INTRODUCTION

The human activity associated with the production, use and disposal of industrial water solutions leads to the pollution and degradation of the world water reserves. The annual volumes of industrial water consumption reach 440 billion cubic meters, which far exceeds the consumption of other raw materials and energy resources. At the same time, the stocks and availability of fresh water are steadily decreasing: the concentration of dissolved pesticides, surface active substances, heavy metal ions, etc., is increasing (Mitryasova et al. 2016, Styskal et al. 2016, Kaleta et al. 2017, Karpinski et al. 2018, Koszelnik et al. 2020). Due to the thermodynamic constraints, the purification systems are not capable of returning water to the original state. Therefore, significant volumes of industrial water consumption and effluent discharges are important factors of the anthropogenic loading on the hydrosphere (Pohrebennyk and Petryk 2017, Michel et al. 2020).

In order to reduce the negative impact on the environment, the strategy of rational water consumption should ensure the minimum involvement in the production and economic activities of
human natural mineral resources, which, spreading in the dissolved form in water compounds, create a real threat to the environment. One of the processes borrowed from nature in accordance with these requirements is the electrochemical transformation of substances (Bahir 2012, Bahir et al. 2005). Numerous scientific studies (Goncharuk and Malyarenko 2001, Kulskiy and Strokach 1986, Plutaxi’n et al. 2013) showed that the potential of electrochemical water treatment is far superior to the traditional methods in terms of environmental, economic and qualitative indicators (Huang et al. 2008, Morita et al. 2000, Hsu 2003).

Moreover, electrochemical activation (ECA) allows for the addition of chemical reagents and, with minimal energy consumption, conversion of fresh or slightly mineralized natural water into a high-performance industrial solution with various functional properties (Ichihara et al. 2004, Thorn et al. 2012, Wang et al. 2019).

The influence of the ECA water solutions on biological molecules, in particular proteins, was analyzed (Prilutskiy et al. 2013, Hsu, S.-Y. 2005, Kim et al. 2000), and the efficiency and safety of their use for disinfection in the diffusion department of sugar production was shown (Miroshnikov 2004). Article (Bordun et al. 2013) describes an environmentally safe technology for the modification of activated carbon (AC) surface, designed to change the composition of surface groups for the production of supercapacitors with increased specific capacitances.

The generalization of the results of scientific research presented in the works (Bahir et al. 2005, Bordun and Ptashnyk 2013, Janich et al. 2014, Goncharuk et al. 2005) allows us to evaluate and systematize the influence of the ECA depth on the properties of activated solutions.

Today, the control of ECA process and analysis of the state of the activated solution is performed using such parameters as time, the temperature in the cells of the electrolyzer, pH, oxidation-reduction potential and electrical conductivity of the anolyte and catholyte (Miyashita 2012, Nakamura et al. 2003, Kurtov et al. 2005).

However, the change in these parameters is due to the effect of the electric field on water, it is not universal, and the result of its use to control the ECA depends on the characteristics of the initial solution (Bryanskiy et al. 2011), [26].

The aim of the work was to develop environmentally safe technologies for the production of industrial water solutions using ECA.

**MATERIALS AND METHODS**

The primary reason for changing the characteristics of the water solution during the ECA is the action of the electric field, thus, monitoring of the current strength flowing through the stationary diaphragm electrolyzer at a constant voltage on the electrodes during the ECA can be used as a method for controlling the depth of activation. Thus, articles (Bordun and Ptashnyk 2013, Janich et al. 2014) showed that the character of the curve of change in the current during the activation of distilled (Fig. 1) and tap water (Fig. 2) displays the physical and chemical transformations in activated solutions. Therefore, this method enables to precisely determine the moment of completion of the activation process, necessary for the achievement of certain properties of industrial solutions with a minimum consumption of both substances and energy.

![Fig. 1. Typical variation of current during ECA of distilled water](image)
Scientific studies and industrial applications often assume the application of water solutions with controlled chemical composition which requires a separate study of the ECA process of such solutions, for example, 0.0001 M KCl solution. The dependences of the current, both for the concentration used in the experiment (Fig. 3) and for concentrations up to 0.1–0.2 M, which is the upper limit of the concentrations for which the effects of the ECA are manifested, are the same and differ only in the time of the saturation – it is decreased as the concentration is increased.

