Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20125

62 (2017) 155–160
February

Countercurrent electrophoretic water purification from ionic and electrically charged colloidal admixtures

Leonid N. Moskvin*, Nina M. Yakimova

Saint-Petersburg State University, The Institute of Chemistry, Saint-Petersburg, Russia, emails: moskvinln@yandex.ru (L.N. Moskvin), yakimovam@yandex.ru (N.M. Yakimova)

Received 25 February 2016; Accepted 1 August 2016

ABSTRACT

As an alternative to the ion-exchange deionization, the new membrane method of fine water purification from electrically charged admixtures based on countercurrent electrophoresis has been suggested. The countercurrent electrophoresis was carried out in the galvanic mode providing a constant rate of ions transfer in a water flow filtered through a porous membrane. The rate of electrophoretic transfer of ions in the membrane pores exceeds the rate of their movement with a hydrodynamic flow. The experimental data on the water impurity composition given by the proposed method confirmed the theoretical assumptions. Being prepared by the suggested method, water is free from soluble organic admixtures that can appear during the ion-exchange deionization and, with relation to the content of inorganic admixtures, is comparable with and even better than water subjected to ion-exchange deionization.

Keywords: Countercurrent; Electrophoresis; High-purity water; Purification

1. Introduction

High-purity water (HPW) is the most demanded solvent both in the practice of chemical analyses and research work and in chemical technologies; however, up to the present, the ion-exchange deionization [1] was the only method applied for its preparation, except for a shot taken by an the author of this paper to break the monopoly of this method, using the effect of water electromigration through a porous membrane [2]. Therefore, the development of the methods of obtaining HPW is still actual. Recently, the new method of the water deionization using a flow-through capacitor has been reported [3]. The flow-through capacitor includes charge barriers, which are used as ion-exchange membranes [4]. The essence of these new water purification methods has attracted the attention of a number of researchers [5–8]. The first flow capacitor used porous carbon and graphite fabrics as electrodes; however, later such most recent materials as carbon nanotubes and graphene gained the main attention [7]. Both the initial and the improved versions of the proposed methods are considered first in terms of the possibilities of their application for water desalination. Obtaining HPW by these methods has not been discussed, as the ion-exchange is still the non-alternative method of water deionization. However, ion-exchange resins on the one hand provide water purification from ionic admixtures and on the other are themselves sources of water contamination with products of their destruction such as organic sulfo-acids and quaternary ammonium bases.

This problem can be solved by the improvement of quality of ion-exchange resins [9] or by searching for alternative methods of water purification. This article is devoted to the development of a new membrane separation method allowing the problem of preparative HPW obtaining to be solved.

2. Materials and methods

To develop the electrical filtration technique, we used Millipore (USA) cellulose acetate membranes with pore diameters of 0.8 and 1.2 μm and a total porosity of 75%,

---

* Corresponding author.

and also porous polytetrafluoroethylene membranes manufactured by proprietary technology, with the average pore radius of 20–50 μm, were used.

An IPE-600-06 (Russia) device was used as a power supply capable of operating in the galvanic mode. Nuclear-grade purity ion-exchange resins cationite KU-2-8chs and anionite AV 17-8chs (Russia) and anionite Dowex Monosphere 550 NC and cationite Dowex Monosphere 650 CN (USA) were used in studying quality of water produced by the ion-exchange deionization. The absorption spectra of aqueous extracts of ion-exchangers were taken on a Shimadzu UV-2550 spectrophotometer. For experimental verification of the proposed scheme of water purification, we used solutions of salts dissociated into ions differing in mobility as much as possible. The cations selected ions were sodium and cesium ions labeled by radioactive ^{137}Cs and ^{22}Na isotopes were selected as reference cations. As reference anions with minimal mobility, picrate ions were selected. Concentrations of sodium and cesium ions were determined radiometrically and those of picrate ions spectrophotometrically. When checking quality of final water produced by the proposed method, metal admixtures were preliminary preconcentrated by electroosmosis [10] and determined by atomic-absorption spectroscopy using a Shimudzu FF-7700 spectrometer. The concentration of chloride ions was determined by ion chromatography on a Stayer A Aquilon ion chromatograph (Russia).

