



Capacitive deionization for simultaneous removal of salt and uncharged organic contaminants from water



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ABSTRACT

Capacitive deionization (CDI) has been solely employed for the removal of charged ions from water, showing limited feasibility compared to other conventional technologies such as reverse osmosis (RO). In this work, we propose to use CDI with activated carbon electrodes for simultaneous removal of inorganic salt and trace organic contaminants (TOCs). This approach is based on the inherent sorption potential of activated carbon CDI electrodes towards organic species. We show that salt removal by CDI is only slightly affected by the presence of different TOCs (bisphenol A, carbamazepine, estrone, and phentoxifylline). Sorption and removal of TOCs (taking place concomitantly) was most effective for the hydrophobic compounds (bisphenol A and estrone) and was not affected by the presence of salt or the applied electric field. Sequential desorption of salt and TOCs into two separated streams was achieved by short-circuiting the two electrodes and washing the electrodes with water and ethanol, respectively. Notably, the described process produces separate waste streams for salts (i.e., water) and organics (i.e., ethanol), which can facilitate their disposal or further treatment. Altogether, the study shows the high potential of the proposed CDI application, which may be valuable for treating water or wastewater streams contaminated with both salt and TOCs.

1. Introduction

Capacitive deionization (CDI) belongs to the class of electrochemical desalination techniques, with potential applications for water and wastewater treatment [1,2]. In a typical CDI process, the treated (salt-containing) water flows through oppositely-charged porous electrodes; salt ions are then extracted by the applied electric field and adsorbed onto the electrode porous surface. Once the electrodes are saturated, they undergo desorption and regeneration by applying zero electrical potential or reverse electric field [3].

Large number of studies were conducted over the last decades on CDI processes, ranging from fundamental mechanistic evaluation (e.g. [4]), electrodes synthesis and optimization [5,6,7], and assessment of different potential applications (e.g. [8]). Presently, it is arguable whether CDI can compete with other common techniques for seawater desalination—such as reverse osmosis (RO) and thermal distillation—mainly due to its higher energy consumption at elevated salt concentration [9,10]. As a consequence, the majority of recent studies focuses on CDI application for brackish-water desalination with total dissolved solids (TDS) of approximately 10,000 mg L⁻¹ with marginal advantages compared to other technologies [11,12].

A review by AlMarzooqi et al. [13] evaluated the energy demand of CDI for brackish-water desalination to be in the range of 0.10–2.03 kWh m⁻³, which is seemingly competitive with RO desalination [14]. However, the values provided in the review were mostly calculated for small-scale systems (labs or pilots), and scale-up typically decreases the process efficiency [11]. For example, Welgemoed and Schutte [3] approximated the specific energy requirement for brackish-water desalination (TDS ~ 1000 mg L⁻¹) by an industrial-type CDI system to be six times higher than that of a laboratory-type module (0.1 kWh m⁻³ versus 0.6 kWh m⁻³). Hence, it is now becoming more acceptable that CDI cannot compete with RO, even for brackish-water desalination. This assumption was more recently confirmed by Qin et al. [10], which determined that RO is significantly more efficient than CDI for brackish-water desalination, using system-scale models for comparing the two technologies over a wide range of operating conditions.

To become competitive and cost-effective, CDI must be employed in alternative applications, rather than desalination, where it is advantageous. Examples for such potential applications include the removal or recovery of industrial wastewater contaminants [15], the selective removal of nutrients (e.g., nitrate and phosphate) (e.g. [16]) and heavy metals [17], and water softening [18,19,20]. In fact, water softening by

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CDI already reached cost-effectiveness and full-scale units are commercially available (e.g., Dutch company Voltea). Noticeably, all the above applications employ CDI for the treatment of charged (inorganic) ions, as implied by the name of the technology.

