solution of the experimental disinfectant according to the exposure period (exposure time being 30 s in the study case). Bactericidal activity of 100 mg L^{-1} $NaOCl$ was used as reference solution. Another reference was 100 mg L^{-1} $NaClO_3$ Three solutions containing 100 mg L^{-1} and 10%, 50% and the same amount of chlorate were investigated.

Results and discussion

The synthesis of hypochlorous acid from low concentrated chloride-containing electrolytes on various oxide materials was carried out at the anode current density of 50 mA cm^{-2}. The results are presented in Table.

As can be seen from the obtained results, boron doped diamond, platinized titanium, and metallic titanium doped with platinum and palladium as well as materials based on lead (IV) oxide modified with fluorine and surfactants turned out to be promising materials for the synthesis of hypochlorous acid by

The effect of anode material on the achieved concentration of ClO^- ions obtained by electrolysis in a sulfate electrolyte (0.5 M Na_2SO_4) additionally containing 0.05 M $NaCl^*$

Material	Concentration of ClO^-, $\times 10^3$, mol dm^{-3}				
	Electrolysis duration, min				
	60	120	180	240	300
Boron doped diamond	1.75	3.5	4.45	6.75	8.58
Ti/Pt	1.5	2	1.65	1.4	1
Pt-doped SnO_2 obtained pyrolitycally	0.5	0.7	0.7	0.7	0.7
Pd-doped Ti/Pt	2.3	2.45	2.79	2.49	2.15
PbO_2 obtained from methanesulfonate electrolyte	1.0	1.6	1.65	1.5	1.3
PbO_2–3 wt.% SLES	1.25	1.6	1.35	1.05	0.8
PbO_2–3 wt.% SLES. Pre-treatment 20 min	1.1	1.95	2.05	1.7	1.35
PbO_2–3 wt.% SLES. Pre-treatment 60 min	0.65	1.4	1.75	1.75	1.6
PbO_2–3 wt.% SLES. Pre-treatment 180 min	0.6	0.95	1.2	1.05	0.95
PbO_2–3 wt.% SLES deposited on Ebonex$^{®}$	1.2	1.4	1.3	1.2	1.25
PbO_2–0.042 wt.% F^-	1.6	2.64	1.95	1.55	1.15
PbO_2–4.2 wt.% SDS	0.95	1.3	1.3	1.3	0.95
PbO_2–2 wt.% SDS	1.15	1.55	1.6	1.45	1.0
PbO_2–3.2 wt.% SLES obtained from nitrate electrolyte	1.1	1.9	2.25	1.7	1.7

*Note: SLES stands for sodium laureth sulfate $(CH_3(CH_2)_{11}(OCH_2CH_2)_nOSO_3Na)$; SDS stands for sodium dodecylsulfate $(CH_3(CH_2)_{11}OSO_3Na)$.

O. Shmychkova, I. Borovik, D. Girenko, P. Davydenko, A. Velichenko

electrolysis. Whereas, given the stability of oxidant synthesis during cumulative electrolysis, titanium modified with platinum and palladium and pre-treated lead (IV) oxide containing surfactants (sodium laureth sulfate) were the best. Thus, these materials are of considerable interest for further development. One should additionally take into account the possibility of the combined use of electrocatalysts for the synthesis of strong oxidants in the reverse current mode in flow systems, when the implementation of the gas cathode will lead to the formation of hydrogen peroxide and hypochlorous acid will be formed at the anode [13]. In fact, such a material can only be a metal electrocatalyst such as titanium, modified by platinum and palladium.

It should be noted that the process of hypochlorite synthesis is catalytic and occurs with the participation of particles adsorbed on the catalyst surface; thus, the change in the concentration of hypochlorite formed (steady state or concentration drop) is due to the passivation of the electrode surface over time, which is characteristic for Ti/Pt surface [13], and for lead dioxide surface. This phenomenon can be explained by both the adsorption of sulfate ions from sulfate solution and recrystallization.

Unlike hydrogen peroxide, the decomposition products of which are effective oxidants only in the presence of catalysts, the main advantage of using hypochlorous acid is its own oxidative activity and combined action. On the one hand, as a strong oxidant, it can interact with hazardous chemicals, leading to their partial or complete destruction. On the other hand, hypochlorites exhibit bactericidal, virulent and fungicidal activity and are widely used for disinfection, which is an additional advantage for the treatment of hospital effluents [1−5]. In addition, the destruction of hypochlorous acid in a photocatalytic system under the action of light leads to the formation of oxygen-containing radicals (one of the options for the implementation of peroxene systems), which will contribute to the destruction of resistance genes in bacteria [3,10]. The general regularities of chemical processes that take place in solutions of hypochlorous acid are quite well studied [14]; however, they still have specificity depending on the structure of the substance with which the oxidant interacts.

