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WATER PREPARATION USING ELECTROCHEMICAL PROCESS

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ABSTRACT

In many technological processes the quality of water is determined by iron ion concentration and hardness.
The effect of electrolysis and electrodialysis processes on iron and calcium ion concentration and the development of microorganisms in water were studied in this work. Experiments were conducted under laboratory conditions using model solutions containing iron and calcium ions. Bacteria Pseudomonas fluorescens were used as model organism for disinfection experiments.
In this work it was found that the solution electrolysis with successive filtration through quartz sand reduces total iron ion concentration 40 - 50 times. If the current intensity applied to the electrodialysis cell is increased, the total amount of iron ion concentration reduced in the solution and the specific work of the process increases.
It was found that calcium and total iron ion concentration in $FeSO_4$ and $CaCO_3$ containing solution decreased during electrodialysis. Rapid concentration decrease is observed at the beginning of the process.
Electrolysis (to remove iron) of water solution containing at least 1 mmol/L of chlorine ions also significantly improves the microbiological situation. No bacteria Pseudomonas fluorescens colony forming unit development in electrolyzed water within five days was found. Using water electrodialysis it is possible to efficiently desalinate solution. The development intensity of bacteria Pseudomonas fluorescens colony forming units in desalinated water is significantly reduced (as far as 1500 times).

Keywords: Demineralization, calcium and iron ions, Pseudomonas fluorescens.

1. INTRODUCTION

In many technological processes the quality of water is of utmost importance. Water in Latvia is usually characterized by high mineral content, hardness and presence of iron ions (Sabiedrības Veselības Aģentūra 2008); this may cause deposition of various substances on surfaces of pipes and equipment (Liu *et al.* 2002). Water should not be corrosive and should not contain organic or inorganic substances that promote the growth of biofilms. The growth of biofilms changes various physical (smell, taste, colour), chemical and biological (biomass and the amount of microorganisms increase) properties. The growth of biofilms within water supply system promotes partial blockage of the pipes (Hallam *et al.* 2001).
Several methods of water treatment are used: filtration, precipitation, adsorption, photocatalysis, chemical disinfection, etc. Electrochemical methods have a considerable potential - electrolysis (EL) and electrodialysis (ED); these methods can be combined with other water treatment methods (Feng *et al.* 2004, Watts *et al.* 2008). There is not enough research that explores the possibilities to use these methods to decrease hardness, iron ion content and the amount of substances that are necessary for development of microorganisms. Additionally during EL disinfectant substances that lessen the development of microorganisms may be formed (Drees *et al.* 2003, Reimanis *et al.* 2008, Reimanis *et al.* 2009).
The aim of this work was to research the influence of EL and ED on iron and calcium ion concentration and the development of microorganisms in water. The experiments were conducted under laboratory conditions using model solutions containing iron and calcium ions. The influence of water treatment methods on the development of microorganisms was investigated using bacteria Pseudomonas fluorescens as model microorganisms.

2. MATERIALS AND METHODS

Model solutions. The model solution containing bivalent iron ions with concentrations 0 – 1.5 mg/L was obtained by dissolving $FeSO_4 \cdot 7H_2O$ in water; such concentrations are characteristic of waters in Latvia (Sabiedrības Veselības Aģentūra 2008).
The model solution containing calcium ions was obtained by dissolving 0.596 mmol/L $CaCO_3$ in water; this corresponds to water of medium hardness.
To assess the influence of treatment on the intensity of propagation of microorganisms in water a culture medium and conditions beneficial for the development of microorganisms were used (Lehtola *et al.* 1999). At first a stock solution containing 4.55 g/L $(NH_4)_2SO_4$, 0.2 g/L KH_2PO_4, 0.1 g/L $MgSO_4{\cdot}7H_2O$, 0.1 g/L $CaCl_2{\cdot}2H_2O$, 0.1 g/L NaCl, 2.27 g/L $CH_3COONa{\cdot}3H_2O$ was made from distilled water. This solution then was diluted with distilled water (1:1000) and treated in autoclave for 45 min in 122°C. Before use prepared solution was cooled to room temperature.

