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Thang Ho[a]; Anju Kurup[a]; Tyler Davis[a]; Jamie Hestekin[a]
[a] Ralph E. Martin Department of Chemical Engineering, University of Arkansas, Fayetteville, AR, USA

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Wafer Chemistry and Properties for Ion Removal by Wafer Enhanced Electrodeionization

Thang Ho, Anju Kurup, Tyler Davis, and Jamie Hestekin
Ralph E. Martin Department of Chemical Engineering, University of Arkansas,
Fayetteville, AR, USA

Electrodeionization is a widely used technology to produce ultrapure water for various applications such as cooling towers, water reclamation for micro-fabrication, and pharmaceuticals. Wafer Enhanced- Electrodeionization (WE-EDI) is a technology which immobilizes resins into wafers allowing for a significant expansion in applications due to a decrease in internal and external channeling and leakage. Although WE-EDI allows for a wide variety of applications in low concentration and selective ion removal, there have been few studies on the effects of various processing variables on WE-EDI performance. This paper investigates the effects of different variables in wafer performance including porosity, capacity, permeability, and ion exchange bead type. Experimental data and predictive modeling shows that thickness and capacity have little effect on the ability of the wafer to enhance cation transport while the ratio of anion exchange to cation exchange resin, the amount of polymer used to bind the resins, and selectivity of the resin beads have a much greater effect. From the experimental and modeling results, it is recommended that the bead chemistry, especially the equilibrium constant K, should be the main consideration for specific ion removal applications.

Keywords electrodeionization (EDI); ion selective removal; ion transport modeling

INTRODUCTION

Ion removal, such as sodium and potassium, is of great interest to the juice and dairy industry because it has the potential to produce higher quality products (1–4). There are two major technologies that have been widely used for ion removal—ion exchange and electrodialysis. Ion exchange operates on the principle of ion selective beads, both cation and anion, operating to remove ions. These beads are contained in ion exchange resin columns which are widely used in juice de-acidification (1,5–10). The advantage of ion exchange is that it is easy and inexpensive to implement on a production scale (5). However, there are several disadvantages that affect the cost of the product. The ion exchange process requires large volumes of chemicals and water in order to regenerate the beads before processing. For instance, a whey demineralization process using ion exchange generates almost six volumes of wastewater per one volume of whey (11).

Electrodialysis (ED) is an electrochemical separation process that uses cationic and anionic ion exchange membranes to remove ions from solution. Cationic membranes allow only cations (Na^+, K^+, Ca^{2+}, etc.) to diffuse through, while anionic membranes allow only anions (OH^-, SO_4^{2-}, Cl^-, etc.) to diffuse through. The driving force for the separation in ED is the current that is applied across the membrane stack. ED consists of cation and anion exchange membranes in different compartments: feed/diluate compartment where ions are removed, the concentrate compartment where ions are transported to, and the rinse compartments (ER) to keep the electrodes clean and prevent chemicals from building up and corroding the electrodes as shown in Fig. 1. ED has been widely used in food processing and desalination applications (4,14–21). ED is more economical to use than ion exchange since it reduces both the volume of chemicals and the amount of water used (17,20). Although it is easy to control the quality of the product with ED, selective ion removal remains dictated by the choice of membrane.

Electrodeionization (EDI) combines the selective removal of ion exchange with the continuous processing of ED. EDI is a modification of ED in which the ion-exchange resin is packed into the diluate or feed compartment in order to enhance the transport of ions across the membrane. Just like the ED system, EDI consists of cation and anion exchange membranes arranged in a particular order to form different compartments. The feed/diluate compartment is packed with cation and anion exchange resins. The concentrate compartment is where the ions are collected as a result of transport through the ion exchange beads. Two rinse compartments (ER) help to keep chemicals from building up and corroding the electrodes. EDI was first used by Walters et al. in cleaning radioactive waste from contaminated water (22), and has

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Address correspondence to Jamie Hestekin, Ralph E. Martin Department of Chemical Engineering, 3202 Bell Engineering Center, Fayetteville, AR 72701, USA. E-mail: jhesteki@uark.edu

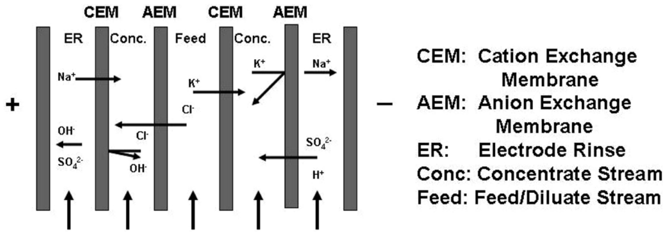


FIG. 1. Schematic of an electrodialysis system.

become a popular technique in the production of high purity water. The major applications of EDI are in the removal of ions at low concentrations (23–27) and the separation of weakly-ionized impurities (28–32). With the promise of ion selective removal, EDI has been widely studied in order to improve its performance. For instance, there have been many studies on flow rates, current, and voltage effects on the performance of EDI (23,24,33,34).

Researchers have also studied how different ion exchange membranes affect the performance of an EDI system. For example, Grabowski et al. studied the effect of anion exchange membrane permselectivity in ultrapure water production using bipolar membranes in two different EDI configurations (35). Both stacks contained separated beds of cation and anion exchange beads with a bipolar membrane separating the beds. In the first configuration, Grabowski et al. separated the diluate and concentrate compartment by an anion exchange membrane. The second configuration has a protective compartment filled with anion exchange beads between the diluate and concentrate compartments. The results showed that the first configuration could not produce ultra pure water (0.055 µS/cm) due to the incomplete permselectivity of anion exchange membranes while the second configuration was able to successfully produce ultra pure water. Moon et al. studied the transport of lithium ions in a nanocomposite membrane EDI system (36). They reported that for low lithium ion concentration ($\sim$5 mg/L) removal, the power consumption was decreased by 40% while switching from a polymeric membrane to a nanocomposite membrane EDI system. However, most of these studies were evaluating ultra-pure water production and how EDI performs in low ion concentrations. There are few if any studies of ion removal in high concentrations and ion selective removal with EDI.

Although there are major advantages over ED, there are also several disadvantages with EDI. First of all, the leakage of ions from compartment to compartment is a major problem (32,37). When the leakage occurs within the EDI system, ions begin to migrate from one compartment to another by convection instead of by diffusion, making it difficult to achieve the target separation. For instance, in ultrapure water production in semiconductor plants, it is difficult to produce the specified qualities when leakage occurs, especially in the presence of weak ions (29). Since the resin is packed loosely between two membranes, it is difficult to have a perfect seal between compartments to prevent leakage. Another disadvantage of EDI systems is the uneven flow distribution in the feed compartment where the ion exchange resins are packed (21). Because of loosely packed ion exchange resin, flow channels are created that decrease the efficiency. Researchers have experimented to eliminate these two problems by using different stack configurations such as spiral-wound configurations (29) or by immobilizing the resin using magnetic fields (38). Menzal et al. used the spiral-wound configuration in which the resins were tightly packed between the two membranes to eliminate the leakage of solution within the EDI system. By charging the cathode, anode, and ion exchange resins, Lacher et al. were able to immobilize the resins and prevent the packed bed from moving when the solution was processed through the system. This eliminated flow channel formation. These technologies were able to eliminate one of the disadvantages of conventional EDI but not both. Moreover, in order to implement these technologies, it is necessary to have a new system specifically designed rather than modifying one of the existing systems.

Wafer Enhanced-Electrodeionization (WE-EDI) was proposed for organic acid removal by Arora et al. in 2007 (39). They used a polymer as the binding agent in order to bind the ion exchange resins together into a wafer (39). The wafer is a mixture of cation exchange resins, anion exchange resins, and elastomeric binder. The wafer was inserted between two membranes as the spacer instead of the loosely packed ion exchange resin found in a conventional EDI system (39–41). WE-EDI helps prevent uneven flow distribution and ion leakage between the compartments. Because of the reduction in leakage, WE-EDI can be used for more selective product separations.

With the combination of ion exchange resins and ED, WE-EDI has potential applications in ion selective removal. However, there are few studies that have taken place concerning ion selective removal using EDI or WE-EDI. This study examines how different wafer compositions—polyethylene, sugar, cation—anion resins ratio and thicknesses (1–2 mm) affect the transport between different ions, especially for potassium ($\sim$2000 mg/L) and calcium ($\sim$1500 mg/L). Moreover, with an in-depth study of wafer characteristics, this paper addresses how different wafer compositions affect the capacity, porosity, and permeability of the wafer. Further, parameters have been obtained for the mathematical modeling of the WE-EDI system for single ion removal. This study creates a foundation for a multi-component model and optimizes several parameters that affect the transport of ions in a WE-EDI system.