It should be noted that the prolonged action of hypochlorites depends on changes in their concentration. It was found that during storage of hypochlorite solutions, in addition to reducing the total content of hypochlorites, there is a gradual increase in the content of chlorate ions in the solution [13]. This phenomenon is due to the fact that hypochlorites exhibit the properties of redox amphotericity, because the chlorine (I) atom can not only reduce the degree of oxidation, but also increase it. The decomposition of hypochlorite is usually described by second-order kinetics. However, we did not experimentally detect significant amounts of ClO_2^-. This is due to the rapid reaction of excess ClO^- ions. Since the concentration of hypochlorous acid decreases with increasing and decreasing pH of the solution and the concentration of ClO^- anions at pH<5 is almost zero, it should be concluded that the fastest disproportionation reaction of HClO should occur at 5<pH<8. This conclusion is well confirmed by experimental data on the dependence of the process rate on the acidity of solutions [13].

Thus, the kinetics of hypochlorite conversion should primarily be related to the pH of freshly prepared solutions, temperature and storage conditions. The kinetics of decomposition is influenced by the presence of organic and inorganic micro-impurities in the solution.

The effect of metal impurities ($5 \cdot 10^{-6}$ M) in the form of simple or complex ions on the stability of NaOCl solutions was investigated. This rather low concentration was chosen based on the amount of micro-impurities that can enter the solution of sodium hypochlorite with NaCl and water. Ions were introduced in the form of appropriate solutions of salts (usually chlorides) into a solution of sodium hypochlorite, which was prepared using double-distilled water and NaCl. The initial pH of the solution was 8.9. At this initial pH, even the initial solution is not stable enough: the decrease in NaOCl concentration was 25% during 160 days. A solution with this pH was prepared specifically to make the effect of micro-impurities as noticeable as possible. It was found that the strongest catalytic action is demonstrated by Co(II), followed by Cu(II) (Fig. 1). Their catalytic action is due to the redox couples Co(II)/Co(IV) and Cu(II)/Cu(I). Next, Mg(II) and Al(III) ions follow the effect on stability. Most likely, there is catalysis of micelles of aluminum and magnesium hydroxides. Probably, other impurities are adsorbed and concentrated on the surface of these micelles, thus forming colloidal catalytic centers. Ni(II), Fe(III), Mn(II), an Ca(II) ions have a similar effect on the stability of the initial solution of sodium hypochlorite.

The following reaction schemes of catalytic action of Ni (II) (Eqs. (1)−(4)) and Co (II) (Eqs. (5)−(6)) have been proposed in the literature [15]:
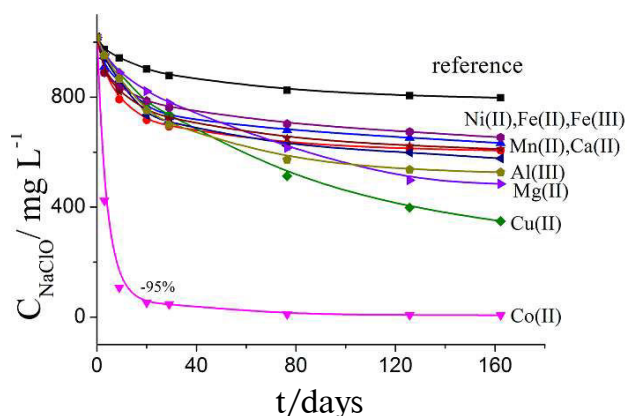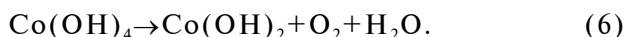
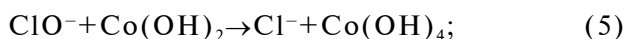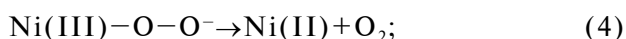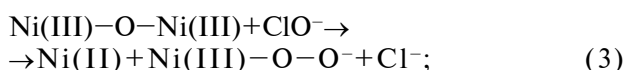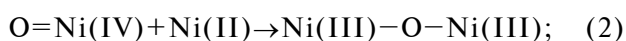$$Ni(II)+ClO^- \rightarrow O=Ni(IV)+Cl^-; \qquad (1)$$
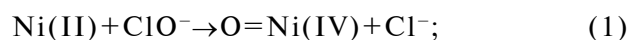
Fig. 1. Kinetic curves of NaOCl concentration drop in the presence of $5 \cdot 10^{-6}$ M cations. Initial pH 8.9

