Chapter 8

Applications of Ion Exchange Resins in Water Softening

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Abstract

Surface and groundwater always contain hardness ions (Ca$^{2+}$ and Mg$^{2+}$). The hardness is an important characteristic that provides the consumer properties of water. This parameter must be taken into consideration by the stations of water treatment, thermal power plants, the enterprises of chemical, food, pharmaceutical industries. Ion exchange resins, which are intended for water softening, are considered in this chapter. The negative effect of hardness ions on human health and equipment is also a focus of attention. Special approaches for increasing the efficiency of water softening are also reported. These approaches involve combining ion exchange with electrodialysis or ultrasound.

Keywords

Water Softening, Hardness Ions, Ion Exchange Resins, Polymer-Inorganic Resins, Electrodeionization

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1. Introduction

Surface and groundwater always contain hardness ions (Ca$^{2+}$ and Mg$^{2+}$), their content is various in different water sources, which are in one or other region. This parameter is an important characteristic that provides consumer properties of water. The hardness must be taken into consideration by the plants, which use a huge amount of water, namely the station of water treatment for household needs, thermal power plants, the enterprises of chemical, food, pharmaceutical industries and so on. The hardness of water determines the possibility to use it for drinking, since the increased content of Ca$^{2+}$ and Mg$^{2+}$ ions adversely affects human health.

For decreasing the content of hardness ions, different softening techniques have been developed. It is necessary to mention baromembrane methods: combination of chemical precipitation with microfiltration [1], polymer-assisted ultrafiltration [2] (as shown in the example of whey filtration, ultrafiltration membrane rejects up to 10-15% of hardness ions [3] without addition of macromolecular compound to the liquid being desalinated), nanofiltration [4], reverse osmosis [5]. Chemical methods (precipitation of insoluble calcium and magnesium compounds with caustic [6] and lime [7] soda) can be related to very old times and are widespread. Distillation has been widely used for a very long time [8]. Modern direction in the field of water softening is membrane distillation [9]. A number of electrochemical methods are also reported: electrodialysis [10], capacitive deionization [11], membrane capacitive deionization [12], electro precipitation [13], electrocoagulation [14].

The most common technique for water softening is ion exchange using polymer resins, since it is relatively cheap, effective and requires no energy consumptions, complex
equipment and expensive materials [15]. The task of the specialists, who occupy the field of material engineering, is to develop ion exchange resins with high capacity, selectivity and fast sorption. Moreover, the resins must be easily regenerated and must be stable against regenerating solutions. Large manufacturing companies (Dow chemical, Bayer etc.) offer a wide range of ion exchange resins, which are intended for one or several purposes.

In this chapter, ion exchange resins (particularly polymer-inorganic composites), which are intended for this purpose, are considered. Negative effect of hardness ions on human health and equipment is also a focus of attention. Special approaches, which allow us to increase the efficiency of water softening are also reported. These approaches involve combining ion exchange with electrodialysis (electrodeionization) or ultrasound.

2. Water hardness

2.1 Salts providing hardness

The permanent hardness is due to multivalent inorganic cations (i.e. cations, a charge of which is higher than +1) [1]. These cations are able to form insoluble compounds due to chemical interaction with different substances, such as soda, alkali and so on. Among multivalent cations, namely Ca$^{2+}$ and Mg$^{2+}$ are found in large quantities in most natural waters. At the same time, Ba$^{2+}$, Sr$^{2+}$, Fe$^{3+}$ and multivalent cations of other metals provide water hardness, however, their contribution is inconsiderable. Thus, only calcium and magnesium cations are related to hardness ions.