EXPERIMENTAL SET-UP

Chemicals and Equipment

Sucrose, low density polyethylene, potassium chloride, sodium chloride, and calcium chloride were obtained from VWR. The cationic and anionic ion exchange resins used were Amberlite IRA-400 and Amberlite IR-120 plus, respectively. Both of these resins were obtained from Aldrich. A Carver Model 3851 Pneumatic Press was used for synthesis of the wafer. The ED stack consists of a Micro Flow Cell (Electrocell, Amherst, NY) which has a PTFE frame, stainless steel electrodes, and a filtration area of approximately 0.001 m^2 per cell pair. Cationic 5B membrane and Anionic ACS membrane from Tokuyama, Japan were used for EDI studies.

Experimental Procedure

Wafer Characterization

Experiments were carried out to investigate the effects of polyethylene and sucrose on the wafer's porosity, capacity, and permeability. A standard wafer consisted of polyethylene, sucrose/sugar, cation exchange resin, and anion exchange resin. Sugar and polyethylene were varied to make seven different kinds of wafers. The wafers were constructed using a pneumatic press set at 237°F and a pressure of 10,000 psi for 90 minutes followed by air cooling for 15 minutes after the wafers were formed. The high pressure helps to bind the mixture together while the high temperature helps to melt the polyethylene without melting the sugar. Polyethylene keeps the resins intact while sugar creates the porosity in the wafer. The heating time of 90 minutes allows polyethylene to melt completely while the air cooling for 15 minutes helps to solidify polyethylene to create a stable structure within the wafer. After sugar removal, the wafer contained a hydrophilic region (ion exchange beads) and hydrophobic region (polyethylene) which helps the wafer to perform as the ion transport enhancer. SEM images of a similar wafer, reported in Arora et al. (39), show polyethylene attached to the sides of beads showing these regions. Each wafer was cut into two 5 cm × 5 cm pieces and soaked overnight in deionized water to remove sugar. The porosity of a wafer is created when the sugar is removed. The dried wafers (taken out of water after soaking) were submerged in solutions of known potassium chloride concentrations for 12 hours. For each step, the concentration of potassium ion and weight of wafers were recorded using ion selective electrodes from Mettler Toledo. These measurements were obtained in order to calculate the capacity of the wafer. The capacity of the wafer is the amount of ion uptake per gram of beads.

The wafer's permeability was measured by using a home built flow-through column. The experimental setup is shown in Fig. 2. Water is pumped from a water tank to the column with a constant flow rate of 15 ml/min. The wafer is inserted in the middle of the column while the flow rate is kept constant, and the pressure is calculated based on the height of the water in the column. The pressure of the column is calculated as the product of the water density, the height of the column, and the gravity constant.

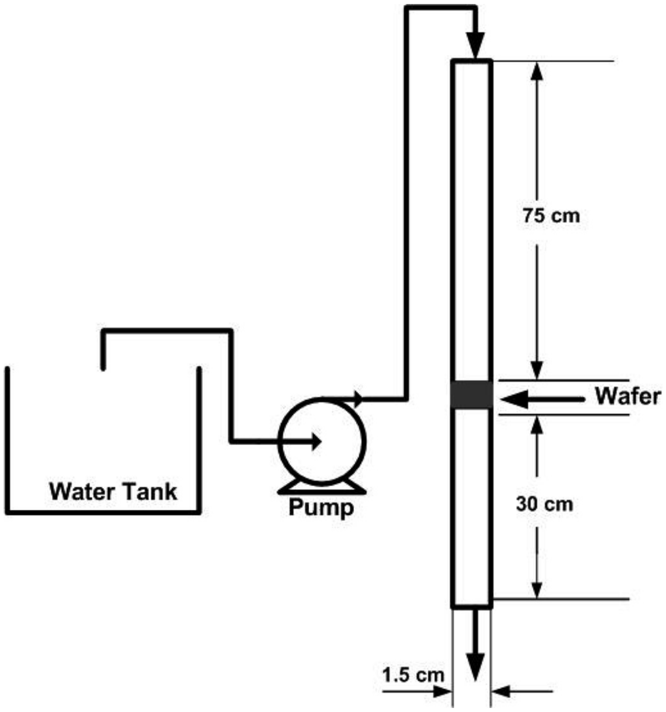


FIG. 2. Home-built wafer permeability experimental system.

The ion exchange selective equilibrium coefficient, K, was determined by using different concentrations of single ion solutions. In this experiment, four different concentrations of potassium were prepared in the range between 100 to 2000 mg/L. A volume of 150 ml of each solution was added into a jar and then 3 mg of cationic exchange beads was then added to the each jar and left in solution for 24 hours. The pH and concentrations of the ion was measured before and after the experimentation. The same procedure was repeated to measure the ion exchange selective equilibrium coefficient, K, for sodium ion.

Ion Selective Removal using WE-EDI

The WE-EDI system was operated in a batch mode with flow rates in all chambers set to 150 ml/min (2.5 ml/sec). The concentration of the rinse solution was 0.3 M Na_2SO_4 for a single component experiment (a standard rinse concentration in industry) and 0.3 M NaCl for multi-component experiments in order to prevent calcium precipitation. Solutions with the same starting concentration were used in diluate and concentrate chambers for each experimental set up. For single ion removal, a solution with a concentration of ~2000 mg/L K^+ (as KCl) was used. For two component experiments, a solution with a concentration of ~1500 mg/L K^+ (as KCl) and ~1500 mg/L Ca^{2+} (as $CaCl_2$) was used. The concentrations of potassium and calcium ions were chosen to correspond to be near their concentration in juice and milk. The volume of the diluate, concentrate, and rinses were 150 ml each. The experiments were operated at a constant current of 0.04 A for 8 hours while the voltage started at 4 V and increased up to 8 V as the solution became more dilute and the membrane fouled. Samples (2 ml) were drawn every hour for the first two hours and every two hours thereafter. Experimental results were corrected for the change in total volume as samples were taken. Samples were diluted ten-fold and sent for analysis of ion profile at the University of Arkansas Poultry Science Department using Inductively Coupled Mass Spectrometry (ICP-MS). Prior to actual sample analysis, standards were used to test the accuracy of the ICP-MS method. Over a variety of concentrations (50–2500 mg/L), the ICP-MS method of Poultry Science Department was within a 3% margin of error based on variations in multiple samples. The current and voltage were recorded at the same time as the samples were collected. For these sets of experiments, the ratio of cation: anion resins were varied from 0:100% to 100%:0 with 25% increments. Also, the thicknesses of the wafers were varied from ~1 mm to ~2 mm. The effects of different ion exchange ratios and thicknesses of the wafers were then evaluated in both single component (potassium) and multi-component (potassium and calcium) systems.

Samples Analysis

For the wafer capacity analysis, the solutions were analyzed for potassium ions using MultiSeven Mettler Toledo ion selective electrodes. For the multi-ion solutions, the samples were analyzed for ion profile by the ICP-MS from the University of Arkansas, Poultry Science Center.

