Water purification by shock electrodialysis: Deionization, filtration, separation, and disinfection ☆

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HIGHLIGHTS

- Experiments demonstrate the multi-functionality of shock electrodialysis.
- Besides deionization and filtration, nano-particles can be separated by charge.
- Bacteria in the feedwater are either filtered or killed by large electric fields.

GRAPHICAL ABSTRACT
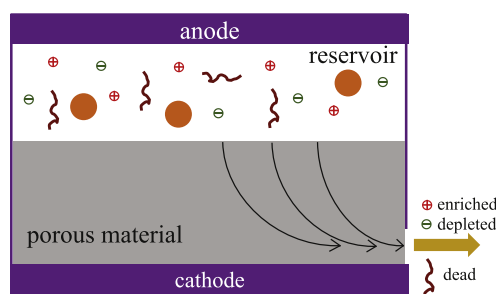
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ABSTRACT

The development of energy and infrastructure efficient water purification systems is among the most critical engineering challenges facing our society. Water purification is often a multi-step process involving filtration, desalination, and disinfection of a feedstream. Shock electrodialysis (shock ED) is a newly developed technique for water desalination, leveraging the formation of ion concentration polarization (ICP) zones and deionization shock waves in microscale pores near to an ion selective element. While shock ED has been demonstrated as an effective water desalination tool, we here present evidence of other simultaneous functionalities. We show that shock ED can thoroughly filter micron-scale particles and aggregates of nanoparticles present in the feedwater. We also demonstrate that shock ED can enable disinfection of feedwaters, as approximately 99% of viable bacteria (here *Escherichia coli*) in the inflow were killed or removed by our prototype. Shock ED also separates positive from negative particles, contrary to claims that ICP acts as a virtual barrier for all charged particles. By combining these functionalities (filtration, separation and disinfection) with deionization, shock ED has the potential to enable highly compact and efficient water purification systems.

1. Introduction

The purification of sea or brackish water is an increasingly important process in areas suffering from water stress or scarcity [1]. State of the art water purification is performed primarily by reverse osmosis (RO) plants and in some cases by electrodialysis (ED) plants [1,2]. In RO and

ED plants, the complete water purification process can be roughly divided into three sequential steps: i) upstream feedwater processing, ii) salt removal (desalination), and iii) downstream processing of the product water [3–5]. In RO plants, to perform desalination, the feedwater is pressurized to above its osmotic pressure, and then flows through an RO membrane which inhibits the transport of salts. In ED, feedwater is flows through an open channel between an anion and cation exchange membrane, and an appropriately directed ionic current is applied to the system, removing anions and cations (dissolved salts) from water [6,7]. Many upstream steps are required in both RO and ED purification system to prevent membrane fouling, including filtration to remove silt (membrane foulants), and pH adjustments of the feedwater [8]. Downstream processes include disinfection of the desalted water through the use of chemical additives such as chlorine [8]. Modern RO plants typically require roughly 4 kWh/m^3 of energy to purify sea water to potable water [3,5], but nearly one third of this total energy is devoted to upstream and downstream processes rather than the desalination itself [4,5]. In some cases, there can also be economic benefits of combining ED and RO in a hybrid desalination process [9].

Shock electrodialysis (shock ED) is a new technique for water desalination that differs from classical ED in several key aspects [10,11]. The theory behind shock ED is a subject of active research [11–17], so here we briefly summarize the basic concepts needed to understand our experiments. In its current realization, a shock ED cell consists of two ion selective elements (ion exchange membranes or electrodes) between which feedwater flows through a charged porous medium with thin double layers that acts as a "leaky membrane" [11,15,16] (Fig. 1). Like ED, when current is passed through the shock ED cell, an ion depleted zone is formed along an ion selective element (the cathode in Fig. 1). As the applied voltage is increased, ion concentration near this element approaches zero, and the system can reach the classical diffusion-limited current [6]. However, unlike ED, in shock ED the presence of a surface charge along the porous media's internal surfaces can enable transport of ions faster than diffusion. There are two theoretically predicted mechanisms [14]: surface conduction by electromigration through the electric double layers of the pores [14,18], which dominates

in submicron pores, and surface convection by electro-osmotic flow vortices in the depleted region [14,17–19], which dominates in micron-scale or larger pores. Experiments in microchannels or pores of different sizes have recently demonstrated and visualized the surface conduction [20] and electro-osmotic flow [11] mechanisms, as well as the transition between them [21]. As a result of this "over-limiting current", the depletion zone can be propagated through the pores as a shock wave (i.e. with a sharp boundary between the depleted and undepleted zones) [12,13,15,16,22,23]. Water flowing through the depletion zone is separated and emerges from the cell as desalinated water [11]. In shock ED [10,11], an ion enrichment or brine zone is formed at the opposite ion selective element, and the formation of enriched and depleted zones at opposite ends leads to strong ion concentration polarization (ICP) [6,7].

Previously, we developed a shock ED prototype using a porous silica glass frit with micron-scale pores as the porous medium, a copper electrode as the anode-side ion selective element, and a Nafion ion exchange membrane as the cathode-side ion selective element [11]. With this device, we demonstrated the deionization of a copper sulfate solution by reducing its concentration by roughly 4 orders of magnitude in two passes (to 10 μM). Further, our measurements of overlimiting conductance suggested that the overlimiting current mechanism in our prototype device was electroosmotic flow rather than surface transport [11]. Compared to recently-developed microfluidic approaches leveraging ICP for water desalination [24,25], shock electrodialysis is a more scalable technology, as its use of porous media can enable high throughput without requiring the fabrication of many parallel microfluidic systems [11]. Another unique feature of shock ED is the ability to propagate the depletion zone controllably through micron-scale frit pores, enabling a tunable ion depletion zone which can extend to millimeters or larger in length to further increase throughput.