Contamination of water sources by anthropogenic organic pollutants that are toxic at trace quantities (i.e., trace organic contaminants, or TORCs), such as pharmaceuticals, polyfluorinated compounds, endocrine disruptors, and pesticides creates a major environmental concern worldwide [21]. Water contamination not only has adverse effects on public health and aquatic ecosystems, but can also lead to the development of antibiotic-resistant bacteria [22]. Conventional methods for water decontamination involve physicochemical separation and oxidation, which both lack selectivity toward pollutants and might be interfered from other water constituents. Hence, development of efficacious technologies to remove TORCs is of paramount importance to ensure clean water.

In this study we propose a new class of CDI application, which relies on the ability of activated carbon (AC) electrodes to effectively adsorb both inorganic salts and hydrophobic TORCs [23]. Using this approach, water contaminated with both salt and TORCs can be treated with a CDI system composed of activated carbon electrodes, applying a typical cycle of desalination and regeneration (Fig. 1). During the desalination step, salt and TORCs are concomitantly removed from the water stream and adsorbed in the carbon electrodes due to electrostatic and hydrophobic interactions, respectively. Following desalination, regeneration cycle takes place in two steps with zero voltage: (i) desorption of inorganic salts into aqueous brine stream and (ii) desorption of organics from the hydrophobic micropores, once they are saturated, into an organic (ethanol) waste stream. Hence, the system eventually results in one product stream (free of salt and TORCs) and two separate waste streams of concentrated salt and organics. The goal of this study was to determine the potential and feasibility of activated carbon electrodes-based CDI to simultaneously remove salt and TORCs from water, proposing a new pathway for CDI application.

2. Materials and methods

2.1. Reagents and chemicals

Four TORCs were selected for this study (Table 1), based on their environmental relevance and their physicochemical properties (mainly octanol/water partition coefficient, $\log K_{ow}$). TORCs were purchased from Sigma Aldrich (St. Louis, MO), at purity level of 99% or higher. NaCl (Sigma Aldrich, 99%) was used to simulate water salinity. Ethanol, acetonitrile, and phosphoric acid (Sigma Aldrich, 99.5% and 99.8%, respectively) were used for TORCs extraction and analysis in high-performance liquid chromatography (HPLC). Tris-EDTA solution (BioUltra, Sigma-Aldrich) was used as a buffer.

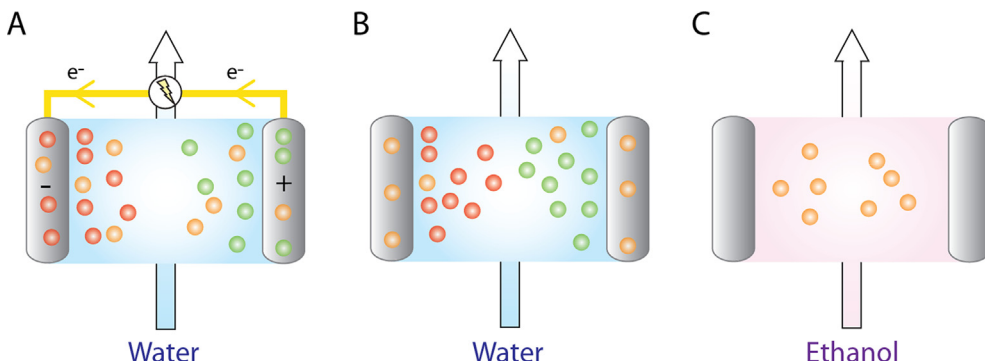


Fig. 1. Schematic diagram of the sequential process: (A) with the application of electric field between the electrodes, sorption of salt (due to electromigration) and trace organic contaminants (TORCs, due to hydrophobic interactions) takes place, (B) when the electrodes are short-circuited, salt is desorbed into an aqueous brine stream, and (C) desorption of TORCs occurs after salt desorption by passing ethanol through the electrodes. Anions, cations, and TORCs are represented as green, red, and orange spheres, respectively.