In order to study the properties of ECA water solutions and the possibility of formation of environmentally hazardous compounds both during their receipt and storage, the activation process can be divided into several stages. The following key points are distinguished during the activation period of the distilled water (Fig. 1): T1dw corresponds to the beginning of the process, which can be described by the Lingan equation for normal electrolysis, T2dw – moment of time when the current in the electrolyte reaches saturation, and T3dw – moment of time when the current in the electrolyzer begins a periodic oscillation process. The following characteristic points are distinguished in the graph of change in current during the activation of tap water (Fig. 2): T1tw corresponds to the moment when the current in the electrolysis reaches the maximum value, T2tw – moment of time when the current strength in the electrolyzer reaches the minimum value, and T3tw – moment of time when the current in the electrolyzer goes to saturation. The following key points were identified for the graph of changes in current during the activation of water solutions with controlled chemical composition (Fig. 3): T1s corresponds to the moment when the current in the electrolysis reaches the maximum value, T2s – time point corresponding to the point of bend on the curve current, and T3s – moment of time when the current in the electrolyzer goes to saturation. These designations were used to identify the duration of the ECA process and T0tw or T0s correspond to the initial state of tap water or water solution with a controlled chemical composition.

It was established that the maximum number of nonequilibrium charges is present in the solutions at the moment of time T1tw (T1s) as well as the formation of the structure and formation of
stable and metastable products of electrolysis begins. The transfer of dissolved ions into the cells of the electrolyzer and the formation of the fine-dispersed phase of the hardness salts are completed at the moment of time \( T_{2\text{m}} \) as well as the maximum deviation of pH and oxidation-reduction potential from the initial value is observed. At the moment of time \( T_{3\text{m}} \) (\( T_3 \)) the number of stable products of electrolysis in the solutions starts to prevail over the quantity of metastable products and the mixing of the solutions from different cells of the electrolyzer begins at the expense of the diaphragm permeation.

Thus, the control of the ECA depth increases the use efficiency of activated water solutions with minimal energy consumption, makes them competitive both in technological and economic indicators and allows reducing the technogenic burden on the environment due to the refusal of traditional industrial solutions of chemical origin.

RESULTS AND DISCUSSIONS

Since it has been established that the ECA water solutions are characterized by high chemical activity and structural ordering, a number of technologies have been selected for the further testing of the proposed ECA depth control technique, in which at least one of these features can be effectively used.

The traditional methods of postmodification of AC surface for the production of supercapacitors’ electrodes include oxidation of the material in the liquid phase of chemically active substances (sulfuric, nitric acid, ammonium peroxysulfate, etc.), oxidation in the gas phase at elevated temperatures, heat treatment in an inert medium, and the like. Such methods allow increasing the specific capacitance of supercapacitors electrodes, but they are energy and resource intensive as well as require complex and costly waste treatment.

An experimental study was carried out using the AC grades of BAU, Ausfer and Norit Supra with particle size of 45–63 μm as well as ECA water \( \text{KCl} \) solutions with different initial concentrations. The selection of activated solutions samples was carried out for each salt concentration at the time of moment \( T_1, T_2 \) and \( T_3 \) (Fig. 3). The AC samples were placed in each selected solution and held for 6–96 hours.

The dependence of the specific capacitance of the modified AC on the initial concentration of the ECA solution of \( \text{KCl} \) with the constant activation and exposure time is given in Table 1 and the effect of exposure time is presented in Table 2.

The possible reason for changing the specific capacitance of AC is the change in the hydrophobic-hydrophilic properties of its surface which are determined by the composition of oxygen-containing surface groups. For the study of hydrophilicity, various types of AC in ECA were exposed to the solutions providing the maximum capacitance of the electrodes (duration of activation – \( T_2\), exposure time – 12 h, initial concentration of solution 0.001 M). A similar exposure was performed in distilled water and a \( \text{KCl} \) initial solution. The results are shown in the Table 3.

The obtained results testify that after the modification of the ECA solution, the hydrophilicity of AC is significantly increased. Such a change is manifested in the emergence of additional or redistribution of the existing surface groups without the application of acid modifiers used in the traditional technologies and posing a significant threat to the hydrosphere due to large volumes of waste.