In this work, we demonstrate that our shock ED cell can perform a number of functions in addition to (and simultaneously with) water desalination, including filtration, disinfection, and ion separations (see Fig. 1). Both filtration and disinfection are important processes in modern water purification plants [3,8]. With our cell, we demonstrate the
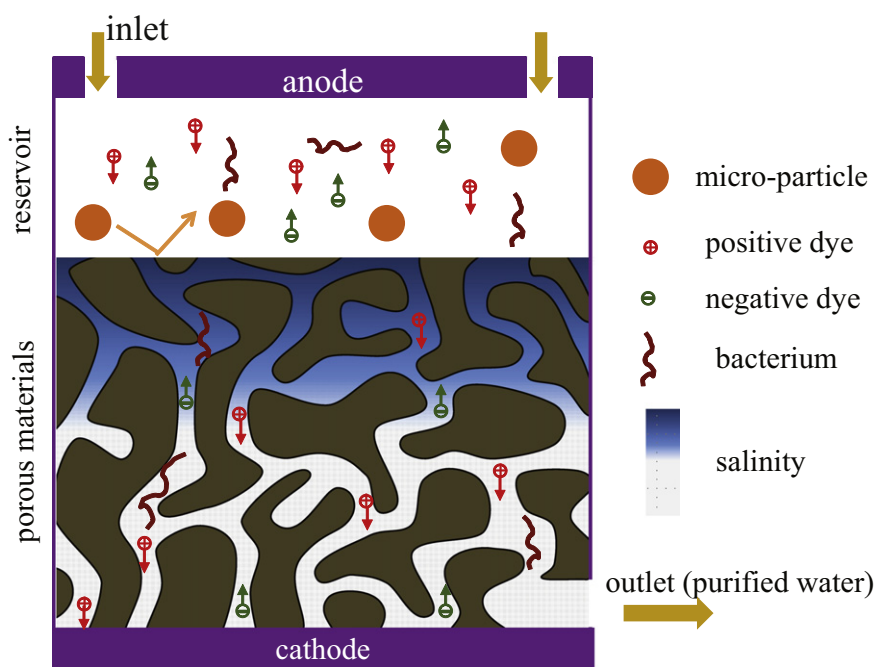

Fig. 1. Schematic demonstrating water purification with our shock ED device. Our shock ED cell consists of two ion selective elements (electrodes or ion exchange membranes) between which is placed a porous media. By passing an ionic current between the ion selective elements, a salt depletion zone is formed near to the cathode. In addition to leveraging the depletion zone to produce desalinated water, the device demonstrates other unique functionalities, including filtration of particulates, spatial separation of species by valence sign, and disinfection.

filtration of micron-scale particles and aggregates of nanoscale particles present in the feedwater, and we hypothesize that this was due to steric hindrance by our microporous frit. We further demonstrate that approximately 99% of *Escherichia coli* bacteria placed in the feedwater were killed or removed upon flow through our shock ED prototype, illustrating the potential for in-situ and additive-free disinfection in shock ED. In addition, we show that our prototype can continuously separate electrochemically inactive ions by charge, consistent with theory [26] but contradicting claims that ICP acts as a "virtual barrier" to all charged species [24].

2. Materials and methods

2.1. Shock ED device

A schematic and a photograph of our shock ED device are shown in Fig. 2a and b. The setup consists of a cylindrical silica glass frit (Adams & Chittenden Scientific Glass), which is 1 mm thick and has a 5 mm radius. The frit is placed against a Nafion membrane, and the membrane is in direct contact with the copper disk cathode. The frit is separated from the copper disk anode by a reservoir of copper sulfate ($CuSO_4$) electrolyte (3 mm thick reservoir). The frit has a random microstructure with pores roughly 500–700 nm in diameter (Fig. 2c, d), an internal surface area (measured via BET) of $a_m = 1.75$ m^2/g, porosity of 0.4, and a density of $\rho_m = 1.02$ g/cm^3. The pore surfaces are negatively charged, and the magnitude of the charge depends on copper sulfate concentration [11]. The charged surfaces promote the (faster-than-diffusion) transport of positive copper ions to the cathode via electroosmotic flows, leading to overlimiting currents [11].

2.2. Sample preparation

A 1 M $CuSO_4$ stock solution was prepared by dissolving 2.5 g of $CuSO_4$ (Science Company) into 10 mL of deionized water. This stock solution was further diluted 10 times to obtain 0.1 M $CuSO_4$ solution, and again diluted to obtain 1 mM $CuSO_4$ solution. To demonstrate size-based filtration, two suspensions were prepared by adding 50 μm diameter green fluorescent polymer microspheres (Thermo Scientific) and 50 nm diameter red fluorescent nanoparticles (Thermo Scientific) into 1 mM $CuSO_4$ solution. The concentration of these suspensions was 20 mg/mL and 2 mg/mL, respectively. To demonstrate charged-based separation, positively and negatied charged fluorescent dye solutions were also prepared. For positively charged dye, 2×10^{-5} g/mL of Rhodamine B fluorescent dye was mixed into 1 mM $CuSO_4$. The pH of this solution was measured to be 4.2, far enough below Rhodamine's isoelectric point of 6 to ensure that the dye is positively charged [27–29]. For negatively charged dye solution, 1 mg/mL of fluorescein dye (Sigma-Aldrich) was mixed into 1 mM $CuSO_4$ [30], and 50% volume of isopropyl alcohol was added to ensure solubility.