Cultivation of model microorganisms. *Pseudomonas fluorescens* are bacteria common in water environment and actively form biofilms. Bacteria used in these experiments were obtained from Microorganism Culture Collection of Latvia (University of Latvia). Bacteria were cultivated on R2A culture medium (LAB M, United Kingdom) for 2 days in 22 ± 0.5°C.

Suspensions of bacteria. A small amount of cultivated *Pseudomonas fluorescens* were transferred into sterile distilled water and suspended.

Samples for microorganism development research. Model solutions were poured into sterile containers and bacteria suspension was added using micropipette. Then containers were covered with aluminium foil and incubated at 22 ± 0.5°C. The amount of bacteria in the solution was determined using colony forming unit (CFU) number.

Determination of CFU number. The changes in development intensity of microorganisms were characterized using CFU number. CFU number was determined using R2A culture medium (LAB M, United Kingdom) and incubation at 20 ± 2^{o}C temperature for 48h (Reasoner and Geldrich 1985).

Iron ion concentration was determined using spectrophotometric method for determining iron ion concentration (LVS ISO 6332:2000).

Calcium ion concentration was determined using volumetric method for determining calcium ion concentration (LVS ISO 6059:1984).

Experimental procedure. EL of water was done in specially made electrolysis cell for water treatment under dynamic conditions with flow velocity 0.01 m/s (fig.1.).

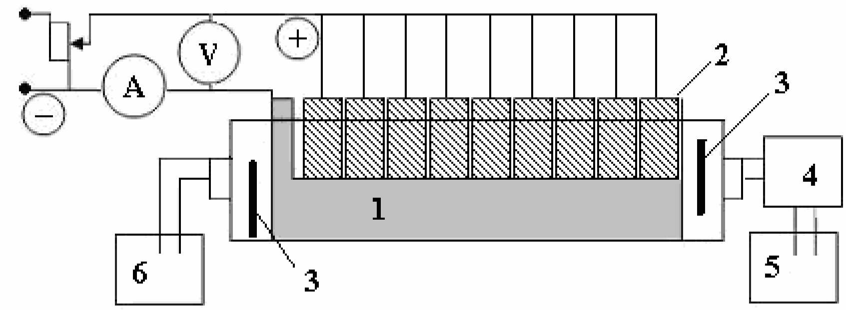

Fig.1. Experimental scheme for EL under dynamic conditions: 1 – stainless steel cathode, 2 – Ti_nO_{2n-1} containing ceramic anodes, 3 – partitions, 4 – pump, 5 – bowl with a stock solution, 6 – bowl with EL solutions

The volume of EL cell is 126 cm^3. 9 anodes containing Ti_nO_{2n-1} with 112 cm^2 large total surface area and a stainless steel cathode with 190 cm^2 large surface area. A rectifier SGS, BCA-5A-K (0 – 65V, 0 – 12 A) was used as a current source.
Model solutions containing iron ions after EL treatment were filtered trough a column of quartz sand (particle size 0.5 – 1.5 mm).
Water treatment with ED was done in a specially constructed ED cell with four chambers. Solution was pumped into lower part of chambers using peristaltic pumps. Current intensity was measured with a ammeter connected with series circuit; voltage was measured with voltmeter connected with parallel circuit. The process was conducted under dynamic conditions and in circulating mode using 25 V voltage (fig.21.).