2.2. Experimental setup and procedure

Removal of salt and TORCs was tested using a cross-flow laboratory-scale two-electrode CDI cell. The electrodes were 0.25 in. apart and had an effective area of 1-inch square. In a typical experiment, 20 mg of NaCl (initial conductivity of $1120 \mu\text{S cm}^{-1}$) were dissolved in 100 mL of buffered deionized water and recirculated across the CDI cell for 90 min, at a flow rate of 100 mL min^{-1} . Salt concentration was selected to allow accurate conductivity and kinetics measurement. During the first 60 min, a voltage of 1.4 V was applied between the cathode and anode to adsorb ions in the electrodes. Following the adsorption stage, the voltage was removed by short-circuiting the cathode and the anode for additional 30 min to desorb the ions. The change in salt concentration was monitored continuously using a conductivity probe located in the 100 mL solution vial, as described in the analytical method section.

Experiments in the presence of TORCs were carried out using the same experimental setup. Here, TORCs were added to the water separately ($C_0 = 20 \text{ mg/L}$) and treated by the CDI reactor. Then, 0.5 mL samples were collected at time zero and after 10, 20, 30, and 60 min for high- HPLC analysis. Control experiments (i.e., with no voltage applied) included TORCs sorption test in DI water alone, buffer solution (50 μM of EDTA at pH 8), and buffer solution with 200 mg L^{-1} NaCl. Desorption of TORCs was carried out by recirculating ethanol through the short-circuited CDI system for 60 min. Samples were collected during desorption after 10, 30, and 60 min.

2.3. Preparation and characterization of the activated carbon electrodes

Activated carbon electrodes were prepared according to the procedure described in details previously [24,25]. In brief, an activated carbon slurry was prepared by mixing carbon powder (CEP-21 k, surface area: $2100 \text{ m}^2 \text{ g}^{-1}$) with 25 wt% glutaraldehyde solution and 6 wt % aqueous polyvinyl alcohol, at a total weight ratio of 90:9:1 (activated carbon:polyvinyl:glutaraldehyde). The slurry was then cast on a graphite sheet using a customized flow coater and dried at room temperature for 12 h. Finally, the electrodes were heated in a vacuum oven at 130°C for an hour for cross-linking.

Surface morphology of the electrodes was characterized by scanning electron microscopy (SEM, Hitachi SU-70 FE-SEM, Hitachi High Technologies America, Inc.). SEM images were obtained at an acceleration voltage of 10.0 kV without any preparation stage and approximate size was calculated based on several micrographs acquired from multiple locations for each sample. Static contact angle measurements of DI water ($\gamma = 72.8 \text{ mN m}^{-1}$) on the carbon electrodes were carried out using a goniometer (OneAttention, Biolin Scientific), using the sessile drop method at ambient conditions. A $3 \mu\text{L}$ water droplet was placed on the electrode sample and photographed using a digital camera for 15 s. The left and right contact angles were analyzed from the digital images by a post-processing software (OneAttention software). The measurements were conducted on a minimum of three

Table 1
Physicochemical properties of the selected TOrcs and HPLC analytical method.

TOrc	Class	log K_{ow} ^a	pK _a ^a	HPLC analytical method			
				ACN:DI ratio	Flow rate (ml min ⁻¹)	Retention time (min)	UV absorption wavelength (nm)
Bisphenol A	Xenoestrogen	3.32	10.29	45:55	2	2.4	230
Estrone	Postmenopausal estrogen	3.13	10.25	55:45	2	2.1	280
Carbamazepine	Anti-epileptic drug	2.45	13.9	35:65	1.3	4.1	285
Pentoxifylline	Muscle pain killer	0.29	0.5	45:55	1	7.1	275

^a Yoon et al. [41].

random locations and the data was averaged. Additional characterization can be found elsewhere [24].