THEORY

Many different approaches for EDI modeling have been proposed (42–45). The most fundamentally based of these models starts with the Nernst-Planck equation. One of these models, modified from (46) was used for modeling WE-EDI performance. In this paper, Glueckauf provided an analytical solution for a mono-valent single component system. To make the model more flexible for a variety of systems, Kurup et al. (47) included an approach that allowed for multi-component systems, multi-valent ions, and allowed the equations to be solved numerically for the first time with WE-EDI. The two main mass equations that were derived were based on ion transport within the diluate compartment. This model assumes that ions are transported from the bulk solution into the ion exchange resins, and that either the cations or anions are limiting. It is important to note that we have assumed that cation transport is limiting in this case since Na^+ and K^+ have conductivities of 50.11×10^{-4} and $73.5 \times 10^{-4}\,m^2S/equiv$ and Cl^- has conductivity of $76.1 \times 10^{-4}\,m^2S/equiv$ (48). However, if multiple anions of high mobility existed in solution this model could be adjusted to account for the transport of both ions. Since the model assumes that half the current goes for transport of cations and half for transport anions, the nearly equal conductivities make this assumption valid. If a more bulky cation or anion was used, this would need to be adjusted. It also assumes that ions transfer along the resins to the membrane via electric current. Further, we assumed that all ion transport happens through the resin and not the solution. For dilute solutions, this is a good assumption, and one of the purposes of this paper was to investigate how well this assumption held with intermediate concentrations. Thus the two governing equations developed are:

$$-a.\ln(1-\eta) - (a-1).\eta = \frac{J}{F} b\overline{C}W \tag{1}$$

$$bWA/f = -a \ln\frac{1-\eta_i}{1-\eta_e} + \ln\frac{\eta_i}{\eta_e} \tag{2}$$

In which, η, a, and b are three parameters defined by

$$\eta = \frac{(C^o)_W}{a\overline{C} - (a-1)(C^o)_W} \tag{3}$$

$$a = \frac{\lambda_3}{\lambda_1 K} \tag{4}$$

$$b = \frac{D}{r^2} \cdot \frac{3\alpha\beta}{2(1-\alpha)} \tag{5}$$

Equations (1) and (2) are solved simultaneously to describe the WE-EDI unit with correlations back to the tank Eq. (48).

$$\overline{C} = C_0 - \frac{A^* W^* (C_0 - C^0_{\text{exit}})}{V} \tag{6}$$

Equations (1), (2), and (6) were solved simultaneously using FORTRAN 90 with ISML library. For more information of the detailed solution procedure of these equations, please see the paper of Kurup et al. (47)

RESULTS AND DISCUSSION

Wafer Characterization: Porosity, Capacity, and Permeability

The porosity is important in a wafer because it indicates how much flow can take place through the wafer, along with the permeability. The porosity (ε) was determined by the ratio of void volume to the total volume of the wafer

(V_w). The total volume was calculated using the product of the area of the wafer (5 cm × 5 cm) and its thickness (2 mm ± 0.03). The void volume was calculated using the total volume and then subtracting the volume of each component, creating the structure of the wafer from the summation of the ratio of the mass of each component (m_i) over the density of each component (ρ_i). In these calculations, sugar was not considered to be part of the wafer's structure since it is removed from the wafer by soaking under water. Thus the porosity is defined as:

$$\varepsilon = \frac{V_w - \sum_i \frac{m_i}{\rho_i}}{V_w} \tag{7}$$

Capacity is an important characteristic in a wafer because it indicates how much enhancement of diffusion the wafer can make. The capacity was defined as the amount of ion uptake in milli-equivalent per gram of resin in a wafer. The wafer capacity was calculated using the concentration difference of ion absorbed (potassium) before (C_0) and after (C_f) soaking, multiplied by the volume of the solution (V) over the total mass of cationic resin (m_{resins}) within the wafer:

$$Capacity = \frac{(C_0 - C_f) * V}{\mathrm{m_{resins}}} \tag{8}$$

The permeability was calculated by using D'Arcy's law (48), in which the permeability (κ) is a function of the fluid flow rate through the wafer (Q), the pressure difference (ΔP), the fluid viscosity (μ), and the contact area (A):

$$\kappa = -\frac{Q}{A} * \frac{\mu}{\Delta P} \tag{9}$$

Considering these three parameters, it is important to point out the range of the experiments conducted. The sugar in these experiments was used to create porosity when it was removed by soaking in water. The polyethylene serves as a binder for holding the beads together. The total ratio for all of components in the wafer was 7.1 when polyethylene is held at 1. For example, the ratio of polyethylene: sugar: cation exchange resins: anion exchange resins in one of the wafers was 1:1.5:2.3:2.3 which give a sum of 7.1. As the ratio of polyethylene to total wafer (7.1) drops below 0.8, the wafer began to fall apart and becomes unviable for further experimentation. The same observation was made as the ratio of sugar to total wafer (7.1) increased above 1.2. Moreover, when the ratio of polyethylene to total wafer was above 1.4, a great deal of pressure drop was required since polyethylene blocks the void volume of the wafer. The same phenomenon was also observed as the ratio of sugar to total wafer dropped below 0.8. Therefore, the permeability and porosity measurements were conducted in the range of 0.8 to 1.4 of polyethylene to total wafer and the range of 0.8 to 1.2 of sugar to total wafer. The results of sugar and polyethylene on porosity and permeability are shown in Figs. 3 and 4, respectively.

As the ratio of polyethylene to total wafer increased, while the amount of cation and anion exchange resins remains constant, the porosity and permeability of the wafer decreased. The main reason was that polyethylene began to block the flow channels as well as cover the resin so that the resin could not make as much contact with the solution. As the ratio of sugar to total wafer increased, the porosity and permeability of the wafer increased due to the increased sugar creating more or larger pores.

Figure 5 shows the capacity as a function of the ratio of polyethylene/sugar to total wafer. The capacity of the wafer is the amount of ions taken up (meq/g) of resin in the wafer. The capacity of the loose resins is the maximum capacity that wafer can have without any site blockage from polyethylene binding. Thus, the maximum capacity of a wafer is dictated by the capacity of loose resin which is 0.051 mg K^+/mg resin for the anion exchange resin used (1.3 meq/g resin, experimentally determined). As shown in

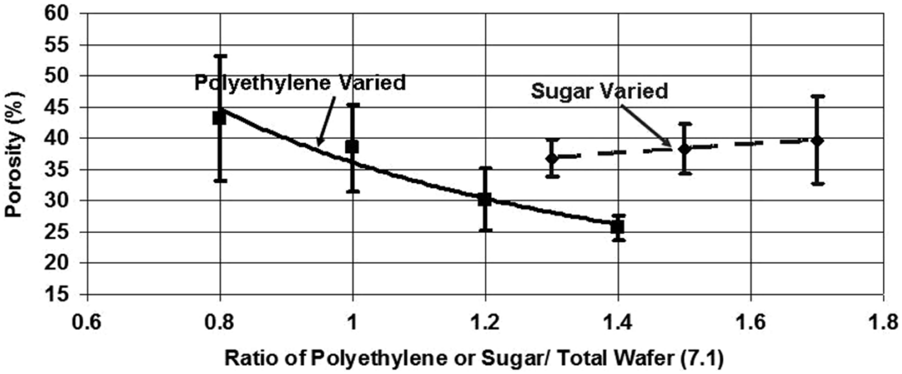


FIG. 3. The effects of polyethylene and sugar on wafer porosity.

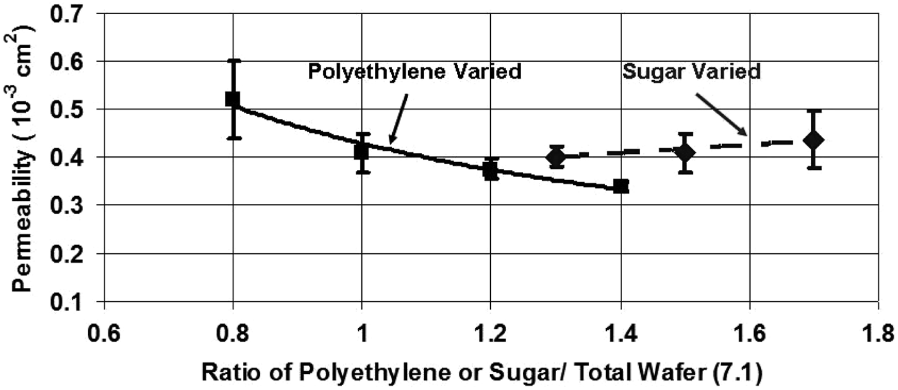


FIG. 4. The effects of polyethylene and sugar on wafer permeability.

the figure, the ratio of polyethylene to the total wafer had the biggest effect on the ion exchange capacity of the wafer. This is because polyethylene, although a binder, is nonconductive and the more polyethylene present in the wafer, the more sites that are blocked from ion exchange capacity.

Decreasing the ratio of polyethylene to total wafer increases the wafer's ability to enhance transport since the wafer porosity, permeability, and capacity all increase. However, the consequence of increased transport is the difficulty to consistently produce wafers with uniform characteristics. Thus, they ultimately fall apart at the ratio less than 0.8 polyethylene. It was necessary to consider both stability and performance in order to optimize the wafer. In this paper, the ratio of 2.3:2.3:1:1.5 for cation exchange resin, anion exchange resin, polyethylene, and sugar, respectively was chosen to perform the rest of the experimentation in single ion removal and multi ions removal. This was the ratio 1 for polyethylene and 1.5 for sugar in Figs. 3–5. It was found that this "magic ratio" gave the best combination of performance and stability in the wafers we tested.