$$O=Ni(IV)+Ni(II)\rightarrow Ni(III)-O-Ni(III); \quad (2)$$

$$Ni(III)-O-Ni(III)+ClO^-\rightarrow$$
$$\rightarrow Ni(II)+Ni(III)-O-O^-+Cl^-; \quad (3)$$

$$Ni(III)-O-O^-\rightarrow Ni(II)+O_2; \quad (4)$$

$$ClO^-+Co(OH)_2\rightarrow Cl^-+Co(OH)_4; \quad (5)$$

$$Co(OH)_4\rightarrow Co(OH)_2+O_2+H_2O. \quad (6)$$

It is known that upon recrystallization of sodium chloride, potassium hexacyanoferrate (II) is added to the mother liquor as an additive that prevents caking and clumping. In this regard, we additionally considered the effect of potassium hexacyanoferrate (II) and hexacyanoferrate (III) additives on the stability of hypochlorite solutions (Fig. 2). If in the presence of Fe(III), the NaOCl concentration decreased rather rapidly during the first 10−20 days; then in the presence of ferrocyanide additives the

nature of the kinetic curves of NaOCl decomposition is close to the reference solution. However, the presence of hexacyanoferrate (II) and hexacyanoferrate (III) increases the rate of decomposition by 1.6 times and 4 times, respectivlay, as compared with the reference solution. The rate of $NaClO_3$ accumulation in the presence of hexacyanoferrate (III) coincides with the action of Fe(III), and the activity of hexacyanoferrate(II) is almost 2 times lower. The kinetic curves of the decomposition of NaOCl and the accumulation of $NaClO_3$ in solutions of sodium hypochlorite, which were obtained from reagent grade and technical NaCl, are shown in Fig. 3. The nature of the curves in Fig. 3 coincides with the nature of the curves 1 and 3 in Fig. 2, indicating the presence of $K_4[Fe(CN)_6]$ impurities in technical NaCl.

The action of Mn(II) cation on the decomposition of hypochlorite is similar to the catalytic action of Ni(II) and Fe(III). There is a sharp decrease in concentration during the first 10−20 days in the presence of these ions, and then the rate is comparable to the rate of decomposition in the reference solution. One can distinguish two linear areas with rate constants of $1.7 \cdot 10^{-5}$ and $1.5 \cdot 10^{-6}$ L/(mg·day) (Fig. 4). Thus, after 70−80 days, the rate of decomposition of NaOCl decreases by an order of magnitude. During this period, there is a main accumulation of chlorate. After 80 days, the chlorate almost ceases to accumulate, and further decomposition occurs only via the oxygen formation.

There is a monotonic decrease in the concentration of NaOCl in the presence of Cu(II). The rate constant of NaOCl decomposition is $1.2 \cdot 10^{-5}$ L/(mg·day) (Fig. 4).

The kinetic curves in the presence of Mg(II) by their nature coincide with similar curves for Cu(II). The rate constant of NaOCl decomposition
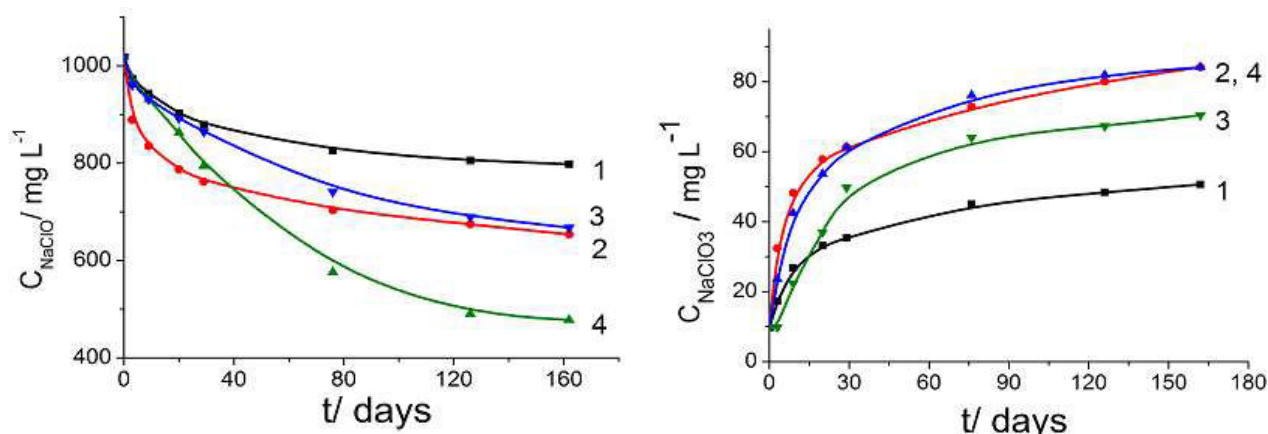