2.4. Analytical methods

Water conductivity was used as a surrogate for NaCl concentration and measured by a calibrated conductivity meter (Oakton Instruments, Vernon Hills, IL). TOrcs concentration was determined using HPLC (Agilent 1260 Infinity Series) coupled with a photodiode array detector (PDA; Agilent 1100). A sample volume of 50 μ L was injected into a C18 column at 20 °C. The mobile phase was an isocratic mixture of water/phosphoric acid (pH 2.3) and acetonitrile. The mobile phase mixture ratios, flow rates, retention times, and UV absorption wavelengths are specified for each analyte in Table 1 (i.e., bisphenol A, estrone, carbamazepine, and pentoxifylline).

3. Results and discussion

3.1. Electrode characteristics

SEM and contact angle measurements were performed to characterize the fabricated activated carbon electrodes and confirm their integrity. Fig. 2A and B shows cross-section and surface SEM images of the activated carbon electrodes, respectively. The activated carbon particle size ranged from 1 to 10 μ m, and the electrodes were approximately 130 μ m in thickness. No cracks or major defects were detected when screening through the entire electrode surface. Contact angle analysis showed a DI contact angle of approximately 14°, indicating a hydrophilic carbon electrode (Fig. 2C), which is crucial in adsorptive material to increase the affinity towards water [26]. Electrochemical impedance spectroscopy was measured in previous studies for the carbon electrodes, presenting ohmic and diffusion resistance of 16.2 and 29.7 Ω , respectively [27].

3.2. Salt removal by CDI in the presence of TOrcs

The goal herein was to examine the impact of TOrcs in water on the removal efficiency of salt during CDI. Fig. 3 illustrates the changes in conductivity (i.e., salt concentration) during CDI operation in the

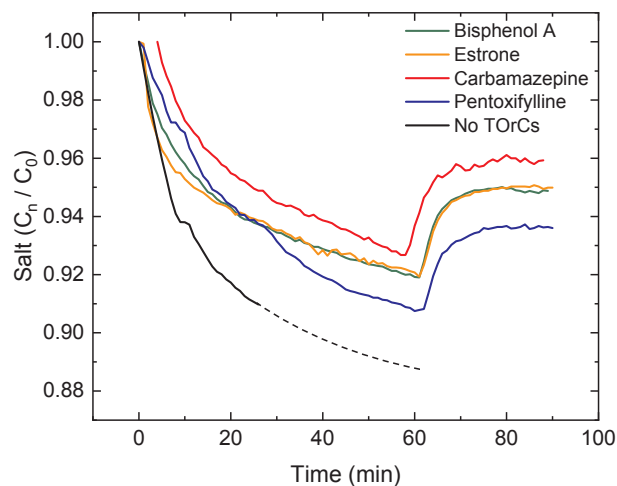


Fig. 3. Salt removal (reported as relative residual concentration) by a typical CDI experiment (i.e., while applying electrical field) in the presence and absence of selected trace organic contaminants (TOrcs). Data was collected during 60 min of CDI experiment at 1.4 V and followed by electrode short-circuiting for additional 30 min.

absence and presence of the examined TOrcs. Each experiment consisted of an initial 60-min phase where the electrodes were electrically charged to adsorb salt, followed by additional 30 min without voltage to desorb the salt. In all cases, concentration of salt decreased rapidly with the application of electrical field. Salt concentration in solution following the desorption stage was lower than the initial concentration, which might be attributed to chemical adsorption occurring in parallel to charge-based sorption. As TOrcs adsorption starts regardless of the applied voltage (depending on K_{ow} rather than electrical field), experiment could not start following equilibrium between salt and pristine electrodes. Addition of TOrcs reduced salt removal by approximately 20% (compared to experiment with salt alone), most likely due to competition on available sites in the micropores and organic fouling of the electrodes [28]. Only minor differences in salt adsorption were observed for experiments with different TOrcs; pentoxifylline least