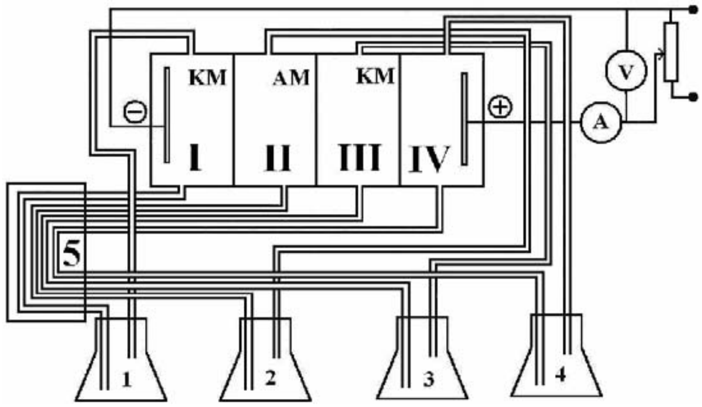

Fig.2. Experimental scheme for ED under dynamic conditions with recirculation: 1, 2, 3, 4 – bowls, 5 – peristaltic pumps; KM – cation-exchange membrane, AM – anion exchange membrane, A – ammeter, V – voltmeter, I, II, III, IV – chambers

Samples for analysis were taken from the third chamber of ED cell; cell construction ensures desalination of the solution in chambers 2 and 3 and saturation of solution in 1 and 4 chambers.

3. RESULTS AND DISCUSSION

Bivalent (Fe^{2+}) and trivalent (Fe^{3+}) iron ions in water can exist in various forms: soluted, suspended (colloids, precipitates and microorganism waste products) and as part of organic and inorganic compounds (Ghosh *et al.* 2008). There exist several methods for iron removal (Das *et al.* 2007); most are based on Fe^{2+} oxidation in presence of air (oxygen) or different oxidizing agent; the precipitated nonsoluble Fe^{3+} compounds then are filtered:

$$4Fe^{2+} + 3O_2 + 6H_2O \rightarrow \mathbf{4Fe(OH)_3}\downarrow \quad (1)$$

There is a considerable oxidation of Fe^{2+} to Fe^{3+} with oxygen soluted in water if the water containing iron ions is filtered through quartz sand (fig.3.). As the water flows through the sand a layer of iron oxides and hydroxides may form on quartz particles; this layer catalyzes oxidation processes of Fe^{2+} ions.

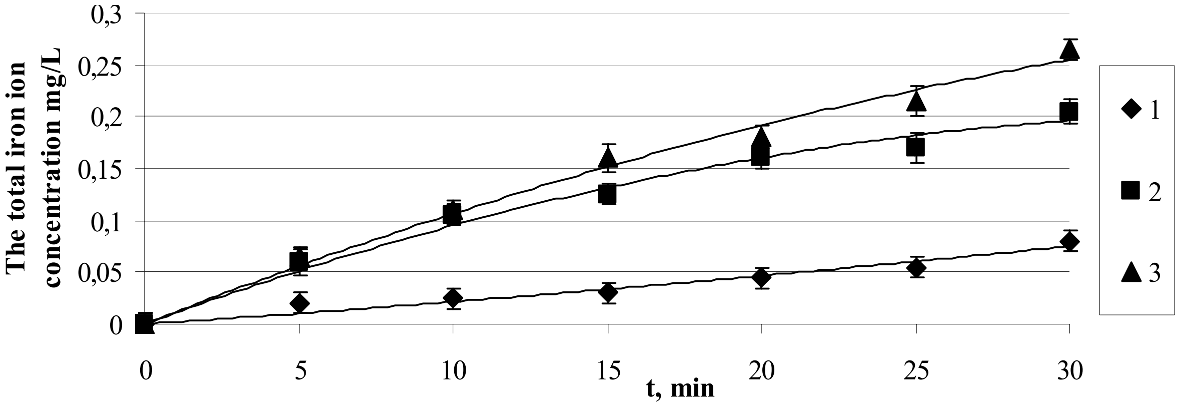

Fig.3. The total iron ion concentration change in the filtrate depending on the filtration time with different iron concentrations in the starting solution: 1 – 0.5 mg/L, 2 – 1.0 mg/L, 3 – 1.5 mg/L

As it can be seen in fig.3., as the filtration period is increased, the total amount of iron ions in the filtrate increases. This tendency is more pronounced if the concentration of iron ions in initial solution is increased. This can be explained by the gradual saturation of the filtering medium.