In order to evaluate the disinfection capabilities of the device, we prepared suspensions of *E. coli* K12 (ATCC). The bacteria were cultured in LB broth at 37° with shaking, and when they reached log phase, were resuspended in 1.5 M NaCl solution. This concentration was selected to minimize osmotic shock upon transfer from the LB broth. After experiments were completed, the bacteria were stained with a BacLight live/dead staining kit as per the manufacturer's instructions (Invitrogen) and thus the live cells could be observed with a microscope. Control samples of *E. coli* were left suspended in the NaCl solution while testing was conducted, and little or no degradation was observed to their viability upon completion of the experiment.

2.3. Device operation

An electrochemical analyzer (Uniscan instruments PG581) was used to apply a voltage to the device. The analyzer's reference and counter electrode leads were connected to the anode, and the working electrode lead was connected to the cathode. After about 10 min, the current reached steady state, and collection of fluid from the outlet of the device began. As indicated in Fig. 2a, the fluid flow was directed towards the cathode side of the device (to force flow through the depletion zone). Flow rate was precisely controlled by a syringe pump (Harvard Apparatus), and the fluid extraction time varied from several minutes to several tens of minutes in order to collect roughly 1 mL of fluid from the outlet for accurate post-experiment analysis.
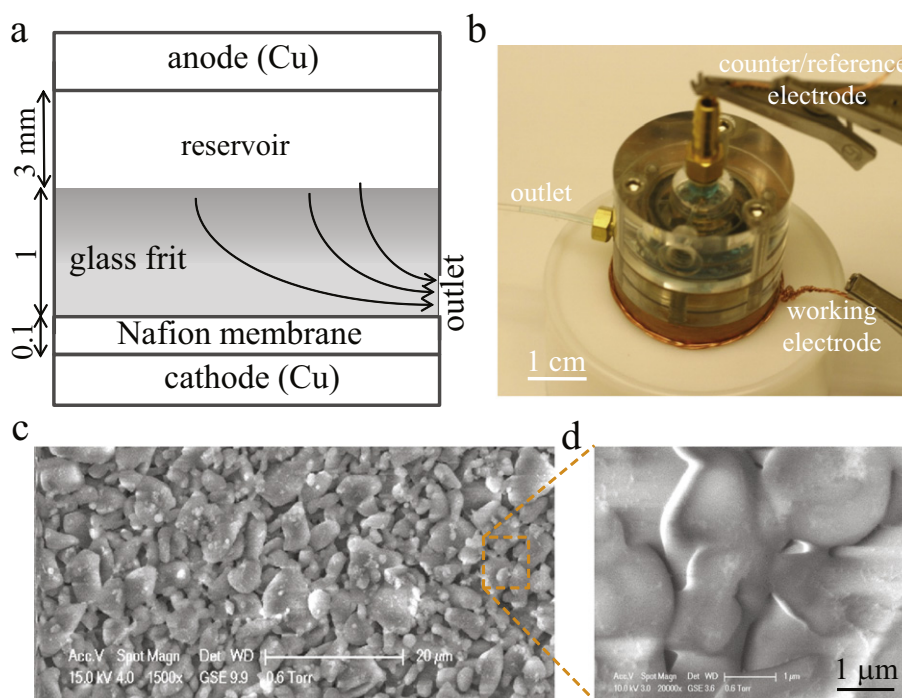

Fig. 2. Description of the prototype shock ED device used in this work. (a) A sketch of the frit/membrane/electrode sandwich structure (not to scale), where arrows indicate the fluid flow direction; (b) a photograph of shock ED device; (c) a SEM micrograph of glass frit showing its pore structure, and (d) enlarged micrographs indicating pore size around 500–700 nm.

2.4. Microscopy

A Nikon Ti–U inverted fluorescence microscope, a 4× or 10× objective, and a Photometrics Coolsnap HQ2 CCD camera were used to capture optical micrographs of samples of fresh solutions or solutions from the outlet of the device 4× and 10× objectives were used in conjunction with a hemocytometer to count the bacteria. To count live *E. coli* cells or particles, samples were loaded into a hemocytometer (INCYTO). The grid pattern on the hemocytometer is explicitly designed for use with lower-powered objectives. In our case, the lower magnification was desirable in order to achieve decent counting statistics on low concentration samples. Illumination was provided by a mercury lamp (Intensilight) for the fluorescence images, and a standard lamp for the bright field images. For *E. coli*, the live/dead cell counting was done using a Nikon C-FL B-2E/C FITC Filter for the live bacteria (dyed with Syto BC, thus appearing green) and a Nikon C-FL Texas Red HYQ for the dead bacteria (dyed with Propidium Iodide, thus appearing red). Image analysis was performed using ImageJ software, either to count the number of particles, count live and dead cells, or to measure the integrated fluorescent intensity of the fluorescent dye solution. In experiments involving fluorescent dyes, any photobleaching effects were not significant as we confirmed that there was no decrease in the integrated fluorescence of a control sample kept next to the device over the course of the experiment.

3. Results and discussion

3.1. Filtration based on size

In contrast to electrodialysis [31], shock electrodialysis utilizes a charged porous glass frit placed between ion exchange membranes to enable overlimiting current [14] and propagate a deionization shock wave [12,13,15,16]. The frit in a shock ED system can also be used as a filter to sterically exclude undesirable particles from the flow (for example, particulates in feedwater in a water purification process). The glass frit in our prototype has pore diameters between roughly 500 and 700 nm, so micron-scale particles can potentially be largely excluded from the fluid at the outlet.