The effect of the ECA mixing water on the physical and mechanical properties of gypsum stone (GS) was investigated. The chemical composition of gypsum is non-toxic, made from natural raw materials and the conversion of calcium sulfate bicarbonate allows obtaining a product with a chemical formula laid in a natural mineral. Due to these properties gypsum is an environmentally friendly substance that allows obtaining finished products based on it without changing the cycles of substances in nature. Therefore, in

<table>
<thead>
<tr>
<th>AC type</th>
<th>Specific capacitance, F/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified AC</td>
<td>38.1</td>
</tr>
<tr>
<td>AC after exposure in distilled water</td>
<td>41.5</td>
</tr>
<tr>
<td>AC after exposure in 0.00007 M KCl solution</td>
<td>42.7</td>
</tr>
<tr>
<td>AC after exposure in ECA water solution of 0.00007 M KCl</td>
<td>46.0</td>
</tr>
<tr>
<td>AC after exposure in 0.001 M KCl solution</td>
<td>42.7</td>
</tr>
<tr>
<td>AC after exposure in ECA water solution of 0.001 M KCl</td>
<td>47.9</td>
</tr>
<tr>
<td>AC after exposure in ECA water solution of 0.003 M KCl</td>
<td>42.4</td>
</tr>
<tr>
<td>AC after exposure in ECA water solution of 0.003 M KCl</td>
<td>46.4</td>
</tr>
</tbody>
</table>

**Note:** ECA was performed before the time point \( t \text{ks2} \), and the exposure time is 12 hours in all cases.
the context of the struggle to restore the ecological balance of the natural and man-made systems, the production of gypsum and products based on them has increased significantly.

However, in order to improve the economic performance of gypsum, various modifiers and plasticizers are used to increase the strength of the final product, to accelerate the timing of achievement of hardness, to reduce the rates of raw material consumption, and etc. In order to achieve this, the use of such environmentally hazardous substances as a mixture of sodium salts of products of polycondensation with formaldehyde sulfated aromatic carbohydrates obtained during catalytic cracking and pyrolysis of petroleum products, and even the simplest of existing modifiers – citric acid, leaves 1.4 tons of waste of cetogypsum per 1 ton of produced acid.

Since during the ECA there is a series of competing processes that cause changes in the various properties of GS, it is advisable to investigate the effect of mixing water obtained at different stages of the ECA and to determine the optimal duration of the process. Gypsum plaster G-5 N II was used for research. As mixing water initial tap water ($T_{0_{tw}}$) and ECA solution, selected in $T_{1_{tw}}$ and $T_{2_{tw}}$, and in the middle of the time interval between $T_{1_{tw}}$ and $T_{2_{tw}}$, (Fig. 2) were used.

It was established that both anolyte and catholyte change the time of solidification of gypsum (Fig. 4). Moreover, the solidification begins and ends the fastest time for the anolyte, and for the catholyte, selected in the middle of the time interval between $T_{1_{tw}}$ and $T_{2_{tw}}$. The greatest time interval between the beginning and end of solidification (4.5 min) was recorded in the study of the sample mixed with catholyte selected in $T_{2_{tw}}$.

The averaged results of the tests of gypsum specimens-balks in the bend are shown in Fig. 5.a, and when compressed – in Fig. 5.b. The best result was obtained by mixing construction gypsum with a catholyte, selected in $T_{2_{tw}}$ – bending strength increased by 31 %, and under compression – by 29 %.

The processes leading to the hardening of gypsum are based on their ability to form supersaturated solutions as a result of the interaction with water. For gypsum plaster, which mainly contains β-modification of gypsum hemihydrate ($\beta$-CaSO$_4$·0.5H$_2$O), this means that its water solubility is greater than the solubility of the product of the reaction of hydration – gypsum dihydrate. Such solutions oversaturated with respect to the gypsum dihydrate are unstable and transform into a more stable state by crystallization of CaSO$_4$·2H$_2$O dihydrate. Consequently, the process of crystallization of gypsum will be influenced by both the chemical composition of water and the presence of nano- and submicron sizes inclusions which act as crystallization centers. These centers may be the CaCO$_3$ particles that are formed in a catholyte from hardness salts during ECA tap water. Moreover, as shown in (Bordun et

<table>
<thead>
<tr>
<th>AC type</th>
<th>Specific capacitance, F/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified AC</td>
<td>38.1</td>
</tr>
<tr>
<td>AC after exposure for 6 hours</td>
<td>43.7</td>
</tr>
<tr>
<td>AC after exposure for 12 hours</td>
<td>47.9</td>
</tr>
<tr>
<td>AC after exposure for 24 hours</td>
<td>42.6</td>
</tr>
</tbody>
</table>

**Note:** The initial concentration of water KCl solution was 0.001 M in all cases; ECA lasted until the moment of time $T_{2_{tw}}$.