Fig. 2. Kinetic curves of NaOCl decomposition (initial pH 8.9) and $NaClO_3$ accumulation in the presence of cations of the iron group ($5 \cdot 10^{-6}$ M): 1 − reference solution; 2 − $FeCl_3$; 3 − $K_4[Fe(CN)_6]$; 4 − $K_3[Fe(CN)_6]$

O. Shmychkova, I. Borovik, D. Girenko, P. Davydenko, A. Velichenko
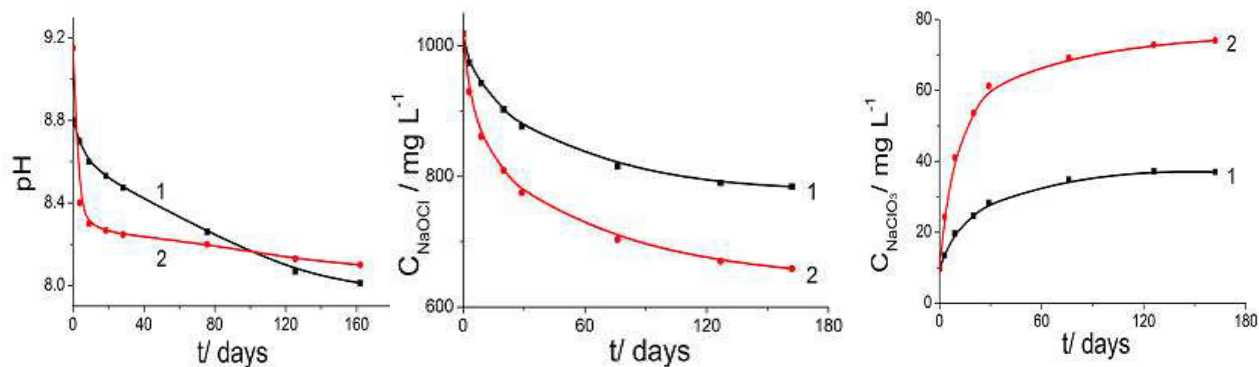
Fig. 3. pH change and kinetic curves of NaOCl decomposition (pH 8,9) and NaClO₃ accumulation in the sodium hypochlorite solution prepared from reagent grade (1) and technical (2) NaCl
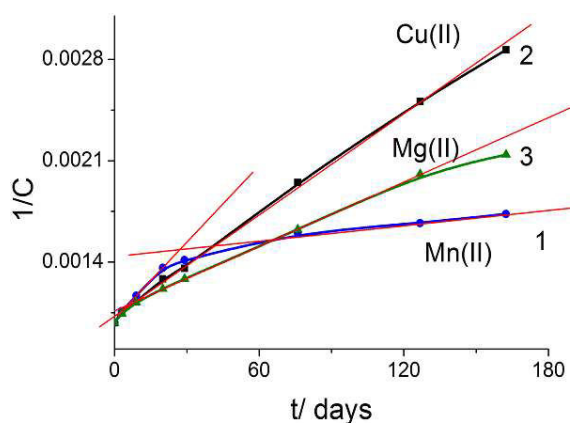