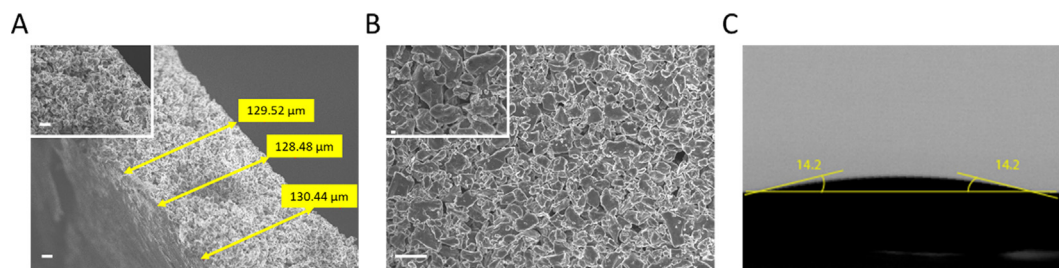


Fig. 2. Characteristics of the activated carbon electrode. Representative scanning electron microscopy (SEM) images of the electrode in (A) cross section and (B) top view. Insets show higher magnification images. Scale bars are 10 μ m. (C) Representative photographs of 3 μ L water droplet controlled by a microneedle on the surface of the activated carbon electrode and water contact angle analysis (in yellow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

affected the CDI salt removal efficiency, owing to its low $\log K_{ow}$ (Table 1), which results in reduced sorption of the compound to the carbon electrodes (compared to the other TOrCs).

Only limited data is available on the impact of organic water constituents on CDI performance. Mossad and Zou [28] showed that salt removal efficiency during CDI (using activated carbon electrodes) decreased by 18% after 30 h, in the presence of 3.1 mg C L^{-1} of humic acid, simulating natural organic matter. For comparison, organic carbon concentration in our tested water was in the range of $11\text{--}16 \text{ mg C L}^{-1}$ (based on the TOrCs molecular formula), more than three times higher than the concentration used by Mossad and Zou. On the other hand, Liu et al. [29] found that humic acid is primarily adsorbed to the mesopores of CDI activated carbon electrodes (2–50 nm), only marginally affecting the electrodes ion storage capacity and salt removal efficiency (taking place predominantly in micropores < 2 nm). Therefore, we believe that with a suitable selection of activated carbon electrodes, the negative effect of TOrCs on salt removal can be minimized.

3.3. TOrCs removal by CDI

The removal of the target TOrCs by CDI setup was performed in parallel to water desalination to demonstrate the feasibility of the proposed process. Concentration of TOrCs gradually decreased during treatment, reaching over 90% removal for bisphenol A after 60 mins (Fig. 4). As expected, the removal rate of the TOrCs follows the order of bisphenol A > estrone > carbamazepine > pentoxifylline, which is in direct correlation with their $\log K_{ow}$ value (Table 1). This agrees well with other studies on water treatment by activated carbon, showing that efficient TOrCs removal is achieved primarily for compounds with high $\log K_{ow}$ [30]. Control experiments showed that TOrCs sorption was not affected by EDTA or salt addition, nor by the applied electrical field, as indicated by the relatively constant TOrCs concentrations in all experiments. Therefore, we can conclude that the sorption mechanism of TOrCs is based on the partition coefficient between solution and the electrode (i.e., hydrophilicity-based) rather than charge interactions.

To regenerate the carbon electrodes, a TOrCs desorption cycle was subsequently applied, where 100 mL of ethanol was recirculated in the CDI system for 60 min. Desorption was most effective for compounds with low $\log K_{ow}$ (e.g., pentoxifylline), which has low sorption affinity