Ca$^{2+}$ and Mg$^{2+}$ ions appear in surface and groundwater (rainwater and distilled water contain a small amount of them) due to a leakage from calcium and magnesium-containing minerals, among which calcite CaCO$_3$, anhydrite CaSO$_4$, alabaster CaSO$_4$·0.5H$_2$O, and gypsum CaSO$_4$·2H$_2$O, dolomite MgCO$_3$·CaCO$_3$ and magnesite MgCO$_3$ are the most widespread. For instance, dissolution of calcium carbonate (bicarbonate formation) occurs as:

$$\text{CaCO}_3 (s) + \text{H}_2\text{O} + \text{CO}_2 (aq) \leftrightarrow \text{Ca}^{2+} (aq) + 2 \text{HCO}^- (aq) \quad (1)$$

Rain water contains dissolved CO$_2$ gas, which interacts with calcium carbonate. As a result, a soluble calcium compound is formed. However, this reaction is reversible. The Ca carbonate can be re-deposited, its morphology strongly depends on the CO$_2$ content in air stalactites and stalagmites can be formed under certain conditions. The biota effect on this process is considerable, since it affects the amount of this gas in air [17].

For the numerical expression of water hardness, the concentration of Ca$^{2+}$ and Mg$^{2+}$ ions is indicated. The SI unit for measuring concentration is mol m$^{-3}$, however, in practice,
degrees of hardness or mg l⁻¹, mmol l⁻¹, mg-eq l⁻¹ are used to measure hardness. In different countries, various non-systemic units are used, they are so-called hardness degrees, which reflect mainly the total content of hardness ions (Table 1).

Table 1. Units of hardness ions

<table>
<thead>
<tr>
<th>Country</th>
<th>Symbol</th>
<th>Definition</th>
<th>Value (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>dH (Deutsche Härte); dGH (degrees of general hardness); °dKH (for temporary hardness).</td>
<td>1 part of CaO or 0.719 parts of MgO per 100 000 parts of water</td>
<td>0.1783</td>
</tr>
<tr>
<td>UK</td>
<td>°e</td>
<td>1 grain CaCO₃ per 1 english gallon of water</td>
<td>0.1424</td>
</tr>
<tr>
<td>France</td>
<td>°TH</td>
<td>1 part of CaCO₃ per 100 000 parts of water</td>
<td>0.0999</td>
</tr>
<tr>
<td>USA</td>
<td>ppm</td>
<td>1 part of CaCO₃ per 1 000 000 parts of water</td>
<td>0.0100</td>
</tr>
<tr>
<td></td>
<td>gpg (grain per gallon)</td>
<td>1 part of CaCO₃ per 1 american gallon of water</td>
<td>0.1710</td>
</tr>
</tbody>
</table>

Total water hardness includes (i) temporary and (ii) permanent hardness (Fig. 1). Temporary hardness is due to soluble calcium bicarbonate and magnesium bicarbonate, which are formed according to scheme (1). This hardness can be removed by boiling, in this case the reaction (1) occurs in an opposite direction. Permanent hardness, which is caused by sulfate and chloride salts, can not be removed by this manner. In this case, the approaches, which are listed above, are used. In general, they are applied to remove the total hardness.

Figure 1. Types of water hardness.
In order to determine water hardness, the standard technique is used. The method is based on titration with ethylenediaminetetraacetic acid (EDTA) [18]. Analytical techniques, such as atomic absorption spectrometry (AAS) and induced coupled plasma analysis (ICP) can be also applied. Potentiometric sensors for monitoring water hardness have been proposed (the sensor also determines the presence of other ions) [19]. Different types of sensors are considered also in [20-22]. The method of quantitative analysis of hardness ions has been invented: it is based on the change of color of silver nanoparticles [23].

According to the amount of Ca$^{2+}$ and Mg$^{2+}$ ions, following water classification has been proposed (Table 2) [18]. Normative content of these ions for drinking water is 25-130 (Ca$^{2+}$) and 5-65 (Mg$^{2+}$) mg l$^{-1}$. Since hardness ions are important for living organisms (calcium is a constituent of bone tissues, magnesium is important for the normal functioning of the cardiovascular, nervous systems, digestive organs, muscles and bones), water with lower content of these species is injurious to health. At the same time, their higher concentration provides negative effects. This problem will be considered further.