3. Results and discussion

3.1. Experimental verification of the level of HPW contamination by ionite destruction products

Research works aimed to develop the alternative method of fine water purification were preceded by experimental verification of the level of HPW contamination with destruction products of ion-exchangers in the water deionized by ion-exchange using a mixed layer of the Russian-made ion-exchange resins (KU-2-8chs and AB-17-8chs) of nuclear-grade purity.

The level of contamination with soluble organic admixtures (SOA) is 20 ± 10 μg/L [2]. The similarity of structure and technology of the synthesis of strongly acidic cationites and strongly basic anionites of various manufacturers suggests that the level of contamination with SOA given above is typical for water produced by the ion-exchange ionization method irrespective of the ionites in use. This assumption was confirmed by the data of the parallel analyses of aqueous extracts from the above-mentioned ionites and from Dowex Monosphere 550 NC and Dowex Monosphere 650 CN ionites. Absorption spectra of the extracts obtained from various ionites are given in Fig. 1, the spectra corresponding to the same time of extraction (48 h) and the same ionite-water volume ratio (1:3).

The dry residues obtained by evaporating equal volumes of the extracts areal so similar as to their mass (Table 1).

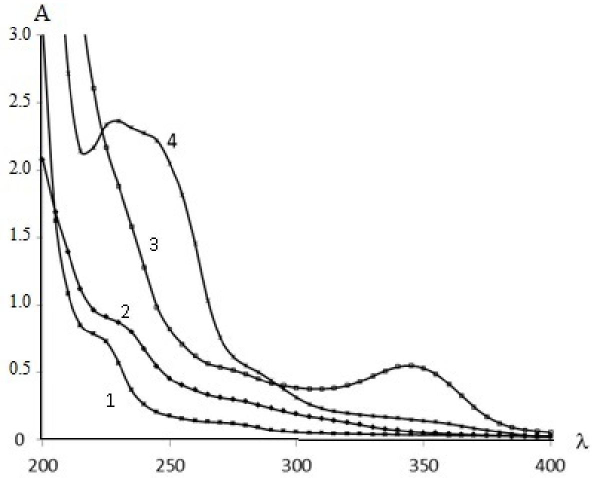

Fig. 1. Absorption spectra of solutions after 48 h contact with: 1 – anionite Dowex Monosphere 550 NC; 2 – cationite KU-2-8chs; 3 – anionite AV 17-8chs; and 4 – cationite Dowex Monosphere 650 CN.

Table 1
Masses of dry residues after evaporating of extracts from ionites

Ionite type	Ionite grade	Dry residue weight after evaporation of 1 mL of the extract, μg
Anionite	AV 17-8chs	170
	Dowex Monosphere 550 NC	60
Cationite	KU-2-8chs	30
	Dowex Monosphere 650 CN	80

Both the absorption spectra and the weights of dry residues allow some differences to be seen in the amounts of SOA that pass into water upon its contact with ionites. Thus, the Dowex Monosphere 550 NC anionite by is somewhat superior to AV-17-8nc in stability, whereas among anionites KU-2-8 (nc) is more stable than Dowex Monosphere 650 CN against destruction. Nevertheless, the observed differences are not essential with regard to the contamination of purified water with SOA. The obtained results confirmed the expediency of the development of an alternative method for fine water purification from impurities.

3.2. Theoretical justification of counter-electrophoretic water purification

The electroosmotic method for water deionization proposed in the above-mentioned article [2] requires special membranes getting in aqueous solutions charges differing in sign, which limits possibilities of its application. However, the found explanation of the mechanism of retention of ionic impurities with a certain charge sign during the electroosmotic water filtration gave occasion to undertake the present study.

The retention of ionic admixtures in electrophoresis is explained by the fact that the electroosmotic flow (EOF) occurs due to a collective movement of ions forming the diffuse part of the double electric layer, which compensates the electric charge of the pore surface in the membrane. In doing so, the ions with the same sign of charge as the surface charge will move in the electric field in the direction opposite to that of EOF, their electrophoretic velocity exceeding the EOF velocity; therefore, such ions are absent from the water transferred with EOF being concentrated in the solution at the membrane boundary on the side of the electrode with the charge of the sign opposite to that of these ions. The proposed explanation of the mechanism of concentrating ions in the course of the electroosmotic water transfer through porous membranes allowed us to assume that the effect of retention of ionic and other electrically charged particles by a porous membrane in an electric field should also appear when the flow through the membrane is formed not by the electric field, but due to the pressure gradient from the side of the electrode responsible for the elecrophoretic transfer of separated particles toward the electrode. The method is based on the fact that instead of the electroosmotic filtration, the electrofiltration in the electric field directed oppositely to the hydrodynamic movement of separated charged particles.