The oxidation of ions may be intensified by EL. Oxygen that is released on anode in the EL process may function as an oxidant. EL of the solution and the successive filtration can essentially reduce the amount of iron ions in the final solution (fig.4.).

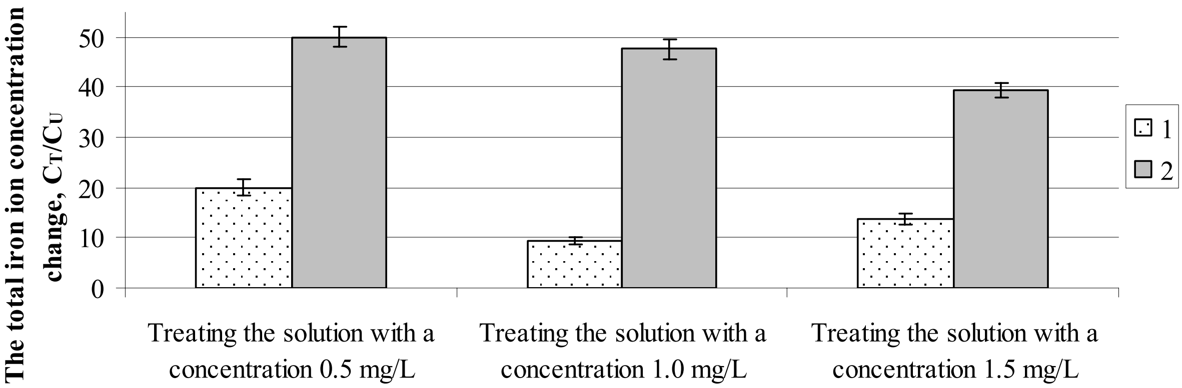

Fig.4. The total iron ion concentration change in the investigated solutions: 1 – filtration through quartz sand, 2 – electrolysis followed by filtration through quartz sand. Filtration time 10 minutes, C_T, C_U - iron concentrations in the treated and untreated solution, mg/L

As it can be seen in fig.4., filtration through quartz sand decreases the amount of iron ions 20 times, but EL with successive filtration through quartz sand decreases the total amount of iron ion concentration 40 – 50 times. This can be explained by saturation of water with oxygen during EL process; only a part of the soluted oxygen is immediately used to oxidize iron ions. During filtration through quartz sand the increased oxygen concentration promotes the oxidation of iron ions. If the iron ion concentration is increased in initial solution, the change in iron ion concentration in EL process is less pronounced.

The efficiency of the of the EL process depending on the current can be characterized by specific work required by the process:

$$A = I \cdot U \cdot t / \Delta m, \quad (1)$$

I – current intensity (A), U – current voltage (V), t – time (s), Δm the amount of the released ion (mg; mmol).

As the total amount of iron ion concentration in initial solution is increased, the specific work required by EL process decreases (fig.5.).

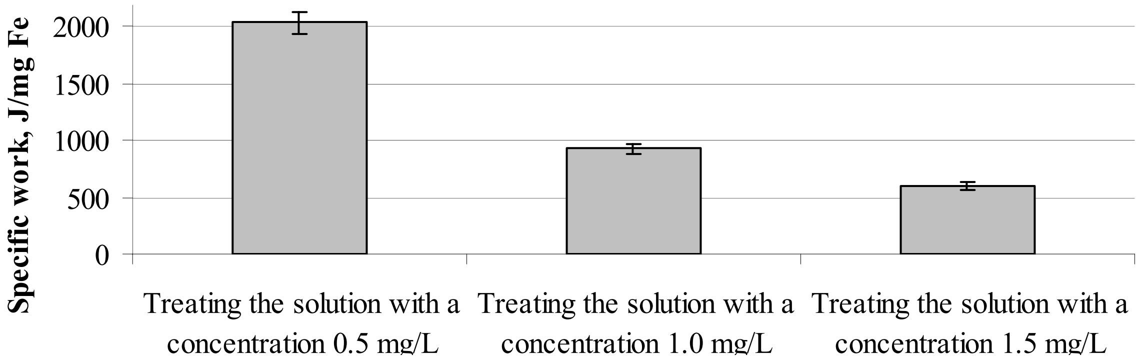

Fig.5. Specific work for total iron concentration reduction by electrolysis from current