<table>
<thead>
<tr>
<th>Type of water</th>
<th>Total hardness (mg l$^{-1}$ of CaCO$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>0-50</td>
</tr>
<tr>
<td>Moderately soft</td>
<td>50-100</td>
</tr>
<tr>
<td>Slightly hard</td>
<td>100-150</td>
</tr>
<tr>
<td>Moderately hard</td>
<td>150-250</td>
</tr>
<tr>
<td>Hard</td>
<td>250-350</td>
</tr>
<tr>
<td>Very hard</td>
<td>&gt;350</td>
</tr>
</tbody>
</table>

Table 2. Types of water according to the content of hardness ions (reproduced according to the permission of Cambridge University Press)

2.2 Negative effect of water hardness

The content of water in human organisms is 70-80%. Namely water provides transport of oxygen, enzymes, hormones, and salts in the body. The chemical composition of water becomes especially important: the more impurities it contains, the worse it dissolves useful substances. As mentioned above, the content of hardness ions in drinking water must be in a strictly determined diapason.
As suggested by the World Health Organization, no fatal health effect of hard water on human health is known [25]. Moreover, hard water provides a contribution to Ca and Mg, since deficiency of which is responsible particularly for cardiovascular and bone diseases and even cancer [26]. Drinking water is more important as a source of calcium and magnesium than diet, since water contains the most digestible compounds of these metals. Nevertheless, soft water is necessary to prepare food beverage productions, such as juices, beer, wines and so on [27]. Hard water sufficiently deteriorates the quality of products. It can be harmful in the case of medical application, for instance, hemodialysis [28] and medicine preparation [29]. In the first case, hardness ions penetrate from physiological solution through the membrane into blood changing its salt composition. In the second case, hardness ions can interact with active components of pharmaceutical drugs. Moreover, they also appear in blood together with drugs for injections. Hard water is undesirable for daily skin and hair care.

However, hardness ions in excess quantities affect human health negatively. First of all, high hardness worsens the organoleptic properties of drinking water, giving it a bitter taste. Ca$^{2+}$ cations interact with phosphate ions directly in digestive organs decreasing the intake of phosphorus, which is also necessary for living organisms [25]. The imbalance between calcium and phosphorus causes hypercalcemia [30]. This disease is characterized by an increase in calcium concentration in blood more than 2.6 mmol l$^{-1}$. As a result, the excessive production of parathyroid hormone occurs. This causes a deficiency of the element in the bone tissue. This pathology can be hereditary and can develop against the background of: growth of malignant tumors; adenomas; benign tumor of the thyroid gland; overdose of vitamins A and D; diseases of the blood and kidneys; taking diuretics.

An excess of Mg causes hypermagnesemia (an increase in the concentration of magnesium in the blood plasma above 1.1 mmol l$^{-1}$ M or 2.9 mmol l$^{-1}$ in severe form). Symptoms include weakness, disorientation, depressed breathing, and decreased reflexes. Hypotension and heart failure are also possible. Increased content of magnesium in water causes diarrhea. Alternatively, water containing high amounts of MgSO$_4$ causes a laxative effect.

No correlation between water hardness and formation of calcium stones in kidneys was found [25]. However, some studies assume that the usage of soft water for drinking prevents calcium nephrolithiasis and the formation of kidney stones [31]. The negative effect of calcium excess on the reproductive system has been shown [32, 33].

At last, the negative effect of hardness ions on equipment (water pipes, heaters, heat exchangers, pumps etc.) due to corrosive effect and formation of insoluble compounds is well known (Fig. 2). Both corrosion and deposition of insoluble compounds damage
equipment. This is another reason for the softening of water before its usage. The ion-exchangers, which are widely used for this purpose, are considered further.