Ion Removal with Different Cation: Anion Exchange Resin Ratio and Thickness

Modeling Single Ion Removal with Standard Conditions

The model used was developed by Kurup et al. (46) for single and multi-component transport. The parameters used are given in Table 1. These parameters are either obtained from the literature or determined from experiments.

The diffusion coefficients for potassium and sodium ions in the solid phase (D) were approximated by using 0.15 times the liquid phase diffusion coefficients as estimated by (49). The average radius of the resin particles were obtained from the mesh size of the particles used (16–60 mesh size), which correlated to an average radius of 0.04 cm (r) using a standard mesh chart (48). The thickness of the wafer (W) was experimentally measured using a caliper. Beta (β) is the fraction of total ion-exchange resin surface area accessible for exchange of ions. Beta was calculated by the ratio of the capacity of the wafer (0.041 mg K^+/mg resins or 1.05 meq/g resins) to the capacity of the loose resins (0.051 mg K^+/mg resins or 1.30 meq/g resins) obtaining the value of 0.8. Lambda (λ) is the equivalent conductance of ions. λ_1 represents the

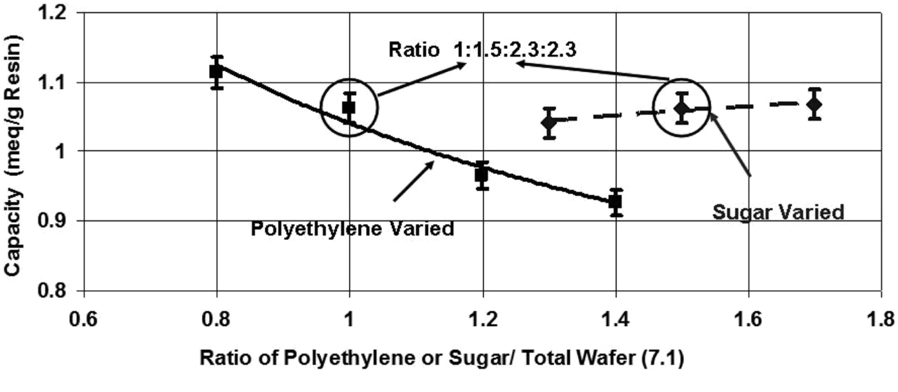


FIG. 5. The effects of polyethylene and sugar on wafer capacity.

TABLE 1
Modeling parameters for potassium and sodium ion removal with wafer enhanced electrodeionization

	Potassium	Sodium
D	$1.957 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{sec}$	$1.334 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{sec}$
r	0.04 cm	
W	0.2 cm	
β	0.8	
α	0.6	
λ_1	$11.43 \times 10^{-5}\,\mathrm{m}^2/\mathrm{V}/\mathrm{sec}$	$7.79 \times 10^{-5}\,\mathrm{m}^2/\mathrm{V}/\mathrm{sec}$
λ_3	$54.396 \times 10^{-5}\,\mathrm{m}^2/\mathrm{V}/\mathrm{sec}$	
K	2.02	0.59
2 J.A	0.04 A	
A	$10\,\mathrm{cm}^2$	
f	2.5 ml/sec	

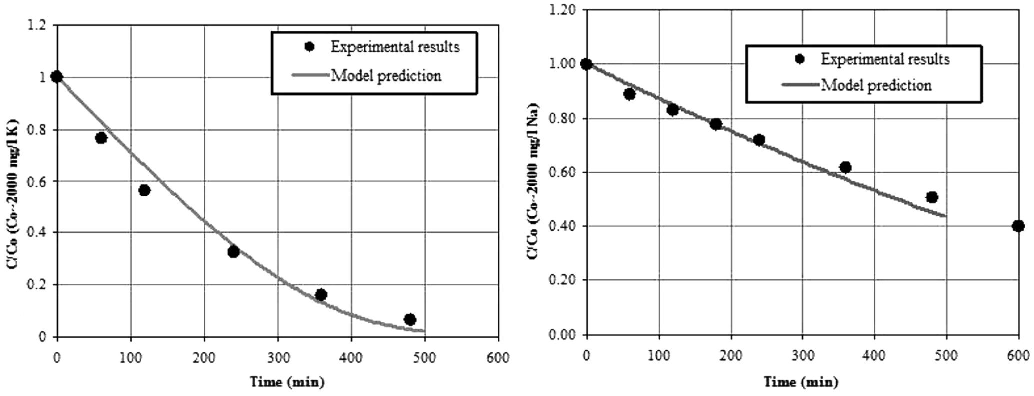
equivalent conductance of potassium or sodium ion while λ_3 represents the equivalent conductance of hydrogen ion (50). The ion-exchange equilibrium selective coefficient (K) was obtained from the ratio of total cation concentration exchanged to the total hydrogen concentration migrated into the solution. The coefficient K of potassium ion or sodium ion is the average of multiple values of K in a range from 100 mg/L to 2000 mg/L ion concentration as discussed on the previous experimental procedure. If a more accurate determination was required, K could be varied as a function of concentration. The operating electrical current of the EDI stack was 0.04 Amps. The assumption was that half of the current is utilized to transport cations and the rest of the current is used to transport anions. The current density (J, Amps/cm^2) is equal to half of the operating current divided by the contact area (A). The contact area (A) is the membrane area given we are using only one cell pair. The flow rate of the diluate stream (f) was 150 ml/minute which was 2.5 ml/sec.

The modeling and experimental results for potassium and sodium ion removal are shown in Fig. 6. It is important to point out that both of these simulations were run with no adjustable parameters and were not based on prior EDI experiments. Given that these experiments ran for over 500 minutes the model fits the experimental data very well. Thus, it was determined that the model was valid over the concentration range we tested and was used to look at other variables effects on WE-EDI performance.

Single Ion Removal: Variation of Wafer Parameters

After the detailed wafer study, it was desirable to see if changes in wafer parameters led to different ion removal rates in WE-EDI. Therefore, the removal of potassium ions with different cation: anion exchange ratios were studied. The computational models were performed in parallel with the experimentation in order to validate both experimental data and numerical modeling. The results for potassium removal with different cation: anion exchange resin ratio is shown in Fig. 7. The results show that when the ratio of cation: anion exchange resins were increased, the removal rate of potassium increased slightly. For instance, after 4 hours of operation, the potassium ion concentration in the diluate/feed compartment is 30% ± 3% of the original potassium ion concentration for the 0% cation exchange resin wafer. For the same operating time, the potassium ion remaining is 20% ± 2.5% of the original potassium ion concentration for 100% cation exchange resin wafer. This small but significant difference in data predicted by the model which shows that as the concentration of the cation exchange resin goes to zero the transport of ions goes to that of ED. Thus with the system where cation exchange is limiting, a wafer with 100% cation exchange resin is optimal or the point where anion exchange becomes limiting.

It was also of interest to examine how different wafer thicknesses would affect the removal rate of ions in a



(a) (b)

FIG. 6. Comparison in single ion removal between modeling and experimentation for (a) potassium and (b) sodium.

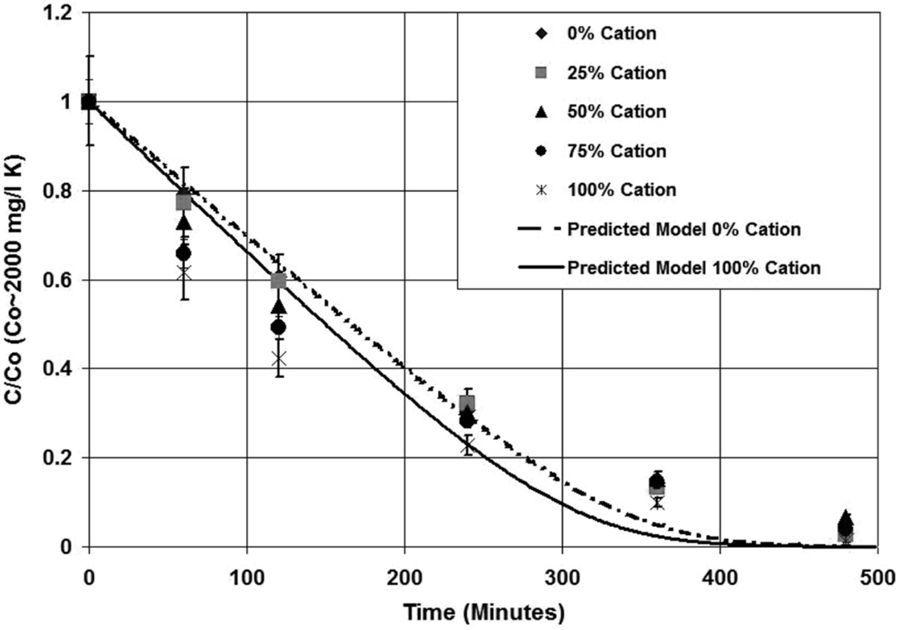


FIG. 7. Potassium ion removal with different cation and anion exchange resin ratios.