In the first experiment, the reservoir was filled with the suspension of 50 μm particles in copper sulfate solution. We then flowed this suspension through the shock ED device (from anode to cathode), without applying electric field, and captured the effluent. The microscopy image taken of the inlet solution is shown in Fig. 3a, and here we can observe the particles as dark dots. As shown in Fig. 3b, the absence of particles was observed in the outflow solution, demonstrating that our shock ED prototype successfully filtered out these particles.

In a similar experiment, we investigated the behavior of particles with diameter less than the frit pore size using the suspension of 50 nm-diameter particles in aqueous copper sulfate solution. From the image of the inlet solution in Fig. 3c, the nanoparticles appeared to flocculate into aggregates due to surface interactions [32,33]. Due to the spatial resolution limitations of optical microscopy, we could not observe directly any unaggregated 50 nm-diameter particles potentially present in solution. However, we observed that the aggregates were large enough to be filtered by porous medium, as no aggregates were observed in the effluent samples (Fig. 3d).

3.2. Disinfection

Removing waterborne pathogens is a critical part of many water purification processes [1,34]. State-of-the-art reverse osmosis (RO) desalination plants utilize dedicated post-treatment procedures for water disinfection, typically the addition of chlorine or chlorine by-products, to eliminate most harmful microorganisms [35]. The shock ED device investigated here utilizes a glass frit with submicron-radius pores that can potentially serve as a filter to remove many biological species during deionization, eliminating the need for any post-treatments. In addition, we postulate that the high electric fields present in the deionization region may further reduce the survival rate of any microorganisms that make it through the glass frit.

To demonstrate the disinfection functionality in our device, we measured the change in concentration and viability of a suspension of *E. coli*
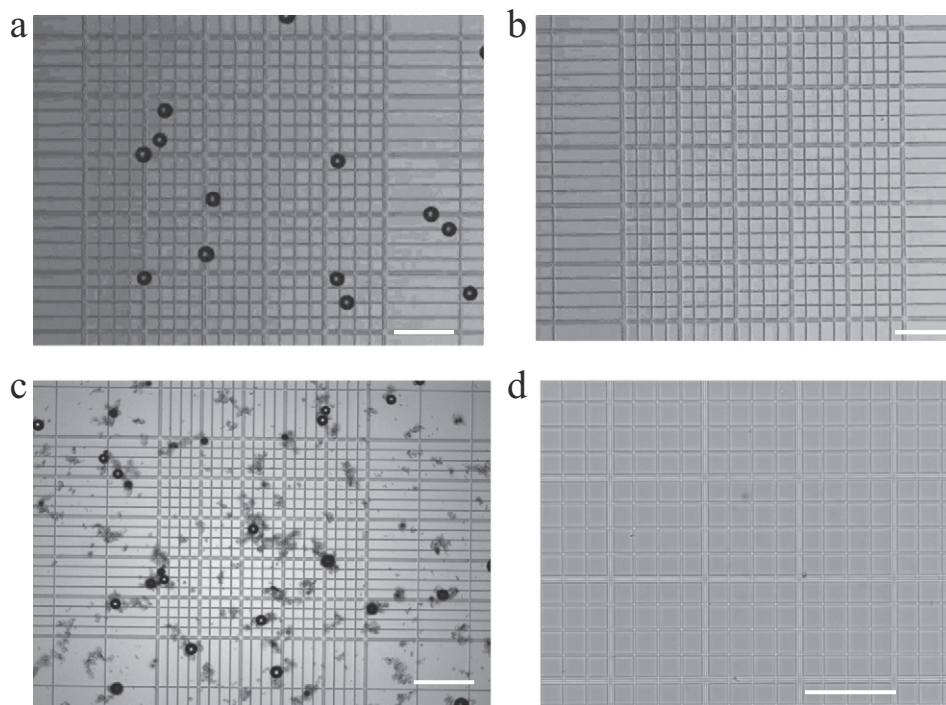

Fig. 3. Results demonstrating the size-based filtration of our shock ED device. Bright field images for the feedwater (a) and (c), and images on a sample from the corresponding outflow (b) and (d). The particles with 50 μm diameter were completely removed from inlet (a) to outlet (b). Aggregates of 50-nm-diameter nanoparticles were also filtered from inlet (c) to outlet (d). Scale bars are 200 μm.

between the inlet and outlet of the device. It is difficult to assess the impact of the shock electrodialysis process for disinfection in the original experiments because copper sulfate solution is not a good medium for cells, so a different electrolyte, 1.5 M sodium chloride (NaCl), was used for these experiments to ensure bacteria viability (see the Materials and methods section.) A sample of the inlet *E. coli* solution is shown in Fig. 4a. The bacteria were stained with a live-dead kit prior to microscopy, and so live bacteria appear green, and dead as red. Using our microscopy setup, we performed a cell counting analysis which showed that the inlet sample contains bacteria which were 99 ± 0.4% viable. Outlet samples were taken under two conditions: one with a flow rate of 0.2 μL/min through the device under the applied voltage at 1.5 V, shown in Fig. 4c, and the other with the glass frit removed and without any applied voltage, as shown in Fig. 4b. When Fig. 4b is compared with Fig. 4a, there is an observable drop in concentration, possibly due to adhesion at points in the system, but the key point is that the bacteria are still largely viable with only very few dead cells.