It is important to clarify the influence of current intensity on the decrease of iron ion concentration in EL process. If the current intensity is increased, more oxygen is released on anode; this intensifies the oxidation processes and the decrease of total iron ion concentration in electrolysed solution (fig.6.). At the same time the specific work required by the process increases.

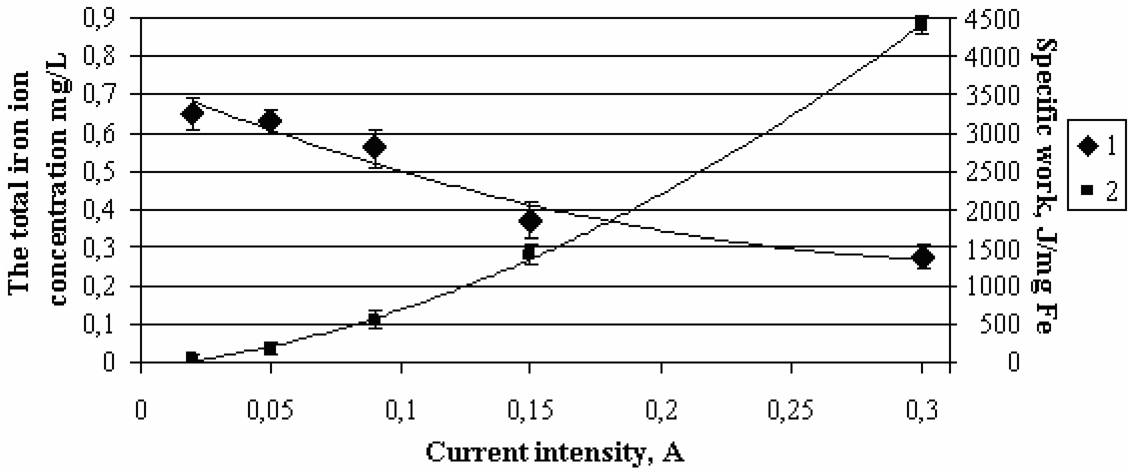

Fig.6. Total iron ion concentration change and specific work change depending on the current intensity of the electrolysis process: 1 – total iron ion concentration changes, 2 – Specific work for total iron concentration reduction. Total iron concentration in the starting solution – 1.5 mg/L. Current 0.09 A

There is interest in water electrodialysis, because ED could not only decrease total iron ion concentration, but also decrease water hardness (Kabay *et al.* 2002).

If $CaCO_3$ and $FeSO_4$ containing solutions are ED with recirculation conditions using 25V both iron and calcium ion concentration decreases if the treatment period is increased (fig.7.) in chamber 3 of the ED cell.