Fig. 4. Kinetic curves of NaOCl decomposition (initial pH 8.9) in the presence of additives ($5 \cdot 10^{-6}$ M): 1 − MnCl₂; 2 − CuCl₂; 3 − MgCl₂

in the presence of Mg(II) is 1.6 less than in the presence of Cu(II) and is $7.5 \cdot 10^{-6}$ L/(mg·day). If the catalytic action of Cu(II) can be explained by the existence of Cu(I)/Cu(II)/Cu(III) redox couples, then the action of micro-impurities of Mg(II) is difficult to explain. The selective action of AlCl₃,

which accelerates the decomposition of hypochlorite but does not affect the rate of chlorate accumulation, is also not easy to explain. A similar situation is observed with the influence of micro-quantities of CaCl₂. As an explanation, one can assume the possibility of the formation of catalytic centers in the form of micelles of the corresponding hydroxides. The micelles themselves act as heterogeneous catalysts or catalytically active micro-impurities from solution can be specifically adsorbed on their surface with the formation of heterogeneous catalytically active colloidal particles.

In addition, the influence of chlorate on inhibition of sodium hypochlorite action as disinfectant was investigated. The data concerning this inhibition are absent in the literature.

The 100 mg L⁻¹ concentration of NaOCl is considered to be effective, at which the experiment repeated three times at the appropriate exposure time ensured the absence of growth of test microorganisms on liquid and solid nutrient media in the presence of typical growth of test cultures in growth controls (Fig. 5).

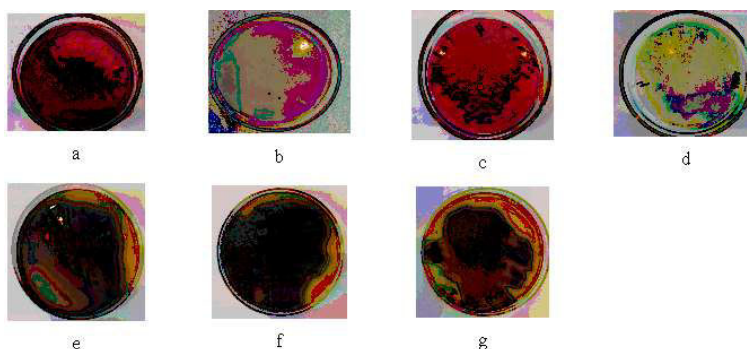The presence of chlorate in the disinfectant

Fig. 5. Typical growth of test cultures in reference solution (100 mg L⁻¹ NaClO₃): a − Escherichia coli (F50) ATCC No. 25922; b − Staphylococcus aureus ATCC No. 25923; c − Salmonella tipymurium 144; d − Pseudomonas aeruginosa ATCC No. 2853(F); e − Listeria monocytogenes ATCC No. 19112; f − Listeria innocua ATCC No. 33090; g − Listeria ivanovi

solution involved leads to the absence of bactericidal activity against S. aureus and P. aeuruginosa, and the growth of P. aeuruginosa colonies becomes more abundant with increasing chlorate content in the disinfectant.

Conclusions

Boron doped diamond, platinized titanium, metallic titanium doped with platinum and palladium as well as materials based on lead (IV) oxide modified with fluorine and surfactants were stated to be effective catalysts for the synthesis of hypochlorous acid by electrolysis. Whereas, given the stability of oxidant synthesis during cumulative electrolysis, titanium, modified with platinum and palladium and pre-treated lead (IV) oxide containing surfactants (sodium laureth sulfate) were the best.

The presence of micro-impurities can affect the stability of the solutions obtained. It has been revealed that Co(II), Cu(II), Mg(II), Al(III), $K_3[Fe(CN)_6]$ demonstrate the maximum negative impact on the stability of sodium hypochlorite solutions, while Ni(II), Fe(III), $K_4[Fe(CN)_6]$ develop it to a lesser extent.

The decomposition of hypochlorite is described by second-order kinetics. There is a sharp decrease in concentration of NaOCl during the first $10-20$ days of storage in the presence of these ions, and then the rate is comparable to the rate of decomposition in the reference solution. The presence of hexacyanoferrate (II) and hexacyanoferrate (III) increases the rate of NaOCl decomposition by 1.6 times and 4 times, respectively, as compared with the reference solution. The rate constant of NaOCl decomposition in the presence of Cu(II) is $1.2 \cdot 10^{-5}$ L/(mg·day), whereas it is 1.6 less than in the presence of Cu(II) and is $7.5 \cdot 10^{-6}$ L/(mg day) in the presence of Mg(II). Such action of micro-impurities on the stability of NaOCl solutions can be explained by the formation of catalytic sites in the form of micelles of corresponding hydroxides.