**Table 2.** Dependence of specific capacitance AC on the time of exposure in ECA anolyte

<table>
<thead>
<tr>
<th>AC type</th>
<th>Hydrophilic surface, %</th>
<th>Hydrophobic surface, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAU</td>
<td>46</td>
<td>54</td>
</tr>
<tr>
<td>AC after exposure in KCl solution</td>
<td>41</td>
<td>59</td>
</tr>
<tr>
<td>AC after exposure in ECA KCl solution</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>Norit Supra</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial AC</td>
<td>39</td>
<td>61</td>
</tr>
<tr>
<td>AC after exposure in KCl solution</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td>AC after exposure in ECA KCl solution</td>
<td>61</td>
<td>39</td>
</tr>
<tr>
<td>Ausfer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial AC</td>
<td>12</td>
<td>88</td>
</tr>
<tr>
<td>AC after exposure in KCl solution</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>AC after exposure in ECA KCl solution</td>
<td>16</td>
<td>84</td>
</tr>
</tbody>
</table>

**Note:** ECA solution anolyte after ECA before time $T_{2_{tw}}$ is used.
Fig. 4. Terms of solidification of gypsum binder, mixed with anolyte (a) and catholyte (b) ECA of tap water

Fig. 5. Bending strength (a) and compression (b) samples of gypsum stone mixed with ECA tap water
al. 2013) in $T_{2_{\text{tw}}}$, their number is maximum, since it is established that, with further activation due to the good permeability of the diaphragm, anolyte enters from the anode chamber into the cathode and causes the dissolution of CaCO$_3$.

In order to check the influence of the dispersed phase of CaCO$_3$ in the mixing water on the mechanical properties of the GS, the catholyte was selected for activation to $T_{2_{\text{tw}}}$. A portion of the solution was filtered through a “blue ribbon” filter with a pore size of 2–4 microns. The changes in the mechanical properties of the GS are shown in Fig. 6. It shows a significant influence of the dispersed phase of CaCO$_3$ on the physical and mechanical properties of GS. In the formation of CaCO$_3$, an important role is played by calcium hydroxide, which is the regulator of terms of solidification. Consequently, the synergy of the effects of carbonate and calcium hydroxide causes a change in the solidification durability and mechanical properties of the GS which allows refusing the use of two types of chemical modifiers – regulators of solidification terms and hardening. Thus, the control of the activation depth determines the properties of the final product and provides the optimal correlation of the products of ECA (Ca(OH)$_2$, CaCO$_3$).

The interaction of the ECA of distilled water and protein molecules was investigated by wedge-shaped dehydration method on model solutions which according to the composition correspond to the serum of human blood (Shabalin and 2001). A picture of the facade of a model solution based on distilled water is shown in Fig. 7.a, and on the basis of the ECA water – in Fig. 7.b – 7.d. For the facies with distilled water a typical picture...

![Graph](image1)

**Fig. 6.** Strength of gypsum stone, mixed with ECA tap water

![Images](image2)

**Fig. 7.** Facies of a model biological solution based on distilled water (a) and anolyte, selected at time $T_{1_{\text{dw}}}$ (b), $T_{2_{\text{dw}}}$ (c), $T_{3_{\text{dw}}}$ (d)
is obtained – the protein roll is placed on the edge and inside the protein-salt zone. The facies based on the ECA of distilled water differ significantly in the protein-salt region. From Fig. 7.b – 7.d it is evident that, along with dendrites, the crystals of salt of the correct form are formed. That is, replacing distilled water with the ECA water leads to a qualitatively new formation in facies.

The structural changes in the protein molecule can be explained by the changes in the pH of the activated solution. Some of the protein’s characteristics reach extreme values with the approach of the solution pH to the isoelectric point which is 4.7 for the albumin. In the facies obtained on the basis of the ECA solutions, where the pH varies from 5.39 for anolyte to 9.31 for a catholyte, the same kind of crystalline inclusions are observed. Consequently, the pH-dependent conformational changes of protein molecules do not affect their formation.

The analysis of the causes of proper crystals formation that arise when drying the protein-salt solutions based on the ECA water allows us to conclude that the main reason for this is the modification of the spatial structure of water molecule associatives – clusters, which, combined with the increased reactivity of ECA solutions, enables the use of activated solutions for environmentally safe influence on the biological processes of biological objects.