Figure 2. Deposits inside the water tube and heater, which are caused by hardness ions.
3. **Ion exchange resins for water softening**

3.1 **Strongly acidic resins**

Strongly acidic resins, such as Dowex 50X8, Dowex HCR-S (Dow Chemical), Purolite C 100E (Purolite International), Lewatit-C249 (Bayer), are often used for water softening. They are gel-like styrene-divinylbenzene polymers containing –SO₃ groups (Fig. 3a). As a rule, the content of cross-linking agent (divinylbenzene) in resins for this purpose is 8-10%. According to the information of producing companies, water content in H-forms of swollen resins is about 50 %, total capacity towards Na⁺ ions is 1.8-1.9 mmol cm⁻³ for singly charged ions. The capacity is independent of solution acidity at pH>2 (potentiometric curve is given in Fig. 4 [34]). The capacity per 1 g of dry resin is 4.8 mmol g⁻¹.

![Figure 3. Polymers, which are a base of (a) strongly and (b) weakly acidic resins.](image)

![Figure 4. Titration curves of cation exchange resins [34]. Reproduced according to the permission of Elsevier Publisher.](image)
Usually Na-forms of resins are used for water softening. Ion exchange occurs according to the scheme:

\[ 2R^-\text{SO}_3^- \text{Na}^+ (s) + \text{Ca}^{2+} (aq) \rightarrow (R^-\text{SO}_3^-)_2\text{Ca}^{2+} (s) + 2 \text{Na}^+ (aq) \]  

(2)

\[ 2R^-\text{SO}_3^- \text{Na}^+ (s) + \text{Mg}^{2+} (aq) \rightarrow (R^-\text{SO}_3^-)_2\text{Mg}^{2+} (s) + 2 \text{Na}^+ (aq) \]  

(3)

Here R is styrene-divinylbenzene matrix. The usage of Na-loaded forms allows one to avoid acidification of water due to releasing H\(^+\) ions (Ca\(^{2+}\)→H\(^+\) and Mg\(^{2+}\)→H\(^+\) exchange).

Isotherm of calcium sorption were obtained for the Purolite C100E cation-exchanger within the interval of CaCl\(_2\) neutral solution of 42 -176 mg·L\(^{-1}\) under different temperatures \[35\]. The Langmuir model was found to be the most suitable to analyze the isotherms. The highest capacity of monolayer has been found to reach 43 mg per 1 g of dry resin at 40\(^\circ\) C, it means a half of total exchange capacity is realized. The \(\Delta G\), \(\Delta H\) and \(\Delta S\) thermodynamic parameters were determined; they show spontaneous endothermic exchange. For the direct Ca\(^{2+}\)→H\(^+\) ion exchange, the selectivity coefficient is 3.9, this value is lower for Mg\(^{2+}\) ions (2.5) \[36\]. Investigation of Ca\(^{2+}\) and Mg\(^{2+}\) sorption on Purolite C100E resin under batch conditions was performed in \[37\]. Modeling chloride solutions and natural groundwater were applied to the study. The resin dosage, at which no change of the resin capacity occurs, is 4 g l\(^{-1}\). The removal degree of hardness ions from groundwater reaches 70%.

The rate of Ca\(^{2+}\) sorption with a Dowex HCR-S /S resin under dynamic conditions was studied in \[38\]. As shown, increasing (i) the superficial velocity of the solution, (ii) the concentration of the feeding solution from 100 to 1000 ppm, and (III) the grain size causes a decrease of sorption rate. Alternatively, increasing the velocity of flow through K-8H resin accelerates sorption \[39\]. These different data are evidently caused by various experimental conditions. As a result, the rate determining stages of sorption are different.

### 3.2 Weakly acidic resins

A number of weakly acidic ion exchangers, for instance, Dowex MAC-3 (Dow Chemical), are based on polyacrylic-divinylbenzene matrix, which contains carboxylic groups (see Fig. 3). The buffer effect caused by them is seen in Fig. 4. The resins are suitable for neutral and alkaline solutions. Thus, they are applied to softening of water, the pH of which is 7 and higher, their usage is ineffective for weakly acidic water.