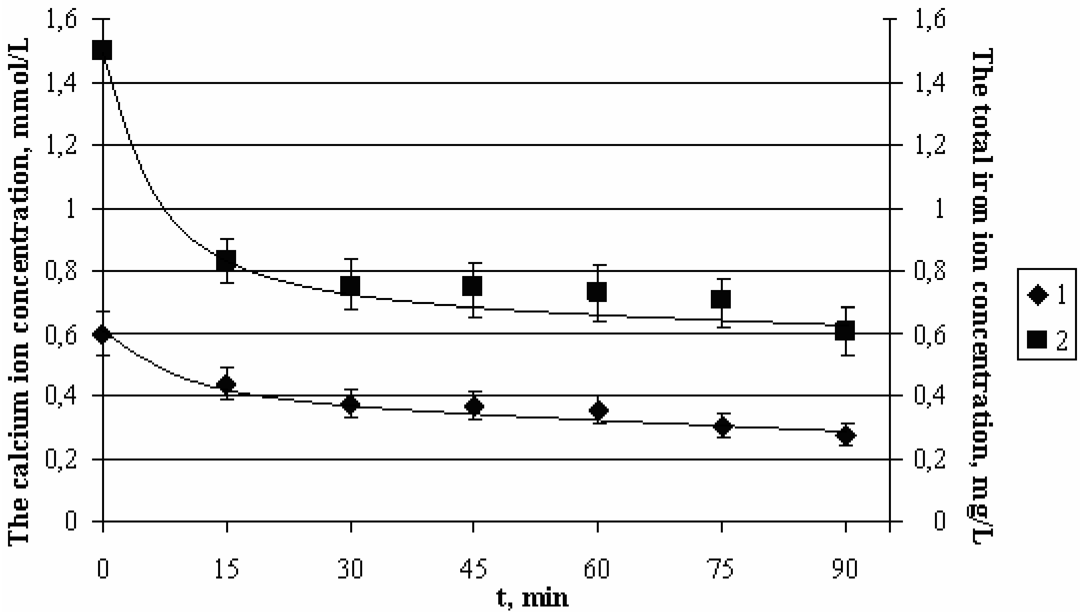

Fig.7. Change of calcium ion and total iron ion concentration during the ED process , with 25 V high voltage: 1 - calcium ions, 2 – iron ions

During the process concentration of Ca^{2+} ions decreases 2.2 times and the total iron ion concentration decreases 2.5 times. The most rapid changes are observed in the beginning of the process.
The specific work depending on the current for ED process was determined in the same manner as for EL process. As it can be seen in fig.8., as the time of the process increases, the specific work also increases.

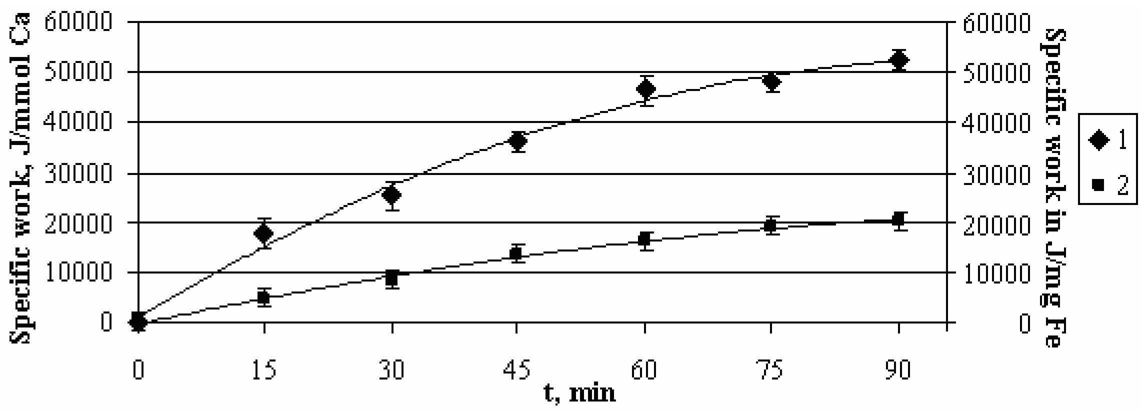

Fig.8. Specific work changes on electrodialysis process from the process time: 1 – calcium ion case, 2 – iron ion case. ED – circuit conditions with 25 V high voltage

In some works (Reimanis *et al.* 2008, Reimanis *et al.* 2009) it was observed that if the water is treated with electrolysis using Ti_nO_{2n-1} containing ceramic anodes there is a marked decrease in the ability of microorganisms to proliferate. This was explained by chlorine being formed during EL process; chlorine has bactericidal properties. The development of microorganisms can be lessened by reducing the amount of nutrients in water; this reduces the increase of total mass of microorganisms (Kapellos *et al.* 2007, Chu *et al.* 2005). In this work the effect of EL and ED under dynamic conditions on the ability of microorganisms to proliferate. A model solution containing culture medium for bacteria *Pseudomonas fluorescens*, Fe^{2+} ions (as $FeSO_4$) and chorine ions was treated with ED and EL. The electrolysed solution contained 1.5 mg/L iron ions and 1 mmol/L chlorine ions. The influence of ED was determined by treating model solution in electrodialysis apparatus for 15 min in circulation mode (fig.9.).