The data demonstrate significant disinfection that depends on forced convection through the porous medium, as well as the action of the applied electric field. When Fig. 4c is compared with Fig. 4a, using the system with the frit results in yet lower concentrations, and larger numbers of dead cells. More quantitatively, with the frit removed, cell viability was measured to be to 96.4 ± 0.9%. With the frit in place, we measured a much reduced viability of the bacteria in the outlet sample, which was 28 ± 8%. We also observed (with the frit in place and under the applied voltage) a strong reduction in the concentration of cells in the outlet sample, as shown in Fig. 4c. Here, in the outlet sample, 96.5 ± 1.8% of bacteria were absent relative to the reservoir sample. Combined with the reduced viability of the outlet sample, roughly 1% of initially viable bacteria remained present and viable in the outlet sample when the frit was in place. We hypothesize that the latter results are due to both steric exclusion of a majority of the bacteria from the frit pore space (*E. coli* have typically micron-scale dimensions [36]), and an inhospitable environment to the bacteria which are able enter the glass frit.

We further hypothesize that the strong electric fields arising in the ion depletion zone can also reduce further the viability of the bacteria passing through the device [37]. Previous studies have shown that an electric field of roughly 0.8–2 V/μm can promote cell death [38,39]. However, we were unable to reliably test this hypothesis in this work, because the use of sodium chloride rather than copper sulfate likely inhibited the formation of a concentration shock (and thus a strong electric field) in our prototype. With sodium chloride (and copper electrodes), our device relied on water electrolysis electrode reactions rather than copper redox reactions to pass a current through the device, which can cause zones of perturbed pH to enter the system [40]. Future work will develop prototypes capable of generating shocks in sodium chloride and other general electrolytic solutions, allowing us to test the effect of depletion zone electric fields on bacteria survival.

3.3. Separation based on charge

In microfluidic devices leveraging ICP to perform molecular sample stacking [41] and water desalination [24], the ion depletion zone was reported to act as a "virtual barrier" for all charged particles (both positively and negatively charged). A possible mechanism for such charge-independent attraction is diffusio-phoresis [42–44], in which charged particles climb a salt concentration gradient in the absence of an applied electric field. When current is being passed, however, this effect competes with classical electrophoresis in the joint phenomenon of electro-diffusiophoresis studied by Malkin and A. Dukhin [45]. Rica and Bazant have shown that electrophoresis generally dominates diffusiophoresis in large concentration gradients due to the enhanced electric field of the depleted solution [26], thus enabling separation by charge in particle flows through regions of ICP. Recently, Jeon et al. analyzed the forces acting on charged particles flowing through the depletion region in microfluidic ICP with negatively charged channel walls and reached consistent conclusions, that negatively charged (counterionic) species are repelled from the depletion zone via strong electrophoretic forces, while positively charged species cannot be repelled
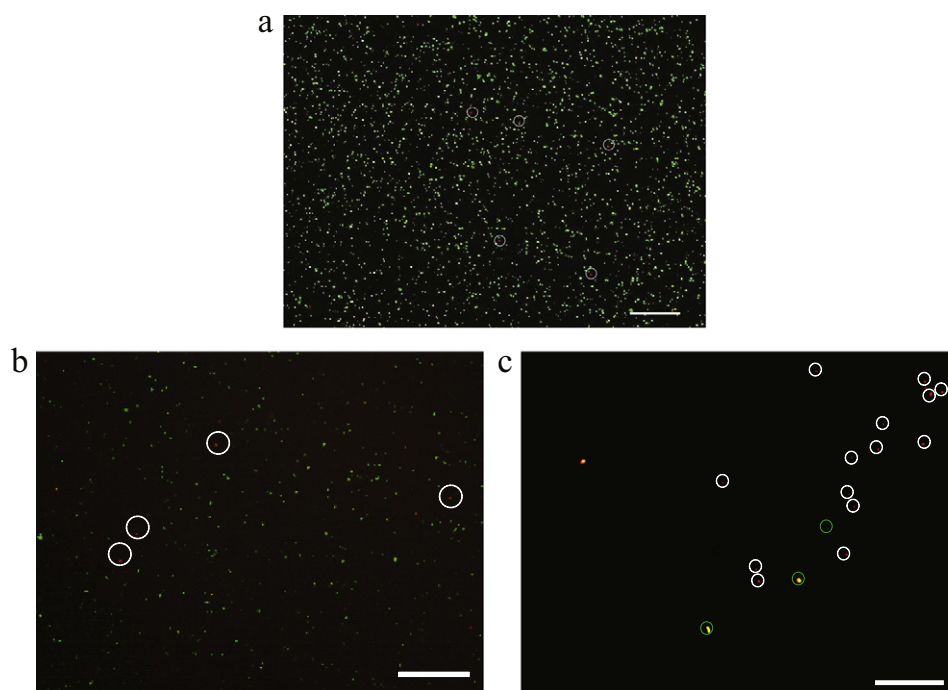
Fig. 4. Results demonstrating the disinfection of a feedwater containing *E. coli* as a model bacteria. (a) Microscopic image of the feedwater, (b) image of a sample from the outlet stream of the device without the porous frit and at zero voltage, showing some cell adsorption but little disinfection (cell death), and (c) an outlet stream image from the device with porous frit included at an applied voltage (1.5 V) and outlet flow rate (0.2 μL/min), showing strong disinfection and filtration. The live bacteria are fluorescent green, and the dead bacteria are red. Scale bar is 200, 500, and 500 μm, for (a)–(c) respectively.

[37]. Jeon et al. further developed a device which separated negatively charged particles via the deflection of their path through the depletion zone (where the extent of deflection correlated to the particles' electrophoretic mobility) [37].