The low concentrated eco-friendly NaOCl can be used as disinfectant agent against multi-resistant strains of microorganisms, however the presence of chlorate in the disinfectant solution involved results in the absence of bactericidal activity against S. aureus and P. aeuruginosa.

Acknowledgments

REFERENCES

1. *Schlager N., Weisblatt J., Newton D.E.* Chemical compounds. − Detroit: Thomson Gale, 2006. − 981 p.

2. *Myers R.L.* The 100 most important chemical compounds: a reference guide. − Westport: Greenwood Press, 2007. − 260 p.

3. *Antibiotic* resistance genes in swine manure slurry as affected by pit additives and facility disinfectants / Hall M.C., Duerschner J., Schmidt A.M., Bartelt-Hunt S.L., Snow D.D., et al. // Sci. Total Environ. − 2021. − Vol.761. − Art. No. 143287.

4. *Efficacy* of chlorine-based disinfectants (sodium hypochlorite and chlorine dioxide) on Salmonella Enteritidis planktonic cells, biofilms on food contact surfaces and chicken skin / Byun K.H., Han S.H., Yoon J.-W., Park S.H., Ha S.D. // Food Control. − 2021. − Vol.123. − Art. No. 107838.

5. *Hypochlorous* acid: an ideal wound care agent with powerful microbicidal, antibiofilm, and wound healing potency / Sakarya S. Gunay N., Karakulak M., Ozturk B., Ertugrul B. // Wounds. − 2014 − Vol.26. − No. 12. − P.342-350.

6. *Characterization* of IrO_2-SnO_2 films prepared by physical vapor deposition at ambient temperature electrocatalysis / Battaglin G., Rosestolato D., Ferro S., De Battisti A. // Electrocatalysis. − 2013. − Vol.4. − No. 4. − P.358-366.

7. *Su D., Ben W., Strobel B.W.* Impacts of wastewater treatment plant upgrades on the distribution and risks of pharmaceuticals in receiving rivers // J. Hazard. Mater. − 2021. − Vol.406. − Art. No. 124331.

8. *Evaluation* of advanced oxidation processes for water and wastewater treatment − a critical review / Miklos D.B., Remy C., Jekel M., Linden K.G., Drewes J.E., Hubner U. // Water Res. − 2018. − Vol.139. − P.118-131.

9. *Persistence* of coronaviruses on inanimate surfaces and their inactivation with biocidal agents / Kampf G., Todt D., Pfaender S., Steinmann E. // J. Hosp. Infect. − 2020. − Vol.104. − P.246-251.

10. *Reduction* of antibiotic resistance genes in municipal wastewater efьluent by advanced oxidation processes / Zhang Y., Zhuang Y., Geng J., Ren X., Xu K., Ding L. // Sci. Total Environ. − 2016. − Vol.550. − P.184-191.

11. *Composite* electrodes PbO_2-Nafion® / Velichenko A., Luk'yanenko T., Nikolenko N., Shmychkova O., Demchenko P., Gladyshevskii R. // J. Electrochem. Soc. − 2020. − Vol.167. − Art. No. 063501.

12. *Girenko D.V., Gyrenko A.A., Nikolenko N.V.* Potentiometric determination of chlorate impurities in hypochlorite solutions // Int. J. Anal. Chem. − 2019. − Art. No. 2360420.

13. *Girenko D., Shmychkova O., Velichenko A.* Electrolysis of sodium chloride solutions on Ti/Pt anodes under current reversal conditions // Voprosy khimii i khimicheskoi tekhnologii. − 2020. − No. 2. − P.36-43.

O. Shmychkova, I. Borovik, D. Girenko, P. Davydenko, A. Velichenko

14. *Unraveling* oxidation behaviors for intracellular and extracellular from different oxidants (HOCl vs. H_2O_2) catalyzed by ferrous iron in waste activated sludge dewatering / Yu W., Wen Q., Yang J., Xiao K., Zhu Yu., Tao Sh., et al. // Water Res. − 2019. − Vol.148. − P.60-69.

15. *Lister M.* Decomposition of sodium hypochlorite: the catalyzed reaction // Can. J. Chem. − 1956. − Vol.34. − P.479-488.