WE-EDI system. Experiments were carried out with four different wafers thicknesses: 1.02 mm, 1.27 mm, 1.78 mm, and 2.03 mm using the same procedure as the previous experiment. The potassium ion concentration was ~2000 mg/L for the diluate chamber. The predicted models were performed with different wafer thicknesses: 1.02 and 2.03 mm. The experiment and model prediction are shown in Fig. 8. When the model parameters were varied from 0.05 to 5 mm, we found very little change in the performance of the wafer. Thus the thinner wafers allow for more active surface area per volume and maximum performance. The thinnest wafer that could be run is the most desirable and is about 0.5 mm. At the wafer thicknesses thinner than 0.5 mm, wafer consistency is a big problem.

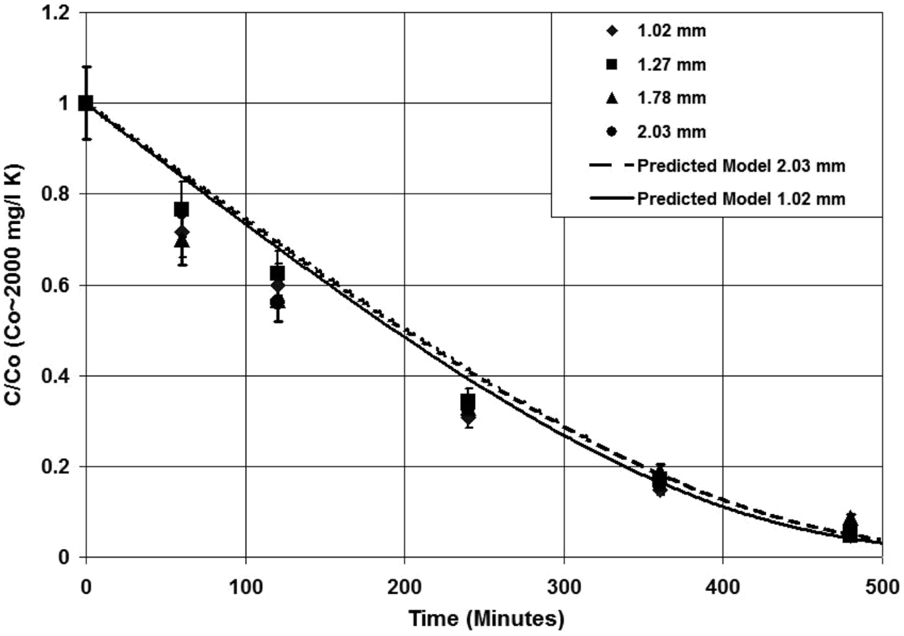


FIG. 8. Potassium ion removal with different wafer thickness.

In earlier experiments of wafer characterization for porosity, capacity, and permeability, the ratio of polyethylene to the total wafer was varied from 0.8 to 1.4. Recalling from Fig. 5, this dropped the ion exchange capacity from 1.05 meq/g resin to 0.95 meq/g resin. Thus, experiments were carried out to investigate how the amount of polyethylene actually affected the performance of WE-EDI in a single component system. The experiments used two wafers with a ratio of polyethylene to total wafers of 1 and 1.4 in ~2000 mg/L potassium ion. The model parameters: packing ratio (α) and fraction of the total ion exchange resin surface area accessible for exchange of ions (β) were calculated from the porosity and the capacity of the wafer, respectively. Packing ratio (1-porosity) turned out to be 0.617 and 0.742 for the polyethylene: total wafer ratio 1 and 1.4, respectively. The fraction β was calculated by the ratio of wafer capacity to the loose resin capacity, which was 0.81 and 0.67 for the polyethylene: total wafer ratio of 1 and 1.4, respectively. The experimental and modeling results are shown in Fig. 9. These results showed that as the ratio of polyethylene to total wafer increased from 1 to 1.4, the removal rate of potassium ion in the WE-EDI system decreased significantly. For instance, after four hours of experimental time, the potassium ion concentration remaining in the diluate compartment was 0.33 ± 0.02 for the ratio of polyethylene to the total wafer of 1 and 0.55 ± 0.02 for the ratio of polyethylene to total wafer of 1.4. The modeling results after four hours show 0.39 for polyethylene: total wafer ratio of 1 and 0.54 for polyethylene: total wafer of 1.4. Although there are some minor differences in experimental and modeling results, both of these results agreed that the more polyethylene that was present in the wafers, the less the wafer enhanced transport in WE-EDI. This happens because as the parameters show, the capacity of the wafer decreases significantly with more polyethylene.

Further, when the capacity of resins was varied from 1.39 meq/g resin to 1.97 meq/g resin (parametric study), the predictive model results are shown in Fig. 10. Figure 10 shows that as the capacity of resins increased the removal rate of potassium increased. For instance, after four hours of experimentation, the potassium concentration remaining in the diluate compartment is 40% the initial potassium concentration for the wafer with ion exchange capacity of 1.39 meq/g resin while the potassium concentration remaining in the diluate compartment is 32% the initial potassium concentration for the wafer with ion exchange capacity of 1.97 mg/g resins. Thus, the wafer capacity was not a major factor in ion transport.

From Figs. 8–10, a discrepancy between the experimental data and model data during the initial period of time are caused by the average equilibrium constant (K) used in the model. In reality, K value varies from high to low as the concentration of ion decreases. Thus the average K value in the model is lower than the actual K value at the initial period of time which caused the model to under predict in the beginning and over predict at the end. It was not thought, however, that the discrepancy was significant enough to justify a K as a function of concentration although this modification could be made.

Moreover, when the equilibrium constant, K, was varied from 1 to 10, the predictive model results show a significant

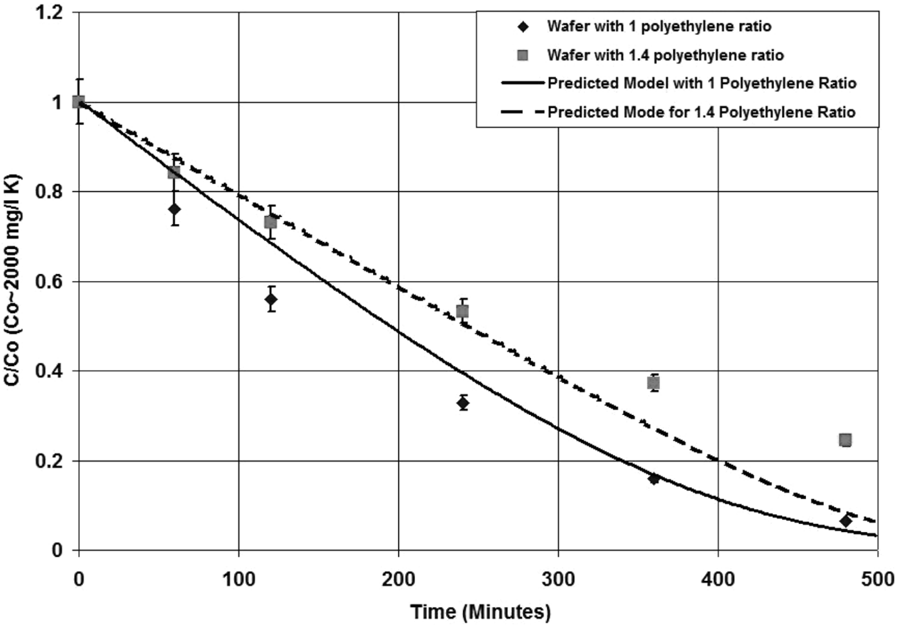


FIG. 9. Potassium ion removal with different polyethylene: total wafer ratio.