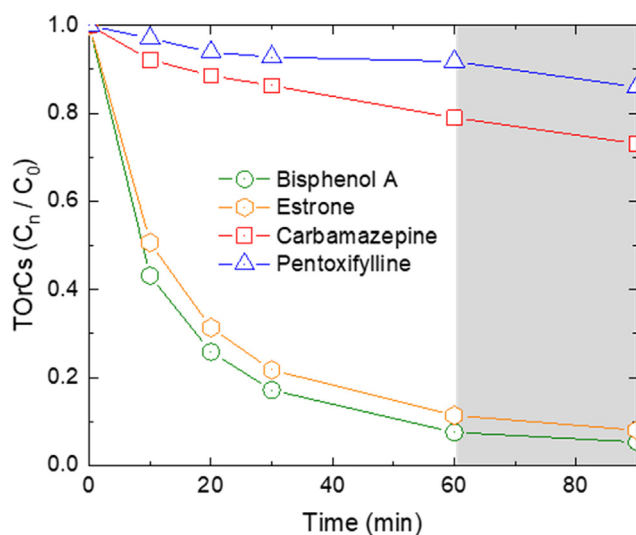


Fig. 4. Trace organic contaminants (TOrCs) removal (tested separately and reported as relative residual concentration) during CDI experiment, in the presence of 200 mg/L salt. The applied electrical field was 1.4 V. Following 60 min, the electrical field was stopped (grey background). TOrC concentration was measured using high-performance liquid chromatography (HPLC).

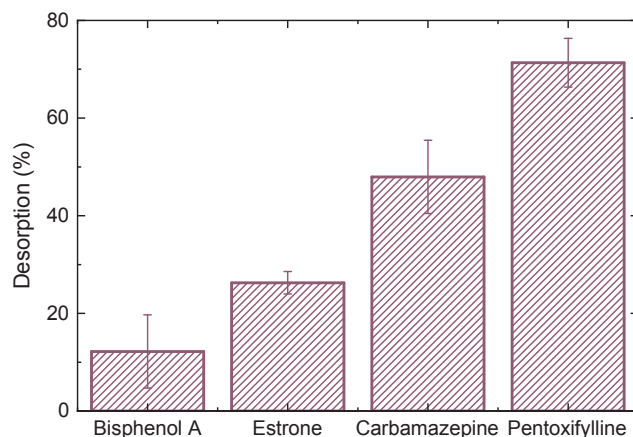


Fig. 5. Trace organic contaminants (TOrCs) percent desorption from the electrodes after 60 min (based on the amount sorbed during experiments presented in Fig. 4) of passing ethanol through the electrodes. TOrC concentration was measured using high-performance liquid chromatography (HPLC).

to the activated carbon (Fig. 5). An alternative method for desorption of organic compounds from activated carbon electrodes is the use of alkaline solution, as was previously demonstrated by Mossad and Zue [28].

An additional set of experiments was carried out to determine the sorption capacity of the electrodes. Here, 100 mL solution of 60 mg L^{-1} Bisphenol A (the compound with highest sorption ability) was passed through the electrodes in a flow-through mode (without recirculation), and the removal of the compound from water was measured (Fig. 6). We have repeated the experiment for 8 cycles (i.e., a total of 800 mL solution of 60 mg L^{-1} Bisphenol A) to determine the sorption capacity of the synthesized electrodes.

Sorption percentage gradually decreased from 82% to 59% after 8 treatment cycles (cycle is equal to the treatment of 100 mL), where electrodes capacity reached 300 mg bisphenol A/g AC. Typical maximum sorption capacity of activated carbon is in the hundreds of mg TOrC per gram carbon [31,32]; more specifically, Pamidimukkala et al. [33] reported maximum sorption capacities for bisphenol A by different types of activated carbon to be in the range of 11 – 456 mg bisphenol/g AC. Hence, we can assume that sorption abilities of the activated carbon were not affected during our specific electrode manufacturing.