To ensure water purification from particles with identical electric charge sign, their total amount, m_e, transferred through the membrane by electric field should exceed their amount, m_F, transferred in the opposite direction by the hydrodynamic flow. This condition is expressed by the equation:

$$m_e > m_F \tag{1}$$

Eq. (1) is a common requirement for the countercurrent electrophoretic isolation of charged particles from a liquid flow. If the amounts of substances transferred by a hydrodynamic flow and by an electric field are expressed via the corresponding mass-transfer parameters, this condition can be presented as follows:

$$It_i / z_iF > C_iv_F \tag{2}$$

where I is the strength of current, at which the filtration takes place; t_i is the transfer number of the separated electrically charged particles; z_i, is their charge; F is the Faraday constant; C_i, is the concentration of the separated particles in the filtered water; and v_F, is the volume rate of the hydrodynamic flow through the membrane.

The process, which meets condition (2), can be realized in both a single capillary for electrophoretic separation of ions and in a porous membrane, which can be considered as a system of parallel capillaries.

To provide separation of electrically charged particles of a certain charge sign irrespective of their electrophoretic mobilities, galvanostatic mode is preferable with an experimentally selected V_F value corresponding to the I value. In this case, all charged particles will return into the volume of water filtered through the membrane, under the action of the electric current flowing through the solution, which fills the membrane pores. Thus, the filtrate will get free from these particles, and the initial solution will be enriched with them up to a certain concentration depending on the ratio of the current strength and the hydrodynamic rate of the solution flow through the membrane in accordance with condition (2).

If the stated prerequisites are assumed to be true, then, to remove electrically charged particles with different charge signs from water according to the proposed scheme, it is necessary to carry out successively filtration processes through inert porous membranes placed in an electric field in directions opposite to those of the electrophoretic movement of these particles under the action of the applied electric field.

3.3. Isolation of admixed cationic and positively charged colloidal species from water by the proposed method of countercurrent electrophoretic purification

A schematic diagram of the proposed method of countercurrent electrophoretic water purification for the stage of isolation of admixed cationic and positively charged colloidal species from water is given in Fig. 2. In our experiments, cells made according to Fig. 2 were used. They contain Millipore (USA) cellulose acetate membranes with pore diameters of 0.8 and 1.2 μm and a total porosity of 75% and also polytetrafluoroethylene porous membranes with the average pore radius of 20–50 μm made by proprietary technology. The data obtained in subsequent experiments were independent of the membrane pore size, as the membranes in all cases only created a laminar flow within their pore space and thus prevent the convective solution mixing.

At the stage of water purification from positively charged admixtures, water to be purified according to Fig. 2 is pumped by peristaltic pumps 3_1 and 3_2 through the cathode chamber of the cell separated from the anode chamber by a porous membrane. Control of the flow through the peristaltic pumps provides conditions for a part of the flow to be filtered through the membrane at the volume rate V_F and for another part of the flow to be discharged from the cathode chamber at the rate V_c by peristaltic pump 3_2 as a concentrate of positively charged particles isolated from water. The discharge of the concentrate prevents the increase in concentration of separated positively charged particles in the cathode chamber over the limiting equilibrium value corresponding to the experimental values of the electric current strength and flow rate of purified water.

As a parameter for the comparison of efficiency of various ions retention, we used the value of breakthrough coefficient K determined as a ratio of separated ion concentrations in the filtrate (C_F) and initial solution (C_0).