ВПЛИВ ДОМІШОК НА СТАБІЛЬНІСТЬ НИЗЬКОКОНЦЕНТРОВАНИХ ЕКОЛОГІЧНО ЧИСТИХ РОЗЧИНІВ NaOCl

О. Шмичкова, І. Боровик, Д. Гиренко, П. Давиденко, О. Веліченко

Досліджено синтез гіпохлоритної кислоти з низько-концентрованих хлоридовмісних електролітів на різних оксидних матеріалах за густини анодного струму 50 мА/см². Алмаз, легований бором, платинований титан, металевий титан, допований платиною і паладієм, а також матеріали на основі свинець(IV) оксиду (модифіковані фтором та поверхнево-активними речовинами) виявилися перспективними матеріалами для синтезу гіпохлоритної кислоти під час електролізу. Однак, враховуючи стабільність синтезу окисників під час кумулятивного електролізу, найкращими були титан, модифікований платиною і паладієм, та попередньо оброблений свинець(IV) оксид, що містив ПАР (натрій лауретсульфат). Слід додатково врахувати можливість комбінованого використання електрокаталізаторів для синтезу сильних окисників у режимі реверсу струму в проточних системах, коли із реалізацією газового катода буде утворюватися гідроген пероксид, а на аноді утворюватиметься гіпохлоритна кислота. Придатним матеріалом може бути лише металевий електрокаталізатор, такий як титан, модифікований платиною і паладієм. Кінетика перетворення гіпохлориту, в першу чергу, визначається величиною pH свіжоприготовлених розчинів, температурою та умовами зберігання. На кінетику розкладання гіпохлориту впливає наявність у розчині мікродомішок органічної та неорганічної природи. Мікродомішками, які мають максимально негативний вплив на стабільність розчинів натрію гіпохлориту, є: Co(II), Cu(II), Mg(II), Al(III), $K_3[Fe(CN)_6]$, в меншому ступені це: Ni(II), Fe(III), $K_4[Fe(CN)_6]$. Досліджено вплив хлорату на інгібування дії натрій гіпохлориту як дезінфікуючого засобу. Наявність хлорату у досліджуваному розчині дезінфікуючого засобу призводить до відсутності бактерицидної активності щодо S. aureus та P. aeuruginosa; ріст колоній синьогнійної палички стає більш рясним із збільшенням вмісту хлорату в дезінфікуючому засобі.

Ключові слова: модифікований платинований титан, дезінфікуючий засіб, натрій гіпохлорит, тест-культури, хлорат, мікродомішки.

THE EFFECT OF IMPURITIES ON THE STABILITY OF LOW CONCENTRATED ECO-FRIENDLY SOLUTIONS OF NaOCl

O. Shmychkova [a], I. Borovik [b], D. Girenko [a], P. Davydenko [b], A. Velichenko [a, *]

[a] Ukrainian State University of Chemical Technology, Dnipro, Ukraine

[b] Dnipro State Agrarian and Economic University, Dnipro, Ukraine

[*] e-mail: velichenko@ukr.net

The synthesis of hypochlorous acid from low concentrated chloride-containing electrolytes has been studied on various oxide materials at the anode current density of 50 mA cm⁻². Boron doped diamond, platinized titanium, metallic titanium doped with platinum and palladium and materials based on lead (IV) oxide modified with fluorine and surfactants turned out to be promising for the synthesis of hypochlorous acid by electrolysis. Whereas, given the stability of oxidant synthesis during cumulative electrolysis, titanium modified with platinum and palladium as well as pre-treated lead (IV) oxide containing surfactants (sodium laureth sulfate) was the best. One should additionally take into account the possibility of combined use of electrocatalysts for the synthesis of strong oxidants in the reverse current mode in flow systems, when the implementation of the gas cathode leads to the formation of hydrogen peroxide and hypochlorous acid is formed at the anode. In fact, only a metal electrocatalyst, such as titanium modified with platinum and palladium, can be a suitable material. The kinetics of hypochlorite conversion is primarily determined by the pH value of freshly prepared solutions, temperature and storage conditions. The presence of different organic and inorganic micro-impurities in the solution also affects the kinetics of the hypochlorite salt decomposition. The following micro-impurities show the most negative impact on the stability of sodium hypochlorite solutions: Co(II), Cu(II), Mg(II), Al(III), and $K_3[Fe(CN)_6]$; Ni(II), Fe(III), and $K_4[Fe(CN)_6]$ influence the stability to a lesser extent. The effect of chlorate on the inhibition of sodium hypochlorite activity as a disinfectant has been investigated. The presence of chlorate in the disinfectant solution involved results in the absence of bactericidal activity against S. aureus and P. aeuruginosa. The growth of pseudomonas colonies becomes more abundant with increasing chlorate content in the disinfectant.