In this work, we show that ICP can in fact accelerate the passage of positively charged species, thus contradicting the virtual barrier claim and demonstrating, apparently for the first time, charge-based separation by the ion depletion zone. Naturally this nonlinear electrophoretic effect only applies to particles small enough to pass through the pores and avoid filtration. In order to demonstrate the effect of the depletion zone on positively charged species, we injected the positively charged Rhodamine dye solution into the device reservoir, and applied a constant voltage of 1.5 V. Note that Rhodamine is considered a non-electrochemically active species, as it does not participate in the electrode reactions (electrode reactions include the positively charged copper ions). The solvated molecule has an effective size of only a few nanometers, so no size-based filtration takes place in our device. Based on the applied electric field, the positively charged dye was expected to move via electrophoretic forces towards the cathode where they accumulate, forming an enrichment region near the outlet. The outlet and reservoir concentrations of Rhodamine were calculated by injecting samples into a hemocytometer chip, and measuring their integrated fluorescent intensities (I) using an optical microscope.

As expected, the dye concentration at the outlet was observed to be greater than at that of the reservoir. Quantitatively, we defined the enhancement ratio of fluorescent intensity as I_{inlet}/I_{outlet}, where I_{inlet} is the integrated fluorescent intensity of solution in the inlet or reservoir, and I_{outlet} is the integrated fluorescent intensity of solution extracted from the outlet. This enhancement ratio is shown in Fig. 5a as a function of extraction flow rate. As the flow rate decreased, the effluent became more enriched in Rhodamine as the integrated fluorescent intensity of solution increased. When no voltage was applied to the shock ED device, as expected, no concentration enhancement was observed in the effluent solution.

The experiment was then repeated with the negatively charged fluorescein dye solution. In contrast to the positively charged dye, the fluorescein was expected to migrate electrophoretically towards the anode, thus being "repelled" from the depletion zone by the large electric field there. When the dye concentration was measured quantitatively at the inlet and outlet (at the cathode-side), we observed a depletion of fluorescein at the outlet as expected. The removal ratio, defined as I_{inlet}/I_{outlet}, is shown as a function of flow rate in Fig. 5b, and this ratio increased with increasing flow rate.

4. Discussion and conclusion

In summary, we have demonstrated that shock ED devices can perform many functions in addition to (and simultaneously along with) water desalination, including filtration, disinfection and separations by charge and by size. As shock ED employs a microporous frit within the flow channel between the membranes, we were able to demonstrate steric filtration of microscale particles and aggregates of nanoscale particles. Further, we were able to kill or remove approximately 99% of viable *E. coli* bacteria present in the feedwater upon flowing through the shock ED device with applied voltage. We hypothesize that further reductions in bacteria viability are achievable via the presumably strong electric fields present within the shock region, and future work will focus on building a prototype capable of testing this hypothesis. Lastly, we demonstrated that our shock ED device can continuously separate positively charged species from negatively charged ones that are small enough to pass into the porous frit.

These demonstrated functionalities can be applied to water purification systems (filtration, disinfection), as well as particulate, molecular or biological separation systems, and demonstrate the potential of shock ED as a versatile new technique for chemical engineering. As in our initial experimental publication [11], here we used a simple first prototype that sustains direct current by electrodeposition/dissolution reactions at copper electrodes and does not separate the brine produced near the anode, as required for continuous operation. We are currently building and testing a proposed scalable prototype capable of continuous desalination and water purification of arbitrary feed water (see Fig. 6 of Ref. [11]). The complete shock ED system consists of a stack of negatively charged porous media separated by cation exchange membranes with electrode streams sustaining the current by water electrolysis.

An important potential application could be to treat produced water from hydraulic fracturing of unconventional oil and gas reservoirs [46]. It has recently been argued that classical ED is an economically viable technology to address this grand challenge in water treatment, if membrane fouling and pre/post-processing were not overly costly issues [47]. Our results suggest that shock ED could be even more attractive, as it retains most of the benefits of classical ED, while incorporating filtration and charge-based colloidal separation in a single compact system. Moreover, the demonstrated electrical disinfection capability should dramatically reduce fouling of the cation exchange membranes, thus eliminating a major lifetime and cost concern. Unlike classical ED, any size-filtered or electrophoretically separated particles
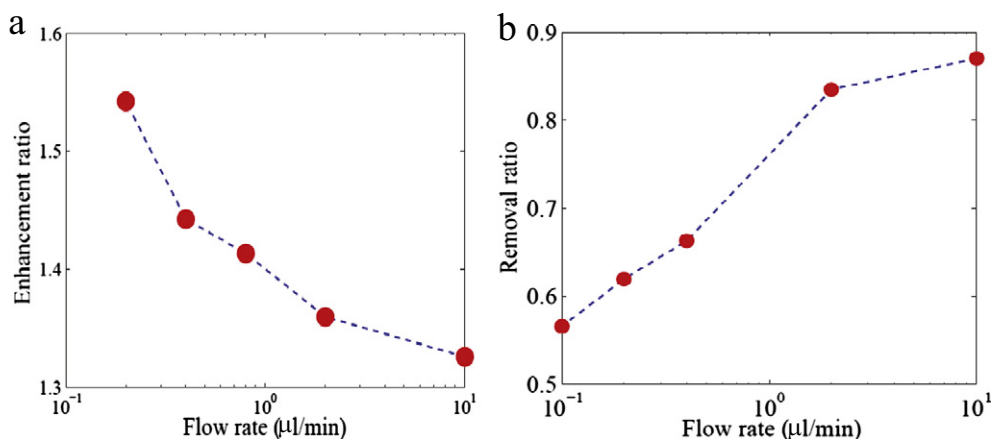
Fig. 5. Results demonstrating the charge-based separation of non-electrochemically active ions by our shock ED device. (a) The observed enhancement ratio of a fluorescent, positively charged dye versus flow rate of feedwater through the device. Enhancement ratio is the ratio of dye concentration (fluorescent intensity) of the outlet sample to the feedwater sample. Enhancement ratio is always greater than unity, indicating that positively charged dye accumulated in the depletion zone of the device. Enhancement ratio decreases as flow rate is increased. (a) The observed removal ratio of a fluorescent, negatively charged dye versus flow rate. Removal ratio is also defined as the ratio of dye concentration (fluorescent intensity) of the outlet sample to the feedwater sample, but in this case, this ratio is always below unity indicating that negatively charged dye was repelled from the depletion zone. Removal ratio increases as flow rate is increased.

are prevented from reaching the membranes, thereby further reducing clogging and fouling of the most expensive component of the system. In contrast, the frit or other porous medium is cheap and could be periodically replaced.