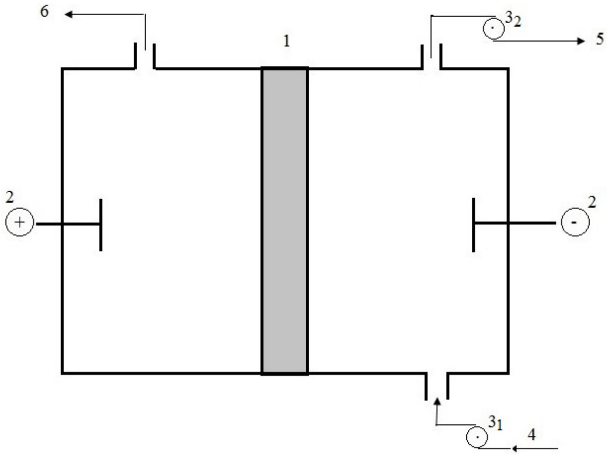

Fig. 2. Schematic diagram of water purification from positively charged admixtures by countercurrent electrofiltration: 1 – microfiltration membrane; 2 – platinum electrodes; 3 – peristaltic pumps; 4 – water to be purified; 5 – discharge of concentrate of separated particles; and 6 – filtrate flow.

The dependencies of breakthrough coefficients *K* for sodium, cesium, and picrate ions on the current density are given in Figs. 3(a) and (b). As follows from these data, for solutions with a comparable conductivity, the maximum breakthrough coefficient at a given current density is observed in the case of the least mobile picrate-ion, the ratio of currents for the complete retention of ions corresponding to $K = 0$ for each of ions satisfactorily agreeing with the ratio of their mobilities in solutions, which also confirms the suggested explanation of the retention mechanism in the proposed method.

The current required for the complete retention of ions depends to a great extent on their concentration in the initial solution (Fig. 3(b)). This is caused by the fact that an increase in the electrolyte concentration and a corresponding increase in the solution electric conductivity result at a specified current in a decrease in the potential gradient on the membrane and causes a decrease in the electromigration rate of separated ions in the solution.

The results obtained have confirmed the validity of the initial prerequisites for the possibility of countercurrent electrophoretic water purification from admixed ionic species.

It is known that admixtures of colloidal and suspended particles present in water as a rule possess an electric charge and have electrophoretic mobility; therefore, it could be expected that the established patterns of the countercurrent electrofiltration can be extended to them. To check the efficiency of water purification from colloidal particles by the proposed method, a used as an example of a colloidal solution of Fe (III) hydroxide. The water purification process was monitored using ^{59}Fe radionuclides added to the system at the stage of the colloidal solution preparation. The colloidal Fe(III) solution was prepared by the titration of an $1\cdot10^{-6}$ M $Fe(NO_3)_3$ solution with an $1\cdot10^{-3}$M NH_4OH solution up to pH = 5. After that the resulting solution was held for 24 h to stabilize size of formed colloidal particles of iron hydroxide. The results obtained by filtration of the colloidal solution through a porous membrane in an electric field are given in Table 2. They confirm the possibility of almost quantitative separation of colloidal admixtures when the corresponding ratio between filtration rate and current density has been selected. Measurement of the membrane radioactivity upon completion of the experiment showed that it remained at the background level, which proves the absence of mechanical filtration of iron hydroxides through the membrane.