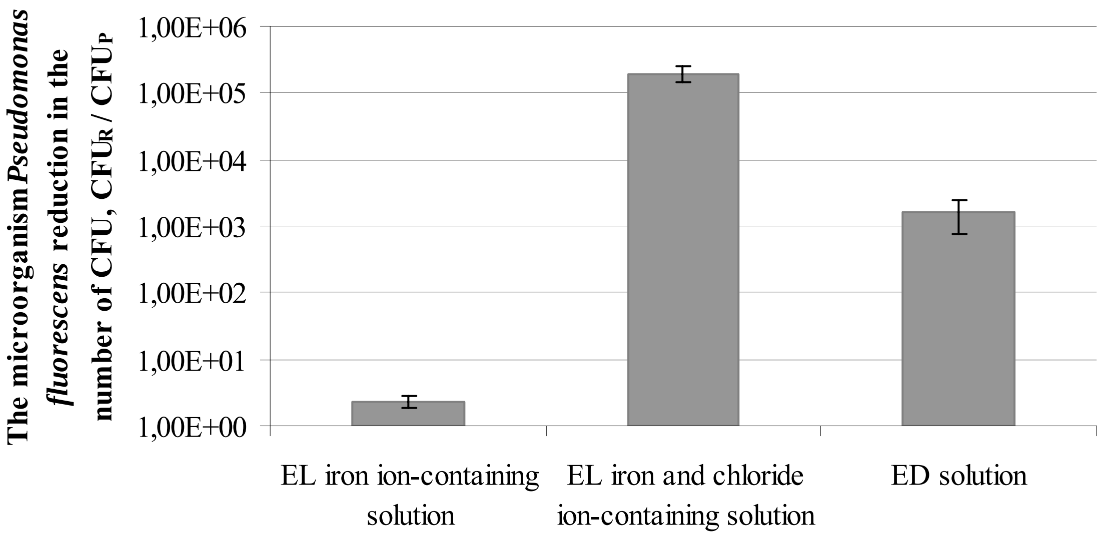

Fig.9. Microorganism *Pseudomonas fluorescens* CFU change after treatment (raw/processed)

As it can be seen in fig.9. if a model solution does not contain chlorine ions, CFU number of *Pseudomonas fluorescens* is nearly constant; if chlorine ions are added to model solution, there is a very marked change in CFU number. In the solution treated with electrodialysis after five days the CFU number is reduced more than 100 000 times – practically equals zero. It was observed that if 0,09 A current is used up to 1 mg/L chlorine can be released, which is enough to disinfect water. A marked decrease of microorganism growth is observed in solution treated with ED. In solution treated with ED after five days the CFU number has decreased for more that 1500 times. This can be explained by reduction of nutrient amount necessary for microorganism growth in the desalinated water.

4. CONCLUSION

1. Electrolysis of water under dynamic conditions and successive filtration substantially reduces the amount of iron ions in the solution. Specific work decreases if the concentration of iron ions in the initial solution is increased; if the current intensity is increased, the amount of iron ions is reduced, but the specific work of the process increases.
2. Iron removal using electrolysis method significantly improves microbiological condition of the treated water if it contains at least 1mmol/L of chlorine ions. In water treated with electrodialysis during five days there is no development of colony forming units of bacteria *Pseudomonas fluorescens*.
3. It is possible to efficiently desalinate solution. In the desalinated water there is a marked decrease (up to 1500 times) in intensity of development of colony forming units of bacteria *Pseudomonas fluorescens*.

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