Other system designs and applications are also possible. For example, in order to avoid the need for Faradaic reactions, such as water splitting, to sustain the current, shock ED could also be performed with blocking porous electrodes to drive salt depletion, as in (membrane [48]) capacitive deionization [49,50]. The use of metal electrodeposition to sustain the current at the cathode, even without a membrane, could also enable selective metal separation to be added as yet another simultaneous functionality. The dissolved molecules or colloidal particles would separate via shock-ED fractionation in the leaky membrane in cross flow, while dissolved metal ions could be selectively removed by "shock electrodeposition" at the cathode [20], all in one continuous unit process.

Acknowledgments

References

[1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marioas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (2008) 301–310.

[2] Y.-M. Chao, T. Liang, A feasibility study of industrial wastewater recovery using electrodialysis reversal, Desalination 221 (2008) 433–439.

[3] B. Sauvet-Goichon, Ashkelon desalination plant — a successful challenge, Desalination 203 (2007) 75–81.

[4] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, Science 333 (2011) 712–717.

[5] R. Semiat, Energy issues in desalination processes, Environ. Sci. Technol. 42 (2008) 8193–8201.

[6] R. Probstein, Physicochemical Hydrodynamics, Wiley Online Library, 1994.

[7] V. Nikonenko, N. Pismenskaya, E. Belova, P. Sistat, P. Huguet, C. Pourcelly, C. Larchet, Intensive current transfer in membrane systems: modeling, mechanisms and application in electrodialysis, Adv. Colloid Interface Sci. 160 (2010) 101–123.

[8] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.

[9] R.K. McGovern, S.M. Zubair, V.J.H.L., The benefits of hybridising electrodialysis with reverse osmosis, J. Membr. Sci. 469 (2014) 326–335.

[10] M.Z. Bazant, E.V. Dydek, D.S. Deng, A. Mani, Method and apparatus for desalination and purification. US Patent Application 2011, 0308953.

[11] D. Deng, E. Dydek, J.-H. Han, S. Schlumpberger, A. Mani, B. Zaltzman, M.Z. Bazant, Overlimiting current and shock electrodialysis in porous media, Langmuir 29 (2013) 16167–16177.

[12] A. Mani, T.A. Zangle, J.G. Santiago, On the propagation of concentration polarization from microchannel/nanochannel interfaces. Part I: analytical model and characteristic analysis, Langmuir 25 (2009) 3898–3908.

[13] A. Mani, M.Z. Bazant, Deionization shocks in microstructures, Phys. Rev. E. 84 (2011) 061504.

[14] E.V. Dydek, B. Zaltzman, I. Rubinstein, D.S. Deng, A. Mani, M.Z. Bazant, Overlimiting current in a microchannel, Phys. Rev. Lett. 107 (2011) 118301.

[15] E.V. Dydek, M.Z. Bazant, Nonlinear dynamics of ion concentration polarization in porous media: the leaky membrane model, AIChE J. 59 (2013) 3539–3555.

[16] A. Yaroshchuk, Over-limiting currents and deionization "shocks" in current-induced polarization: local-equilibrium analysis, Adv. Colloid Interf. Sci. 183–184 (2012) 68–81.

[17] I. Rubinstein, B. Zaltzman, Convective diffusive mixing in concentration polarization: from Taylor dispersion to surface convection, J. Fluid Mech. 728 (2013) 239–278.

[18] C.P. Nielsen, H. Bruus, Concentration Polarization, Surface Currents, and Bulk Advection in a Microchannel, 2014. (arXiv:1408.4610 [physics.flu-dyn]).

[19] A. Yaroshchuk, E. Zholkovskiy, S. Pogodin, V. Baulin, Coupled concentration polarization and electroosmotic circulation near micro/nanointerfaces: Taylor–Aris model of hydrodynamic dispersion and limits of its applicability, Langmuir 27 (2011) 11710–11721.

[20] J.-H. Han, E. Khoo, P. Bai, M.Z. Bazant, Over-limiting current and control of dendritic growth by surface conduction in nanopores, Sci. Rep. 14 (2014) 7056.

[21] S. Nam, I. Cho, J. Heo, G. Lim, M.Z. Bazant, G. Sung, S.J. Kim, Experimental Verification of Overlimiting Current by Surface Conduction and Electro-osmotic Flow in Microchannels, 2014. (arXiv:1409.2956 [physics.flu-dyn]).

[22] T.A. Zangle, A. Mani, J.G. Santiago, On the propagation of concentration polarization from microchannel/nanochannel interfaces. Part II: numerical and experimental study, Langmuir 25 (2009) 3909–3916.

[23] M.E. Suss, A. Mani, T.A. Zangle, J.G. Santiago, Electroosmotic pump performance is affected by concentration polarizations of both electrodes and pump, Sensors Actuators A Phys. 165 (2011) 310–315.