A Pure PC200FD weakly acidic resin (Pure Resin Co.) was investigated in \[37\] and compared with strongly acidic resin Purolite C100E. No sufficient difference in exchange capacity towards Ca\(^{2+}\) ions has been found, when sorption was performed from a one-component solution. Slightly higher removal degree was realized, when both Ca\(^{2+}\) and Mg\(^{2+}\) ions were removed from groundwater. FTIR spectra showed no shifts of stripes,
which are attributed for carboxylic functional groups (1600 – 1700 cm\(^{-1}\)). This indicates no complex formation both for strongly and weakly acidic resins. No sufficient effect of types of anions (Cl\(^-\), NO\(_3\)^-, SO\(_4^{2-}\)) on calcium uptake by weakly acidic resin is suggested [40].

New commercially available weakly acidic resins were tested in [41] under batch and dynamic conditions. Unfortunately no commercial designation of the resins is specified. As found, the static capacity towards Ca\(^{2+}\) ions reaches 70-120 mg g\(^{-1}\) under batch conditions. The column test showed high run time (1200-1700 bed volume) in the case of desalination of water containing (mg l\(^{-1}\)): Ca\(^{2+}\) (20), Mg\(^{2+}\) (2), Na\(^+\) (4300). In other words, soft water containing a large amount of sodium ions was treated. The hardness ions were removed practically completely: their residual concentration was <1 mg l\(^{-1}\) in the effluent. At the same time, a decrease of Na\(^+\) was 0.16-0.28 % indicating high selectivity of tested resins towards hardness ions. Higher selectivity towards Ca\(^{2+}\) ions compared with Mg\(^{2+}\) is stressed.

Ca\(^{2+}\) sorption on the Na-form of Dowex MAC-3 resin under batch conditions was studied in [42]. The sodium-loaded resin was obtained by a treatment of the H-form of the resin with a NaOH solution. The isotherms, which were obtained in solutions of a wide concentration interval, are related to the “L” or “H” types of isotherms depending on the concentration of Ca\(^{2+}\) ions in equilibrium solution. If the content of these ions is lower than \(\approx 80\) mg l\(^{-1}\), the isotherm shows a plateau, further a growth of ion exchange capacity is observed. This phenomenon is explained as the effect of residual content of NaOH, which remained in the resin grains after the transformation of H-form into Na-form. The residual alkali provides an increase of the solution pH inside grains enhancing exchange capacity of weakly acidic resin. The isotherms are fitted by the Langmuir–Vageler model.

Weakly acidic cation exchange resin Lewatit S 8528 (Bayer) has been proposed as an alternative to strongly acidic resins for Ca\(^{2+}\) removal even from sugar beet juice [43].

3.3 Polymer-inorganic resins

The usage of polymer-inorganic resins [44-54] are directed to the removal of toxic ions (Ni\(^{2+}\) [44,47,49,50], Cd\(^{2+}\) [47,48], UO\(_2^{2+}\) [46], cationic dye [50]) from water containing also Mg\(^{2+}\) and Ca\(^{2+}\) ions. However, the hardness ions are removed simultaneously. Thus, the composites are suitable for water softening. Anion exchange resins remove arsenite [52] and chromate [53] anions from the solution containing also an excess of Cl\(^-\) or SO\(_4^{2-}\) anions.

Strongly acidic Dowex HCR-S [44-50] and weakly acidic Dowex MAC-3 [50] cation exchange resins were applied after modifying with inorganic constituents. Zirconium
hydrophosphate was used as a modifier, since its functional groups were able to form complexes of multicharged ions being sorbed [54].

A very important problem is the modifier morphology. It is determined by the precipitation conditions (from deposition of zirconium hydroxophosphate from the ZrOCl₂ solution or from sol of hydrated zirconium hydroxocomplexes) and porous structure of polymer matrix. As described in reviews [55,56], porous structure of ion exchange polymers occurs as a result of swelling. It is formed by hydrophilic and hydrophobic voids. Micropores and partially mesopores are hydrophilic, they are caused by the fragments of polymer chains, which contain functional groups. The fragments that are free from them are responsible for the formation of hydrophobic meso- and macropores. Structure defects are also attributed for ion exchange polymers, their size is several tens micrometers.