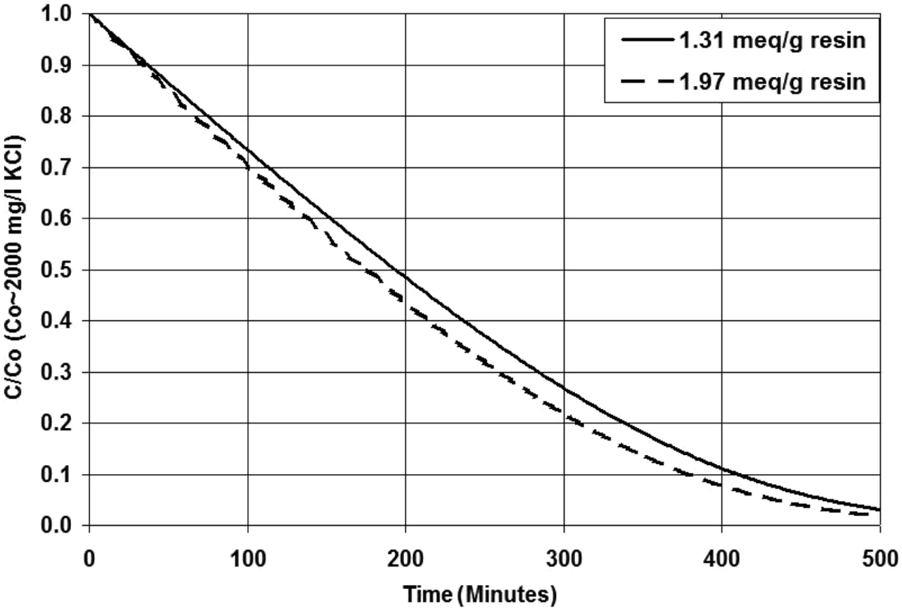


FIG. 10. Parametric study of potassium ion removal with different ion exchange resin capacities.

difference as seen in Fig. 11. Figure 11 shows that as the equilibrium K of the resin increases, the removal rate of potassium increases significantly. For instance, after four hours of experimentation, the potassium ion concentration remaining in the diluate compartment is 48% the initial potassium concentration for K = 1. With the same four hours of experimentation, the potassium ion concentration remaining in the diluate compartment is 30% the initial potassium concentration for K = 10. Thus for future wafer choice, it is recommended that resins with high equilibrium K be chosen (K = 10). With thousands of ion exchange resins to choose from, this is quite possible in WE-EDI. For single ion systems, K was the most significant factor in the rate of transport by WE-EDI.

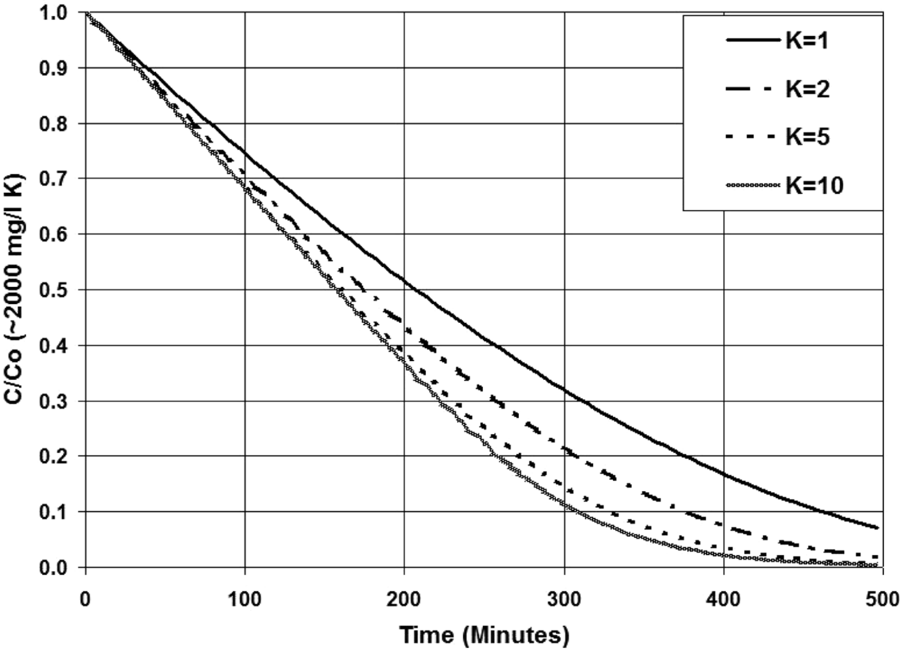


FIG. 11. Parametric study of potassium ion removal with different equilibrium constant (K).

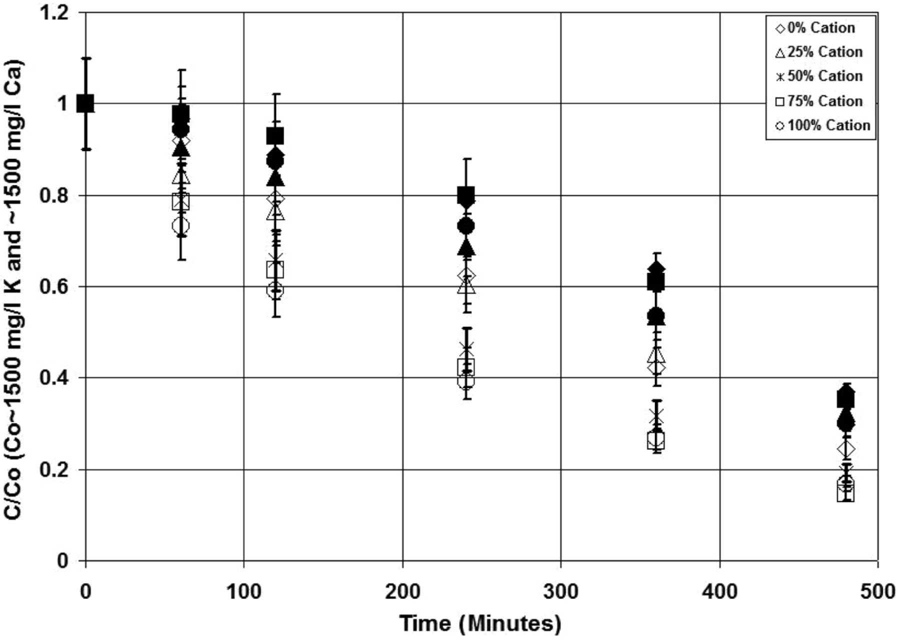


FIG. 12. Potassium (outline) and calcium (filled) ion removal with different cation and anion exchange resin ratios.

Multi-Ion Removals

In many different juice and dairy systems, multi-component separations such as potassium from calcium, are important. Thus, experiments were carried out with ~130 mg/L K^+ (as KCl) and ~1300 mg/L Ca^{2+} (as $CaCl_2$) solutions. The same experimental procedure was followed as described earlier. The total volume of the diluate compartment was 150 ml, the flow rate was 150 ml/min, and the electrical current was 0.04 Amps. The cation: anion exchange resin ratio was varied from 0:100% to 100:0%

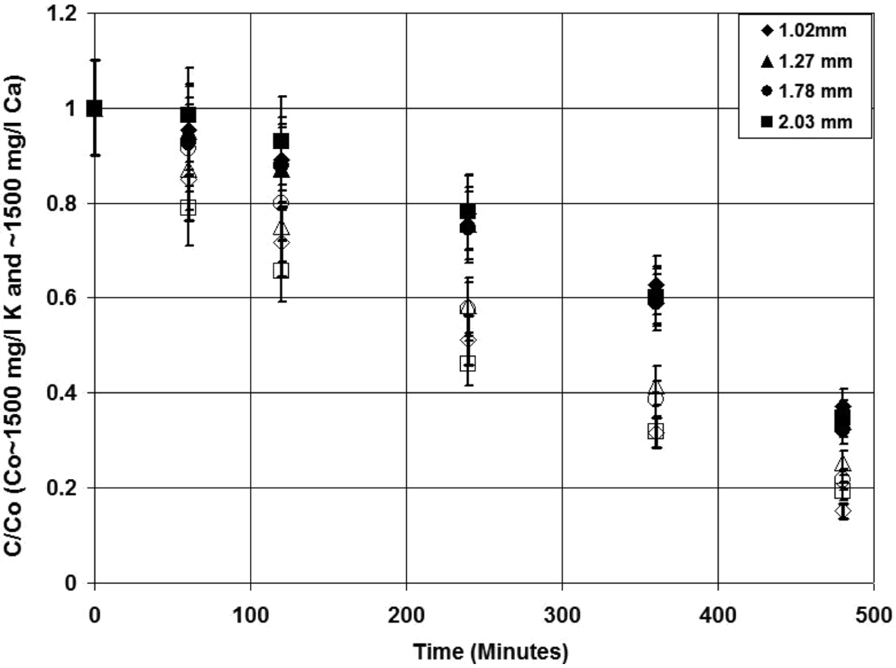


FIG. 13. Potassium (outline) and calcium (filled) ion removal with different wafer thicknesses.