The basis of the ECA solutions use for disinfection is that for the normal life of various microorganisms, pH and the oxidative-reduction potential of the environment in which they are located play an important role. In a neutral environment, the existence of microbes is possible in a sufficiently wide range of values of the oxidation-reduction potential but as a result of a relatively small shift of pH to the alkaline or acidic side, this range substantially decreases. For each microorganism, there is a certain optimum of pH and oxidation-reduction potential as well as their critical values. The reason for this is that in all the biological processes associated with cell activity, catalysts (enzymes) play an important role. The physiological processes of the cell depend heavily on the activity of the enzymes; thus, any factor that affects the enzymes will have a direct effect on the cell as a whole. The mechanism of destruction of the microorganism ECA solutions is to create stable compounds with active centers of enzymes, which leads to the “starvation” and death of microorganism cells. Human and other higher organisms produce and actively use a number of high-level antioxidants for their functioning; therefore, their somatic cells possess a powerful system of antioxidant protection that is not inherent to microorganisms which makes the ECA disinfectant solutions safe for human and the environment.

The effectiveness of using disinfectants on the basis of ECO anolyte of sodium chloride solution with an initial concentration of 0.01 M and duration of activation of T3, on the examples: Escherichia coli, Candida pseudotropicalis, Aspergillus niger, Geotrichum candidum. The results of microbiological studies are given in Table 4.

If Escherichia coli is used as a standard indicator, then the fight against the rest of the microorganisms is a real technological problem of sugar production, which is usually solved using the chemical reactants of the II–III classes of danger (Kulskiy and Strokach 1986, Hsu 2005, Kim et al. 2000, Bugaenko and Tuzhilkin 2007). Thus, for the processing of 1000 tons of sugar beet, more than 150 kg of formalin, 150 kg of bleach, 200 kg of sodium hypochlorite and up to 30 kg of antibiotics and foam extinguishers are used. Taking into account significant volumes of sugar production, even a slight decrease in the use of the above-mentioned disinfectants will have a positive effect on the environment and public health. More detailed results of approbation of this method in the production conditions are presented in

<table>
<thead>
<tr>
<th>Microorganisms</th>
<th>ECA duration</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>T1 s</td>
</tr>
<tr>
<td>Escherichia coli</td>
<td>low expressed</td>
</tr>
<tr>
<td>Bacillus subtilis</td>
<td>not observed</td>
</tr>
<tr>
<td>Pseudomonas denitrificans</td>
<td>not observed</td>
</tr>
<tr>
<td>Candida pseudotropicalis</td>
<td>not observed</td>
</tr>
<tr>
<td>Aspergillus niger</td>
<td>not observed</td>
</tr>
<tr>
<td>Geotrichum candidum</td>
<td>low expressed</td>
</tr>
</tbody>
</table>

Table 4. Disinfectant effect of ECA solutions of sodium chloride
the article (Bordun et al. 2014). Consequently, the ECA water solutions can be effectively used to solve a number of actual problems that exist in the sugar production. Such decisions will be characterized by high environmental friendliness, low cost of equipment and solutions themselves, as well as simplicity of implementation in the existing production schemes.

CONCLUSIONS

The technology of increasing the capacitance of electrochemical supercapacitors based on the modification of the surface of activated carbon by low-mineralized ECA by the solutions of potassium chloride was developed. It ensures the increasing of the hydrophilic volume of carbon powder of the BAU brand in 2.16 times, Norit Supra – 1.52 times and brand Ausfer – in 1.3 times. This allows increasing the specific capacitance of the received electrodes which are made from such carbon by 15–25 % and to refuse to use traditional ecologically dangerous methods of modification of the carbon surface.

The technological scheme of the use of a catholyte as a mixing water for gypsum on the basis of a definite optimal ratio of the products of the ECA (Ca(OH)₂, CaCO₃) is proposed, which provides both the regulation of the solidification terms of the gypsum dough and the processes of gypsum dihydrate crystallization to obtain a stone with increased durability. This technology makes it possible to effectively replace the regulators of solidification terms and other gypsum modifiers of chemical origin due to the growth of the strength of gypsum stone with bending by 31%, and with compression – by 29%.

The mechanisms of interaction of the activated water solutions with protein molecules and the technology of obtaining an ecologically safe disinfectant based on the ECA solutions of sodium chloride were investigated. It was established that the main reason for this interaction is the structural changes in the resulting water solutions due to the action of the electric field. A disinfectant effect of anolyte was confirmed on the example of Escherichia coli, Candida pseudotropicalis, Aspergillus niger, Geotrichum candidum. It was shown that such a disinfectant will be characterized by environmental friendliness and safety for higher organisms, low cost of equipment and solutions themselves, simplicity of implementation in the existing technological schemes.

Acknowledgment

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