Thus, the modifier particles of different morphological features can be formed. They can be precipitated in the form of non-aggregated nanoparticles, their aggregates and agglomerates (Fig. 5). Depending on the size, they can be located in different types of pores. Thermodynamic approach to deposition of the particles of one or other size is reported in [57].

Figure 5. Non-aggregated (a [45]) and aggregated (b [47])nanoparticles of zirconium hydrophosphate in strongly acidic resin. Reproduced according to the permission of Springer (a) and Elsevier publishers.

The location of inorganic constituents affects properties of composites. Nanoparticles enhance sorption of Ca²⁺ions [48], as sorption isotherms show (Fig. 6). They are fitted with the Langmuir model. In other words, the curves involve a rapid growth followed by a plateau. At the same time, no sufficient improvement of Ca²⁺ sorption is observed, when
the modifier is in the form of large aggregates that are located in hydrophobic pores [47]. These phenomena are explained from the point of view of osmotic pressure of counter- and fixed ions of the modifier. When it is located in hydrophobic pores, the osmotic pressure squeezes hydrophilic pores of the polymer matrix. This is suggested based on porosimetry measurements. As a result, some hydrophilic pores are excluded from ion exchange. The selectivity towards Ni\(^{2+}\) and Cd\(^{2+}\) ions is due to the inorganic constituents. When the modifier nanoparticles are placed in hydrophilic pores [48], they evidently form additional centers of selective sorption. These centers can involve phosphate and sulfo groups simultaneously. Other advantages of the composites containing nanoparticles are the reproducibility of their composition [51]. Thus, the composite ion exchangers containing non-aggregated nanoparticles of the modifier are the most suitable for water softening.

![Graph](https://example.com/graph.png)

**Figure 6. Isotherms of Ca\(^{2+}\) sorption on polymer and polymer-inorganic strongly acidic resin. Plotted based on the data of [48].**

Polymer-inorganic strongly basic anion-exchanger containing magnetic particles (MIEX resin, Orica Watercare) was mixed with an Amberlite 200C strongly acidic cation exchanger (Dow Chemical) [58]. The cation exchanger contained no inorganic modifier. Unfortunately the modifier morphology as well as the composition of the ion-exchanger were not reported. The tested hard and very hard water contained 300–1000 mg l\(^{-1}\) of hardness ions (relatively CaCO\(_3\)) and 2.9–56 mg l\(^{-1}\) of dissolved organic carbon. The ion exchange technique allowed one to reach 97 % removal of total hardness as well as 76 % of organic carbon. As suggested, Ag nanoparticles were embedded to strongly acidic cation exchangers to provide their antimicrobial activity during water softening [59]. However, the suggestion about morphological features of the silver particles was not approved.
4. Regeneration of ion exchange resins and their fouling

According to the recommendation of the producing company, following reagents are needed for regeneration of resins: H$_2$SO$_4$ (1-8 %), HCl (4-8%) or NaCl (8-12%). Water softening requires a solution of NaCl to avoid the formation of acidic effluent. Moreover, this reagent is suitable to regenerate a mixed bed of cation exchange resin and anion exchange resin [58]. The problem is fouling of the resins with organic compounds during water softening. The loading of ion-exchangers with organic substances decreases the efficiency of the removal of hardness ions. As mentioned above, anion exchange resins contain magnetic particles. It means a simple procedure is required for the separation of cation- and anion exchangers. However, it is possible to regenerate the mixed bed without the resin separation, A 2% NaCl solution has been recommended to remove organic compounds from the resins over regeneration. The composition of the waste solution involves high amounts of NaCl, calcium, magnesium, organic compounds and trace contaminants. CaSO$_4$ is precipitated in the waste concentrate, this solid could be removed by filtration. Coagulation or membrane processes are recommended for the recovery of dissolved salts. After the treatment, the regenerating solution can be used repeatedly. The method of the treatment of brine, which is formed after water softening, has been proposed in [60]. The technique involves nanofiltration followed by double-stage crystallization and distillation. A concentrated solution is formed over distillation, it can be used for the regeneration of ion exchange resins.