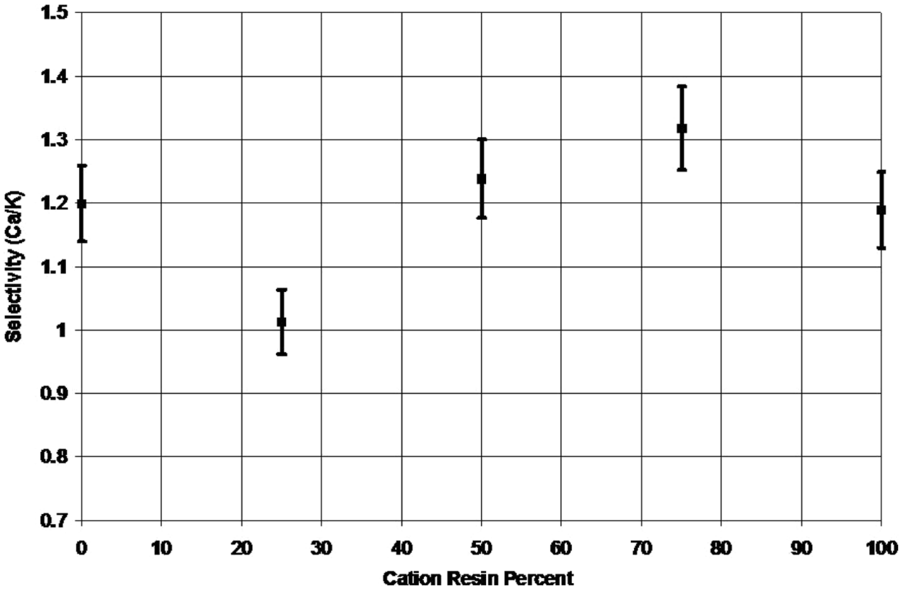


FIG. 14. Selectivity of calcium/potassium with different cation and anion resin ratios.

with 25% increments. Four wafer thicknesses: 1.02, 1.27, 1.78, and 2.03 mm were also tested in these experiments. The experimental results are shown in Figs. 12 and 13.

Figure 13 shows that there was little change in the removal rate of either potassium or calcium ions when the wafers thicknesses were increased from 1.02 to 2.03 mm. However, in Fig. 12, the removal rate of calcium and potassium ions did vary as the ratio of cation to anion resin was adjusted from 0:100% to 100:0%. For instance, after four hours of experimentation, the calcium concentration remaining was 60% the initial calcium concentration, and the potassium concentration remaining was 70% the initial potassium concentration for 25%:75% cation:anion exchange resin wafer. For the same four hours of experimentation, the calcium concentration remaining was 40% the initial calcium concentration, and the potassium concentration remaining was 75% the initial potassium concentration for 25%:75% cation:anion exchange resin wafer. The selectivity of calcium ion over potassium ion in WE-EDI was calculated using Eq. [10]:

$$Selectivity = \frac{(C_{Ca\_initial} - C_{Ca\_final}) * C_{K\_initial}}{(C_{K\_initial} - C_{K\_final}) * C_{Ca\_initial}} \qquad (10)$$

where the removal rate of calcium ion was compared with the removal rate of potassium ion when the ratio of cation to anion resin was varied. The selectivity versus the percentage of cation exchange resin is shown in Fig. 14. Figure 14 shows that when varying the cation: anion exchange resin ratio, the selectivity of ion was minimized at 25% cation exchange resin, although this effect was found to be minor. Since K is the most significant factor in single ion removal, future work will center around the variation of K for the selective removal of ions.

CONCLUSIONS

This study deals with how different wafer properties affected ion removal in a WE-EDI system. From the wafer characterization, the effect of sugar and polyethylene were evaluated in capacity, porosity, and permeability to optimize the ratio of polyethylene and sugar to the total wafer. The optimized wafer composition was 1 polyethylene: 1.5 sugars: 2.3 cation exchange resin: 2.3 anion exchange resin. The wafer characterization also provided enough information to obtain the packing ratio (α) and the fraction of total ion-exchange resin surface area accessible for exchange ions (β) to use in the mathematical modeling.

This paper also demonstrated that when the cation: anion exchange resin ratios and the wafer thicknesses were varied, the removal rate for a single ion system had minimal change. However, increasing the capacity of the resins did have a significant effect on the removal rate of ions. Moreover, the single component model was successfully developed to predict the removal rate for single ion WE-EDI systems.

From the modeling results, for single ion removal, it is recommended to use ion exchange resins with high capacity and high equilibrium constant K for the best ion removal.

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NOMENCLATURE

A	Contact area, cm^2
$\overline{C}$	Bulk or liquid phase concentration of counter-ion species, mg/L
C^0	Counter-ion concentration at the interface between liquid and resin/solid particle, mg/L
C^0_{exit}	Counter-ion concentration exiting the EDI system, mg/L
C_0	Initial concentration in diluate compartment, mg/L
$(C_o)_w$	Initial concentration at the wafer surface, mg/L
C_f	Final concentration, mg/L
D	Diffusion coefficient of ion in the solid face, cm^2/sec
F	Faradays constant, s Amp/mole
f	Flow rate, ml/sec
J	Current density, Amp/cm^2
K	Ion-exchange equilibrium selectivity coefficient
r	Radius of resin particle, cm
m_i	Mass of component I, g
m_{resins}	Mass of the resins in wafer, g
N	(Buffer volume added)/(fixed diluate volume)
Q	Flow rates through the wafer, ml/sec
S_i	Observed solute passage of component i
V	Volume of solution, ml
V_w	Total volume of wafer, cm^3
W	Width of the cell, cm
X	(Initial diluate volume)/(final diluate volume)
ΔP	Change in pressure, N/m^2
α	Packing ratio
β	Fraction of total ion-exchange resin surface area accessible for exchange of ions
η	Current efficiency
η_i	Current efficiency inlet
η_e	Current efficiency outlet
λ_1	Equivalent conductance of counter-ion, $m^2/V/sec$
λ_3	Equivalent conductance of H^+ ion, $m^2/V/sec$
ε	Porosity
ρ_i	Density of component j, g/cm^3
κ	Permeability, cm^2
μ	Viscosity of liquid, g/cm/sec