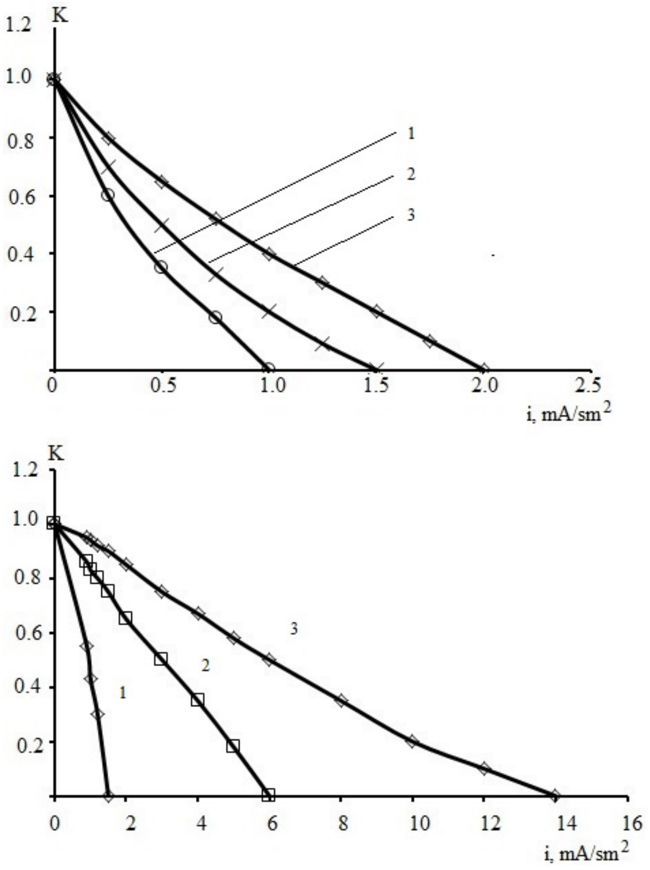

Fig. 3. Dependence of breakthrough coefficients of: 1 – cesium, 2 – sodium, and 3 – picrate ions on current density at a fixed filtration rate of 6.0 L/min: (a) for 5.10^{-5} M solutions (1 – CsOH; 2 – NaOH; 3 – NaPic) and (b) for NaCl solutions (1:10^{-4} M; 2: 5.10^{-4} M; 3: 10^{-3} M).

Table 2
Efficiency of countercurrent electrophoretic water purification from colloidal particles of Fe(III) hydroxide at a constant current density of 6.4 mA/cm^2

Filtration rate, mL/c·cm^2	Membrane voltage, V	Filtrate specific radioactivity, Bq/L	Breakthrough coefficient, %
0.37	410	$5.3\cdot10^4$	13
0.33	390	$3.7\cdot10^4$	9
0.29	340	$1.3\cdot10^4$	3
0.107	310	≤20	<1
0.11	250	≤20	<1

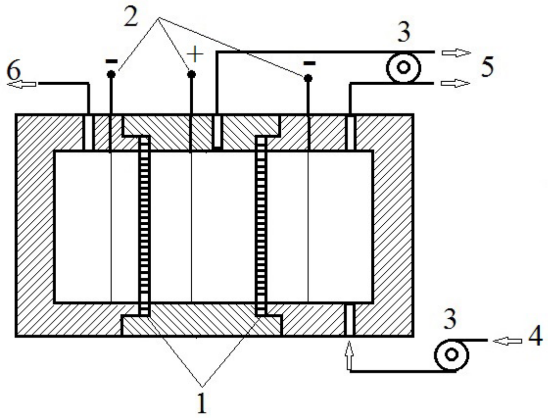

Fig. 4. Schematic diagram of electrophoretic cell for water purification from positively and negatively charged impurities: 1 – micro filtration membranes; 2 – platinum electrodes; 3 – peristaltic pumps; 4 – water to be purified; 5 – discharge of admixture concentrate; and 6 – purified water.

Table 3
Contents of admixtures in water purified ion-exchange deionization and countercurrent electrophoresis through porous membranes

Method	Admixture	Na	Mg	Ca	Zn	Cu	Cl
Ion-exchange deionization	Content, μg/L	2.4 ± 0.3	1.0 ± 0.5	3.4 ± 2.0	1.8 ± 1.0	0.10 ± 0.05	4.0 ± 2
Countercurrent electrophoresis		≤0.03	≤0.2	≤0.2	0.4 ± 0.2	0.05 ± 0.01	<1.0

3.4. Countercurrent electrophoretic water purification from electrically charged admixtures

To put into practice the countercurrent electrophoretic water purification from both positively and negatively charged admixtures, we propose a single three-chamber cell with two porous polytetrafluoroethylene membranes (Fig. 4) to be applied as a prototype of the purification setup instead of a device based on successive separation of positively and negatively charged particles. The working area of the membrane was 200 cm^3, thickness 3 mm, and average pore radius 50 μm.

The cell (Fig. 4) contains a single anode placed in the central chamber and two cathodes in the other two chambers. Water to be purified is fed by a peristaltic pump into one of the cathode chambers. Another variant, i.e., a combination of one cathode and two anode chambers, is also possible. For the arrangement of chambers shown in Fig. 4, positively charged particles are separated in the first (in relation to the water flow direction) chamber, as is the case with the experiments in two-chamber cells (Fig. 2), and when water is filtered from the central chamber into the second cathode chamber, anionic admixtures are separated. The admixture concentrates, which were isolated from the flow of purified water in the first cathode and the central anode chambers, are discharged owing to the experimental selection of the water flow rate, which should be sufficient for generating solution flows along all the lines simultaneously. Such conditions are provided if the flow rate of solution pumped to the chamber is higher by a factor of 5–10 than the total rate of flows of concentrates discharged from the first cathode and the intermediate anode chambers and of purified water taken from the second cathode chamber.