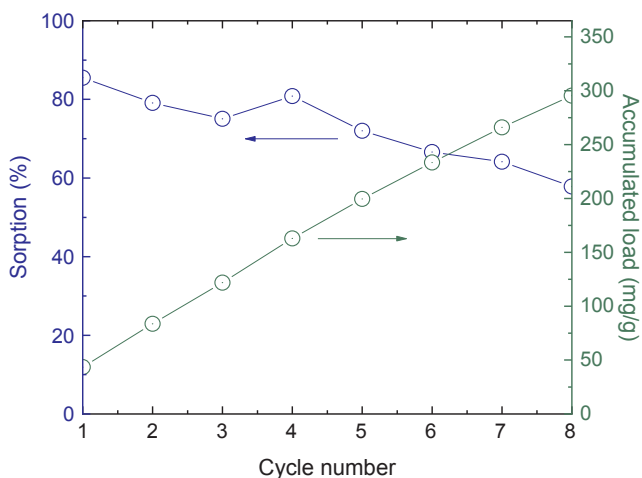


Fig. 6. Percent sorption of bisphenol A (left axis) and its corresponding accumulated load on the electrodes (right axis) in a set of repeated experiments. In each experiment, Bisphenol A initial concentration was 60 mg/L at a volume of 100 mL.

3.4. Potential applications for water treatment

Natural water is often contaminated by both inorganic ions and organic contaminants, especially in densely populated areas. Our innovative mode-of-application for CDI, i.e., the simultaneous treatment of salt and TORCs, may be beneficial for a wide range of applications: from treating brackish groundwater contaminated with TORCs (as it is often the case in Israel and elsewhere; [34,35], to tertiary wastewater treatment. For example, California regulations for wastewater reuse entails the application of a tertiary treatment, which includes reverse osmosis and UV advanced oxidation, with the objective of removing salt and TORCs [36]. Our proposed CDI process presents an alternative for the RO-UV/H₂O₂ tertiary treatment, removing salt and TORCs in a single reactor. Other interesting applications may be the treatment of specific industrial wastewater stream, often containing high levels of salt and organic contaminants [37].

4. Conclusion

Removing TORCs from water and wastewater has been the focus of intense scientific and regulatory efforts over the past two decades [38,39,21,40], as such compounds are continually discharged into the sewage system and find their way to the environment and into drinking water supply [21]. In fact, TORCs are often targeted during advanced wastewater treatments, together with salt and other regulated contaminants, especially when wastewater reuse is considered. Developing a cost-effective process for the simultaneous removal of salt and TORCs may present an attractive wastewater treatment. Capacitive deionization (CDI)—a desalination process which cannot compete with other desalination techniques—may stand out in the context of co-treatment of salts and TORCs from water. The reason for that is the frequent use of activated carbon electrodes during CDI desalination, which are also known for their high sorption capacity towards organic contaminants. Subsequently, we propose herein the use of CDI with activated carbon electrodes to remove both salt and (hydrophobic) TORCs from water/wastewater.

We show that combining two known processes, CDI desalination and TORCs sorption, into one treatment reactor, result in the removal of both salt and TORCs, and that the processes do not affect the efficiency of one another. Furthermore, we show that electrode regeneration can be achieved by two desorption cycles: without applying voltage using aqueous solution for salt desorption and ethanol/alkaline solution for TORCs desorption. The two generated waste streams are much more homogenous than a combined stream, and therefore can be treated, discharged or reused more effectively. For example, a waste stream containing only salt can be directly discharged into the ocean (unlike waste stream containing both salt and TORCs). The waste stream containing TORCs and ethanol on the other hand, can be easily treated by biological means (since ethanol is environmentally friendly and not toxic). Altogether, this study presents a proof-of-concept for a new cost-effective CDI application for treatment of water/wastewater streams contaminated with salt and TORCs. This application may promote the use of CDI and open the door for new research pathways, mainly with regard to treatment optimization and application in natural water and wastewater effluent.

Author contributions

E.S., R.E., and I.Z. designed research; E.S., and I.Z. performed research; E.S., R.E., Y.L., and I.Z. analyzed data; and Y.L. and I.Z. wrote the paper.

CRedit authorship contribution statement

Yaal Lester: Data curation, Writing - original draft. **Evvyatar Shaulsky:** Conceptualization, Methodology, Investigation. **Razi**

Epsztein: Conceptualization, Methodology. **Ines Zucker:** Conceptualization, Methodology, Investigation, Writing - original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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