REFERENCES

1. Bidikar, M.S. (1974) Ion exchange process in food technology. *Indian Chemical Manufacturer*, 13 (1): 89–97.
2. El Khattabi, M.O.; Aloaui, H.; Midaoui, A.E. (1996) Reduction of melassigenic ions in cane sugar juice by electrodialysis. *Desalination*, 107 (2): 149–57.
3. Jirapinyo, P.; Thammonsiri, N.; Suwanthol, L.; Phosuya, P.; Pidacha, P.; Patrarat, S. (2001) Carbohydrate and electrolyte contents in commercial fruit juices. *Journal of Medical Association of Thailand*, 84 (7): 942–7.
4. Leiva, M.; Lopez, H. (1988) The use of electrodialysis in food processing part 2: Review of practical application. *LWT-Food Science and Technology*, 21 (4): 177–82.
5. Bhatia, A.K.; Dang, R.L.; Gaur, G.S. (1979) De-acidification of apple juice by ion exchange resins. *Indian Food Packer*, 33 (1): 15–20.
6. Kochergin, V.; Tzschatzsch, O. (2005) Ion exchange thin juice softening using fractal technology. *Internation Sugar Journal*, 107 (1278): 342–53.
7. Sun, Y.; Grevillot, G.; Tondeur, D. (1990) Modelling and optimiztation of the cyclic regime of an ion-exchange process for sugar juice softening. *The Chemical Engineering Journal*, 43 (2): B53–66.
8. Zanto, L.T.; Bichsel, S.E. (1970) The direct production of liquid sugar from ion exchange treated thick juice. *Journal of the American Society of Sugar Beet Technologists*, 16 (2): 149–54.
9. Bagal, M.V.; Bapat, J.D. (2004) Fouling of ion-exchange resins during deionization of sugarcane juice. *International Journal of Chenical Science*, 2 (2): 241–50.
10. Palacios, V.M.; Caro, I.; Perez, L. (2001) Application of ion exchange techinques to industrial process of must acidification. *Separation and Purification Method*, 30 (1): 143–56.
11. Houldsworth, D.W. (2007) Demineralization of whey by means of ion exchange and electrodialysis. *International Journal of Dairy Technology*, 33 (2): 45–51.
12. Adhikary, S.K.; Harkare, W.P.; Govindan, K.P. (1987) Deacidification of fruit juices by electrodialysis- part II. *Indian Journal of Technology*, 24 (1): 24–7.
13. Mondor, M.; Lam Quoc, A.; Lamarche, F.; Ippersiel, D.; Makhlouf, J. (2005) Assessing ionic transport during apple juice electro-acidification: Influence on system effficiency. *Journal of Membrane Science*, 246 (2): 217–26.
14. Tragardh, G. (1991) Membranes application in the food industry. *Polymer Journal*, 23 (5): 521–9.
15. Bazinet, L.; Lamarche, F.; Ippersiel, D. (1998) Bipolar-membrane electrodialysis: Applications of electrodialysis in the food industry. *Trends in Food Science & Technology*, 9 (3): 107–13.
16. Edmonds, C.; Salem, E. (1998) Demineralization. An economic comparison between EDI and mixed-bed ion exchange. *Ultrapure Water*, 15 (9): 43–9.
17. Zang, J.A.; Moshy, R.J.; Smith, R.N. (1966) Electrodialysis in food processing. *Chemical Engineering Progress Symposium Series*, 62 (69): 105–10.
18. Vu, H.T.; Koshchuh, W.; Novalin, S. (2005) Electrodialysis versus chromatography for desalting silage juice: Comparison of both processes with regard to energy consumption. *Journal of Membrane Science*, 256 (1–2): 78–88.
19. Kang, Y.J.; Rhee, C.K. (2002) Deacidification of mandarin orange juice by electrodialysis combined with ultrafiltration. *Journal of Food Science and Nutrition*, 7 (4): 411–6.
20. Vera, E.; Ruales, J.; Dornier, M.; Sandeaux, J.; Sandeaux, R.; Pourcelly, G. (2003) Deacidification of clarified passion fruit juice using different configurations of electrodialysis. *Journal of Chemical Technology and Bitechnology*, 78 (1): 918–25.
21. Vu, H.T.; Koshchuh, W.; Kulbe, K.D.; Kromus, S.; Krotscheck, C.; Novaldin, S. (2004) Desalination of high salt content mixture by two-stage electrodialysis as the first step of separating valuable substances from grass silage. *Desalination*, 162 (1–3): 343–253.
22. Walters, W.R.; Weiser, D.W.; Marek, L.J. (1995) Concentration of radioactive aqueous wastes - electro-migration through ion exchanges membranes. *Industrial Engineering Chemistry*, 47 (1): 61–7.

23. Jones, C.P.; Pierce, A.; Roberts, B. (2006) Deionization: The use of EDI technology of recycle HF acid wastes from scrubbers and thermal treatment units. *Ultrapure Water*, 23 (5): 34–9.
24. Matzan, E.; Maitino, P.; Tate, J. (2001) Deionization: Cost reduction and operating results of an RO/EDI treatment system. *Ultrapure Water*, 18 (8): 20–4.
25. Wang, J.; Wang, S.; Jin, M. (2000) A study in the electrodeionization process- high-purity water production with a RO/EDI system. *Desalination*, 132: 349–52.
26. Dallbauman, L.; Sirivedhin, T. (2005) Reclamation of prodcuced water for beneficial use. *Separation Science and Technology*, 40 (1): 185–200.
27. Park, J.S.; Song, J.H.; Moon, S.H. (2007) Removal of hardness ions from tap water using electromembrane processes. *Desalination*, (202): 1–8.
28. Mahmoud, A.; Muhr, L.; Grevillot, G.; Lapicque, F. (2007) Experimental tests and modeling of an electrodeionization cell for the treatment of dilute copper solutions. *Can. J. Chem. Eng.*, 85 (2): 171–179.
29. Menzal, T.; Beusshausen, S. (2006) Deionization improvements of semiconductor water treatment using sprial-wound EDI. *Ultrapure Water*, 23 (4): 31–5.
30. Parker, R. (1999) Electrodionization evaluation in a semiconductor fab recycle system. *Semiconductor Pure Water and Chemicals Conference Proceedings*, Pittsburgh, PA.
31. Barber, J.H.; Towe, G.; Tessier, D.F. (2000) EDI operattion for removal weakly-ionized impurities. *Paper presented at International Water Conference*, Pittsburgh, PA.
32. Meyer, N.; Parker, W.J.; Van Geel, P.J.; Adiga, M. (2005) Development of an electrodeionization process for removal of nitrate from drinking water. Part 2: Multi-specices testing. *Desalination*, 175 (2): 167–77.
33. Bouhidel, K.E.; Lakehal, A. (2006) Influence of voltage and flow rate on electrodeionization (EDI) process efficiency. *Desalination*, (193): 411–21.
34. Lee, J.W.; Yeon, K.H.; Song, J.H.; Moon, S.H. (2007) Characrerization of electroregeneration and determination of optimal current density in continuous electrodeionization. *Desalination*, (207): 276–85.
35. Grabowski, A.J.; Zhang, G.; Strathmann, H.; Eigenberger, G. (2006) The production of high purity water by continuous electrodeionization with bipolar membranes: Influemce of the anion-exchange membrane permselectivity. *Journal of Membrane Science*, (281): 297–306.
36. Moon, P.; Sandi, G.; Kizilel, R.; Stevens, D. (2003) Computational simulation of lithium ion transport through polymer nanocomposite membranes. *Journal of New Materials for Electrochemical System*, 6 (4): 237–44.
37. Konduri, S.; Nair, S. (2006) Atomistic simulations of diffusion of small molecules in a Polymer/Nanoporous layered silicate nanocomposite membrane. *Polymeric Materials: Science and Engineering*, 94 (1): 93–4.
38. Lacher, C.; Franzreb, M.; Holl, W.H. (2004) Improving the efficiency of electrodeionization by means of magnetic ion exchange resins. *Powerplant Chemistry*, 6 (8): 465–71.
39. Arora, M.B.; Hestekin, J.A.; Snyder, S.W.; St. Martin, E.J.; Lin, Y.J.; Donnelly, M.I.; Millard, C.S. (2007) The separative bioreactor: A continuous separation process for the simultaneous production and direct capture of organic acids. *Separation Science and Technology*, 42 (1): 2519–38.
40. Arora, M.B.; Hestekin, J.A.; Lin, Y.J.; St. Martin, E.J.; Snyder, S.W. a. Porous solid ion exchange wafer for immobilizing biomolecules. Patent 7306934, filed a, and issued 2007b.
41. Arora, M.B.; Hestekin, J.A.; Lin, Y.J.; St. Martin, E.J.; Snyder, S.W. b. Immobilized biocatalytic enzymes in electrodeionization (EDI). Patent 7306934, filed b, and issued 2007c.
42. Spoor, P.B.; Koene, L.; Janssen, L.J.J. (2002) *J. Appl. Electrochem.*, 32: 369–377.
43. Helfferich, F. (1966) *Ion-Exchange*; McGraw-Hill: London.
44. Verbeek, H.M.; Furst, L.; Neumeister, H. (1999) *Comp. Chem. Eng.*, 22: S913–S916.
45. Danielsson, C-O.; Dahlkild, A.; Velin, A.; Behm, M. (2006) *J. Electrochem. Soc.*, 153 (4): D51–D61.
46. Glueckauf, E. (1959) *British Chemical Engineering*, 1 (1): 646–51.
47. Kurup, A.; Ho, T.; Hestekin, J. (2009) *Ind. Eng. Chem. Res.*, 48 (20): 9268–9277.
48. Perry, R.H.; Green, D.W. (2007) *Perry's Chemical Engineers' Handbook*; 8th Ed.; McGraw Hill: New York, NY.
49. Newman, J.S.; Thomas-Alyea, K.E. (2004) *Electrochemical Systems*; Wiley, New York.
50. Baker, R.W. (2004) *Membrane Technology and Application*, 1st Ed.; Wiley, New York.