In our model experiments with sodium picrate solutions containing the least mobile anions ($u = 3.15 \cdot 10^{-2}$ m^2/Vs), the salt concentration was such that provides specific conductivity of the solution of 2.10^{-6} Ohm^{-1}·cm^{-1} (that is equivalent to the averaged value of specific conductivity of distilled water). It was found that picrate-ions are completely retained at a filtration rate of 10 L/h, flow rates providing the admixtures discharge of ~ 1,5 L/h, and a current strength in the cell of 200 mA, which testifies that the energy consumption for the purification is moderate. Further, we checked a possibility for distilled water purifications at the process mode providing the solution purifications from picrate-ion. The voltage applied at the first purification stage was 400 V and at the second 550 V. Usually, the main parameter used to characterize HPW is its electric conductivity. Water obtained by the proposed method was substantially inferior by this parameter to water obtained by ion-exchange ionization at the same composition of distilled water to be purified. This is due to the fact that electric conductance of water purified by electrofiltration is defined by dissolved carbon dioxide, which is almost completely removed in the case of the ion-exchange ionization because in the case of sorption by an anionite in the H-form the equilibrium $CO_2 \Leftrightarrow HCO_3^-$ is shifted to the side of anionic species sorbed by the anionite. The corresponding increase in the completeness of removing dissolved CO_2 was achieved by shifting the pH of the treated water up to pH ≥ 8 by adding a NaOH solution. In this case, the quality of water purified by the proposed method and by the ion-exchange deionization became equal, as determined by the integral characteristic, i.e., conductivity. We did not checked the purified water quality with respect to the content of SOA since in the case of countercurrent electrophoretic water purification there are no sources for entering SOA in the finished product. Hence, the most typical for HPW inorganic admixtures were chosen as the quality criteria (Table 3).

The data of Table 3 show that, except for SOA, the proposed method ensures the high quality of water by other criteria.

4. Concluding remarks

The idea of preparing HPW on the basis of countercurrent electrophoresis principles has found its experimental proof. Water prepared by the proposed method is free from SOA that can appear during the ion-exchange deionization and, by the content of inorganic admixtures, is at a comparable and even a lower level in relation to water obtained by the method of ion-exchange deionization.

Acknowledgements

The authors gratefully acknowledge the Russian Science Foundation (projects no. 16-13-10117) for supporting research presented in this article.

References

[1] J. Paul Guyer, Introduction to Ion Exchange Techniques for Water Desalination, Engineers Edge, LLC, USA, 2012.

[2] L.N. Moskvin, L.A. Godon, L.V. Epimachova, Water purification by electroosmosis, Russ. J. Appl. Chem., 59 (1986) 527–529.

[3] Patent USA No. 6,781,817, Fringe-Field Capacitor Electrode for Electrochemical Device, 2004.

[4] Patent USA No. 6,709,560, Charge Barrier Flow through Capacitor, 2004.

[5] Y. Zhao, Y. Wang, R. Wang, Y. Wu, S. Xu, J. Wang, Performance comparison and energy consumption analysis of capacitive deionization and membrane capacitive deionization processes, Desalination, 324 (2013) 127–133.

[6] H. Li, L. Zou, Ion-exchange membrane capacitive deionization: a new strategy for brakish water desalination, Desalination, 275 (2011) 62–66.

[7] F.A. AlMarzooqi, A.A. AlGhaferi, I. Saadat, N. Hilal, Application of capacitive deionization: a review, Desalination, 342 (2014) 3–15.

[8] K.N. Knust, D. Hlushkou, U. Tallarek, R.M. Crooks, Electrochemical desalination for sustainable water future, ChemElectroChem, 1 (2014) 850–857.

[9] M.M. Nasef, O. Guvanc, Radiation-grafted copolymers for separation and purification purposes: status, challenges and future directions, Prog. Polym. Sci., 37 (2012) 1597–1656.

[10] L.N. Moskvin, V.S. Gurskii, L.V. Epimakhova, Electroosmotic concentration of cations and anions for the analysis of high purity water, J. Anal. Chem., 47 (1992) 1265–1268.