In comparison with strong acids, the disadvantage of regenerating neutral NaCl solution is that it is impossible to prevent uncontrolled reproduction of microorganisms in the ion exchange column. As found, the microbial composition of water becomes worse after passage through the bed of strongly acidic resin: the amount of microorganisms increases several times [61]. However, it should be noted that the regeneration with back-wash streams depresses them in softened water. This is due to the mechanical destruction of biofilm on the resin grains.

At the same time, it is suggested that the resin loaded with microorganisms cannot be sanitized by flushing, backflushing or other rinsing procedures [62]. Regeneration removes the microorganisms only partially, but it is not enough for sanitation. Recirculation of the regenerating solution promotes fermentation providing bacterial growth. Addition of silver-containing solution to the regenerating liquid depresses bacterial growth. It is necessary to avoid loading of ion-exchangers with silver cations, i.e. to use only low-concentrated solutions. Another way is the disinfection with 0.01% peracetic acid, the combination of silver and peracetic techniques gives better results. As mentioned above, embedding the particles of metal Ag to the resins provides their antimicrobial activity [59].
The regeneration of ion-exchangers is also complicated by the formation of a film, which consists of humic matters, HM [63]. The main reactions, which occur during water softening, are assumed: (i) Na\(^+\) ions in resins are replaced with Ca\(^{2+}\) ions, (ii) Ca\(^{2+}\) ions in a solution interact with HM, positively charged HM–Ca\(^{+}\) species are formed, (iii) these species are adsorbed by the resin, weakening the electrostatic interaction between Ca\(^{2+}\) ions and functional groups of the ion-exchanger. According to the experience of the author of this chapter, this film could be removed only with a solution of strong acid. On the other hand, inorganic modifiers embedded to resin grains can prevent fouling of ion exchange resins [51]. This is an especially valuable advantage of polymer-inorganic ion-exchangers, when they are applied to desalination of biological liquids.

5. Ion exchange in a combination with other processes

5.1 Ion exchange and ultrasound

Ultrasound is a longitudinal wave, a frequency of which is above 20 kHz [64]. This value is higher than the sonic range (20 Hz - 20 kHz). Humans can hear sounds namely of this frequency diapason. Ultrasound causes cavitation: this process involves formation, increase and collapse of cavities or microbubbles. These processes occur during milliseconds. During the bubble collapse, energy is released in accordance with the theory of “hot spots”. The pressure reaches up to 500-10,000 bar, the temperature can reach up to 3000-5000 K. Under these tough and extreme conditions, the radicals of hydroxyl and hydrogen are generated as a result of thermal dissociation of oxygen and water. These radicals occur in water, oxidizing organic compounds preventing fouling of ion-exchange resins, which is realized, for instance, according to the mechanism [63]. In order to prevent the fouling of polymer materials, ultrasound can be applied to water disinfection, removal of algae, and membrane filtration [64]. It can also be used to decrease the turbidity and total suspended solids.

The application of ultrasound for water softening is considered in [65]. Strongly acidic cation exchanger was used for sorption of Ca\(^{2+}\) and Mg\(^{2+}\) ions under batch conditions. As confirmed by FTIR spectroscopy, no effect of ultrasound on functional groups occurs. The amount of the ion-exchanger is sufficient: the ultrasonic treatment enhances sorption, when the resin amount is small. Increase in the dosage deteriorates sorption affected by ultrasound, this is probably by the screening of grain surface with rather large bubbles, which cannot be removed from the resin bed. Increase of temperature from 35\(^\circ\) to 55\(^\circ\) C slightly improves sorption: the growth of the capacity of the Langmuir monolayer is from 26.3 to 27.7 mg g\(^{-1}\) towards Mg\(^{2+}\) ions (ultrasound), and from 23.2 to 27 mg g\(^{-1}\) (no
ultrasound). The limiting stage of sorption is the reaction of pseudo-first order. As found, ultrasonic activation accelerates sorption.