Keywords: doped platinized titanium; disinfectant; sodium hypochlorite; test culture; chlorate; micro-impurities.

REFERENCES

1. Schlager N, Weisblatt J, Newton DE. *Chemical compounds*. Detroit: Thomson Gale; 2006. 981 p.

2. Myers RL. *The 100 most important chemical compounds: a reference guide*. Westport: Greenwood Press; 2007. 260 p.

3. Hall MC, Duerschner J, Gilley JE, Schmidt AM, Bartelt-Hunt SL, Snow DD, et al. Antibiotic resistance genes in swine manure slurry as affected by pit additives and facility disinfectants. *Sci Total Environ*. 2021; 761: 143287. doi: 10.1016/j.scitotenv.2020.143287.

4. Byun KH, Han SH, Yoon JW, Park SH, Ha SD. Efficacy of chlorine-based disinfectants (sodium hypochlorite and chlorine dioxide) on Salmonella Enteritidis planktonic cells, biofilms on food contact surfaces and chicken skin. *Food Control*. 2021; 123: 107838. doi: 10.1016/j.foodcont.2020.107838.

5. Sakarya S, Gunay N, Karakulak M, Ozturk B, Ertugrul B. Hypochlorous acid: an ideal wound care agent with powerful microbicidal, antibiofilm, and wound healing potency. *Wounds*. 2014; 26(12): 342-350.

6. Battaglin G, Rosestolato D, Ferro S, De Battisti A. Characterization of IrO_2-SnO_2 films prepared by physical vapor deposition at ambient temperature electrocatalysis. *Electrocatalysis*. 2013; 4: 358-366. doi: 10.1007/s12678-013-0137-2.

7. Su D, Ben W, Strobel BW, Qiang Z. Impacts of wastewater treatment plant upgrades on the distribution and risks of pharmaceuticals in receiving rivers. *J Hazard Mater*. 2021; 406: 124331. doi: 10.1016/j.jhazmat.2020.124331.

8. Miklos DB, Remy C, Jekel M, Linden KG, Drewes JE, Hubner U. Evaluation of advanced oxidation processes for water and wastewater treatment - a critical review. *Water Res*. 2018; 139: 118-131. doi: 10.1016/j.watres.2018.03.042.

9. Kampf G, Todt D, Pfaender S, Steinmann E. Persistence of coronaviruses on inanimate surfaces and their inactivation with biocidal agent. *J Hosp Infect*. 2020; 104: 246-251. doi: 10.1016/j.jhin.2020.01.022.

10. Zhang Y, Zhuang Y, Geng J, Ren X, Xu K, Ding L. Reduction of antibiotic resistance genes in municipal wastewater efыluent by advanced oxidation processes. *Sci Total Environ*. 2016; 550: 184-191. doi: 10.1016/j.scitotenv.2016.01.078.

11. Velichenko A, Luk'yanenko T, Nikolenko N, Shmychkova O, Demchenko P, Gladyshevskii R. Composite electrodes PbO_2-Nafion®. *J Electrochem Soc*. 2020; 167(6): 063501. doi: 10.1149/1945-7111/ab805f.

12. Girenko DV, Gyrenko AA, Nikolenko NV. Potentiometric determination of chlorate impurities in hypochlorite solutions. *Int J Anal Chem*. 2019; 2019: 2360420. doi: 10.1155/2019/2360420.

13. Girenko D, Shmychkova O, Velichenko A. Electrolysis of sodium chloride solutions on Ti/Pt anodes under current reversal conditions. *Voprosy Khimii i Khimicheskoi Tekhnologii*. 2020; (2): 36-43. doi: 10.32434/0321-4095-2020-129-2-36-43.

14. Yu W, Wen Q, Yang J, Xiao K, Zhu Yu, Tao S, et al. Unraveling oxidation behaviors for intracellular and extracellular from different oxidants (HOCl vs. H_2O_2) catalyzed by ferrous iron in waste activated sludge dewatering. *Water Res*. 2019; 148: 60-69. doi: 10.1016/j.watres.2018.10.033.

15. Lister MW. Decomposition of sodium hypochlorite: the catalyzed reaction. *Can J Chem*. 1956; 34(4): 479-488. doi: 10.1139/v56-069.