[24] S.J. Kim, S.H. Ko, K.H. Kang, J. Han, Direct seawater desalination by ion concentration polarization, Nat. Nanotechnol. 5 (2010) 297–301.

[25] K.N. Knust, D. Hlushkou, R.K. Anand, U. Tallarek, R.M. Crooks, Electrochemically mediated seawater desalination, Angew. Chem. Int. Ed. 52 (2013) 8107–8110.

[26] R. Rica, M.Z. Bazant, Electrodiffusiophoresis: particle motion in electrolytes under direct current, Phys. Fluids 22 (2010) 112109.

[27] Kimberley F. Schrum, S. E. J., Joseph M. Lancaster, S.D. Gilman, Monitoring electroosmotic flow by periodic photobleaching of a dilute, neutral fluorophore, Anal. Chem. 72 (2000) 4317–4321.

[28] A.L. Garcia, L.K. Ista, D.N. Petsev, M.J. OBrien, P. Bisong, A.A. Mammoli, S.R.J. Brueck, G.P. Lopez, Electrokinetic molecular separation in nanoscale fluidic channels, Lab Chip 5 (2005) 1271–1276.

[29] Y.-J. Oh, T.C. Gamble, D. Leonhardt, C.-H. Chung, S.R.J. Brueck, C.F. Ivory, G.P. Lopez, D.N. Petseva, S.M. Han, Monitoring FET flow control and wall adsorption of charged fluorescent dye molecules in nanochannels integrated into a multiple internal reflection infrared waveguide, Lab Chip 8 (2008) 251–258.

[30] E.M. Buharova, I. M. V., A.M. Saletsky, Structure of molecular associates of fluorescent probes in solutions of human serum albumin, J. Appl. Spectrosc. 75 (2008) 785–790.

[31] H. Strathmann, Ion-exchange Membrane Separation Processes, vol. 92004. (Access Online via Elsevier).

[32] Ernest M. Hotze, T. P., G.V. Lowry, Nanoparticle aggregation: challenges to understanding transport and reactivity in the environment, J. Environ. Qual. 39 (2010) 1909–1924.

[33] Adamo R. Petosa, I. R. Q. M. E., Deb P. Jaisi, N. Tufenkji, Aggregation and deposition of engineered nanomaterials in aquatic environments: role of physicochemical interactions, Environ. Sci. Technol. 44 (2010) 6532–6549.

[34] D.T. Schoen, A.P. Schoen, L. Hu, H.S. Kim, S.C. Heilshorn, Y. Cui, High speed water sterilization using one-dimensional nanostructures, Nano Lett. 10 (2010) 3628–3632.

[35] C.A. Martinez-Huitle, E. Brillas, Electrochemical alternatives for drinking water disinfection, Angew. Chem. Int. Ed. 47 (2008) 1998–2005.

[36] K. Asami, T. Hanai, N. Koizumi, Dielectric analysis of Escherichia coli suspensions in the light of the theory of interfacial polarization, Biophys. J. 31 (1980) 215–228.

[37] H. Jeon, H. Lee, K.H. Kang, G. Lim, Ion concentration polarization-based continuous separation device using electrical repulsion in the depletion region, Sci. Rep. 3 (2013).

[38] H. Hulsheger, J. Potel, E.G. Niemann, Killing of bacteria with electric pulses of high-field strength, Radiat. Environ. Biophys. 20 (1981) 53–65.

[39] T. Grahl, H. M., Killing of microorganisms by pulsed electric fields, Appl. Microbiol. Biotechnol. 45 (1996) 148–157.

[40] A. Persat, M.E. Suss, J.G. Santiago, Basic principles of electrolyte chemistry for microfluidic electrokinetics. Part II: coupling between ion mobility, electrolysis, and acid–base equilibria, Lab Chip 9 (2009) 2454–2469.

[41] Y.-C. Wang, A.L. Stevens, J. Han, Million-fold preconcentration of proteins and peptides by nanofluidic filter, Anal. Chem. 77 (2005) 4293–4299.

[42] B.V. Deryaguin, S.S. Dukhin, A.A. Korotkova, Diffusiophoresis in electrolyte solutions and its role in the mechanism of film formation from rubber latexes by the method of ionic deposition, Kolloidn. Zh. 23 (1961) 53.

[43] S.S. Dukhin, B.V. Derjaguin, Surface and Colloid Science, vol. 7, Academic Press, New York, 1974. (Ch. 2).

[44] D.C. Prieve, J.L. Anderson, J.P. Ebel, M.E. Lowell, Motion of a particle generated by chemical gradients. Part 2. Electrolytes, J. Fluid Mech. 148 (1984) 247–269.

[45] E.S. Malkin, A.S. Dukhin, Aperiodic electrodiffusiophoresis, Colloid J. 44 (1982) 225.

[46] M.M. Bomgardner, Cleaner fracking, Chem. Eng. News 15 (Oct. 2014) 13–16.

[47] R.K. McGovern, A.M. Weiner, L. Sun, C.G. Chambers, S.M. Zubair, V. J. H. Lienhard, On the cost of electrodialysis for the desalination of high salinity feeds, Appl. Energ. 136 (2014) 649–661.

[48] P. Biesheuvel, A. van der Wal, Membrane capacitive deionization, J. Membr. Sci. 346 (2010) 256–262.

[49] S. Porada, R. Zhao, A. van der Wal, V. Presser, P. Biesheuvel, Review on the science and technology of water desalination by capacitive deionization, Prog. Mater. Sci. 58 (2013) 1388–1442.

[50] M.A. Anderson, A.L. Cudero, J. Palma, Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: will it compete? Electrochim. Acta 55 (2010) 3845–3856.