Unfortunately, the disadvantage of this technique is a strong dependence of the hardness removal efficiency on the resin dosage. This makes impossible the usage of ultrasound for ion exchange columns.

### 5.2 Ion exchange and electrodialysis

The electrochemical method, which combines ion exchange and electrodialysis, is called “electrodeionization”, EDI. It consists of two main stages: (i) extraction of ions by ion-exchange resin, (ii) migration of species being sorbed through the ion exchanger and membrane towards the electrode compartment of the electrodialysis cell (Fig. 7). The bed of ion-exchanger (cation, or anion exchange resins, or their mixture) is placed between cation and anion exchange membranes. As opposed to traditional ion exchange, EDI can be considered a continuous process. The necessary condition of continuity is the equality of rates of sorption and migration [66]. Regarding divalent ions, a high rate of their migration can be achieved only in flexible resins. Different fields of the EDI application are considered in reviews [67-69].

It should be noted that the EDI method is the most suitable for water containing no hardness ions. When ions, which are present in water, form insoluble compounds, the EDI process is complicated with deposit formation on the surface of both resin grains and membranes, since water dissociation occurs on the solid-liquid interface. H\(^+\) ions enter the ion-exchanger bed, OH\(^-\) ions remain at the surface of cation exchange grains and separator. Precipitation is a result of the solution alkalization. In order to solve this problem, acidification of feeding solution has been proposed [70]. Acidic solution was also used in concentrating compartments of the EDI cell. Flexible Dowex WX-2 resin was applied to the EDI process. However, leakage of acid through the membranes (especially through anion exchange separator) is possible, as a result, the solution being desalinated is acidified. However, this approach is not suitable for the softening of water, since its neutrality must be provided.

In order to prevent the deposit formation, periodic change of the polarity of the EDI cell (electrodeionization reversal, EDIR) has been proposed [70]. A mixed bed of the Amberlite IRA 402 Cl and Amberlite IR 120 Na resins, which were produced by Rohm and Hass Co. (USA) was placed between membranes. The model solutions, the hardness of which varied from 250 to 1250 mg l\(^-1\) relative to CaCO\(_3\), were passed through the resin bed. The removal degree of calcium and magnesium ions exceeded 99 %, when the period of polarity reversal was 10 min. This approach allowed one to perform a long-time operation of the EDIR system and to minimize scale formation (the deposit contains mainly CaCO\(_3\) and
MgCO₃). However, water was acidified down to pH 4 during the passage from the bed indicating preferable removal of cations. The removal degree of hardness ions reached about 20% during the EDIR process [72]. However, the energy consumption was ≈20 kWh per 1 kg of CaCO₃ indicating low economical efficiency of the process. For instance, in the case of electrodialysis, the energy consumption is 1 kWh per 1 kg of salts.

Figure 7. Scheme of the EDI process [67]. Reproduced according to the permission of Elsevier Publisher.

Conclusions

Among various methods of water softening, ion exchange possesses a special position, since it requires no expensive and complex materials and equipment. A wide range of strongly and weakly acidic cation-exchange resins are proposed by producing companies.
Thus, the ion-exchange resins are easily accessible. The mentioned advantages of ion exchange techniques allows one to use them for various application fields despite discontinuity of these processes. As opposed to traditional ion exchange, continuous water softening (EDI, EDIR) requires high energy consumption.

Ion exchange resins are easily regenerated with NaCl solution, the brine is eco-friendly. Fouling and biofouling, which occur over water softening and resin regeneration, can be prevented by modifying resins with inorganic ion-exchangers or silver particles. Economical aspects of the usage of composite resins should be considered for each case.

References


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