Biomorphic microchanneled electrodes for enhanced water desalination through capacitive deionization
Jaqueline O. Brotto, Natan Padoin, Carlos R. Rambo and Cíntia Soares

ABSTRACT

This work reports the preparation of rattan-derived carbon electrodes and their application in capacitive deionization technology for desalination. Desalination tests were performed with different concentrations of simulated seawater in a continuous mode with gravity as the driving force and applied voltages of 0.8 and 1.2 V. Electrosorption kinetics were performed to verify desalination of the saline solutions over time. Scanning electron microscopy revealed that the microstructure of the biomorphic carbon is composed of porous microchannels with diameters of around 300 mm, which allowed both fluid flow and ion retention. The kinetics of the electrosorption presented excellent results concerning desalination of highly concentrated solutions using low voltages.

Key words | biomorphic carbon electrodes, biotemplating, capacitive deionization, desalination

INTRODUCTION

The World Health Organization (WHO) predicts that by 2050 a lack of potable water will affect up to 4 billion people, not counting the 11% of the world’s population that currently do not have access to adequate drinking water (Ahmed et al. 2015). In this context, researchers are attempting to develop feasible methods for desalination of sea water as a solution for this problem (Ghaffour et al. 2016).

Among the existing technologies, there are some that are well-established, such as reverse osmosis, flash distillation, and multi-effects distillation. However, one of the major disadvantages of all of these technologies is the high cost associated with their operation. Therefore, researchers have been studying more efficient methods to reduce the costs associated with the energy required for their use.

One of the promising techniques that fulfill all of these requirements is capacitive deionization, also called electrosorption. It is based on the attraction of the ions contained in the salt water through the application of a potential difference in electrodes, which results in the formation of a double electric layer on the wall of the electrodes, causing the ions to move to this surface, thus reducing the concentration of salt in the solution (Li et al. 2016; Fang et al. 2018). There are two modes of operation that can be used in analyzing the efficacy of this technique: batch and single pass. Batch operation involves a simpler analysis; however, as the solution is measured several times in the same reservoir, there is a difficulty in comparing the electrosorption equilibrium data. In the simple pass mode, it is possible to obtain well-defined values of the salinity of the feed and final streams, since in this operation the withdrawn samples are not in the same reservoir (Porada et al. 2013a).

The great advantage of electrosorption is the low energy consumption required for its operation because only a low applied voltage is required to generate the potential difference. The key point of this technology lies in the choice of material used to manufacture the electrodes because it must exhibit high conductivity and porosity.

Currently, researchers have been developing electrodes based on graphene and mesoporous carbon compounds...
Other studies indicate carbon composites along with other materials, such as polypyrrole (Wang et al. 2015) and oxides, have potential application as electrodes. In addition, researchers have also used graphene/SnO2 nanocomposite systems (El-Deen et al. 2014) as well as ion exchange polymers on carbon nanotube electrodes (Díaz et al. 2014).

Yu et al. (2016) pointed out that electrosorption has advantages related mainly to its low energy demand and low environmental impact. However, when taking into consideration the electrodes used and the chemicals used to make them, a considerable environmental impact could be revealed. On the other hand, the microarchitecture of some natural plants can be used as an attractive template for the design of complex porous carbon-based materials that cannot be engineered by conventional techniques (Ota et al. 1995). In recent years, different biotemplating technologies have been developed for conversion of plant structures into biomorphous materials (Cao et al. 2004; Rambo et al. 2005). Rattan, for instance, a climbing palm belonging to the subfamily Calamoideae, exhibits a microstructure characterized by a homogeneous profile comprised of uniformly distributed long porous-walled microchannels that allow fluid flow along its stem (Uhl & Dransfield 1987) and it can be used as a biotemplate. These features can be useful for applications that make use of capillary flow to obtain high volumetric yields.

This work reports the use of rattan-derived biomorphic carbon electrodes for desalination of saline solutions through electrosorption.

**MATERIALS AND METHODS**

To perform the desalination process proposed in this research, rattan (*Calamus rotang*) was used as a starting template for electrode fabrication. For laboratory-scale capacitive deionization technology to desalinate saline water, it is suggested to use a single salt solution containing NaCl or KCl, simulating sea water (Porada et al. 2013a). Here, we used NaCl. Furthermore, the choice of concentration used herein was based on previous literature data. NaCl solutions with concentrations of 5 and 10 g·L$^{-1}$ were used for the desalination tests and 25 mL saline solutions were prepared from the dissolution of the NaCl salt P.A. in distilled water.

Rattan pieces (cylinders with 2.5 cm diameter) were pyrolysed at 800°C for 1 h at a heating rate of 1.5 °C·min$^{-1}$, under a flowing argon atmosphere, for complete decomposition of the cellulose, hemicellulose, and lignin chains into carbon. At 800°C, the bio-derived carbon exhibits a pseudo-amorphous structure with a very low degree of crystallization (Rambo & Sieber 2005). The oven was allowed to cool naturally. Finally, the rattan samples were cut into disks with dimensions of 0.500 ± 0.002 cm thick, a diameter of 2.60 ± 0.01 cm, and a weight of 0.95 ± 0.01 g.

The desalination test system consisted of two rattan disks, two paper filters with the same diameter, two sealing rings, two copper wires, and tubes and connections. Figure 1 illustrates the assembled system used in all of the tests performed in the present work.

The desalting process of the NaCl solutions was performed using gravity as the driving force for the passage of the solution through the biomorphic electrodes. The main reason to use a flow-through pattern was to make use of the natural orientation of the vessels of rattan, with the main objective being taking advantage of the porous, channeled microarchitecture of the natural biotemplate. For the desalination tests, the voltages were set to 0.8 or 1.2 V, delivered through a DC power supply (iCEl, PS-4100).

A digital conductivimeter (CON-500 - Ion) was used to determine the initial and final NaCl concentrations. It is noteworthy that at each stage of the tests, the initial and final conductivities of the solutions were monitored. In addition, the solution was always homogenized, before and after the passage through the electrodes, to avoid salt precipitation. The pH of all solutions before and after desalting remained between 8.5 and 9.

Electrosorption is a process like adsorption, i.e. it is a surface phenomenon. However, the main difference is in the application of an electric potential to form the double layer of electrons. The kinetics of electrosorption were obtained from the combinations of the concentrations of 5 g·L$^{-1}$ and 10 g·L$^{-1}$ with the voltages of 0.8 V and 1.2 V. The concentration of the ions contained in the electrodes, the volume of solution treated, and the amount of ions removed during electrosorption kinetics can be obtained.
by Equations (1)–(3), respectively (Porada et al. 2013a).

$$q_{eq} = \frac{Q C_0}{m_e} \left[ t_{sat} \left( 1 - \frac{C(t)}{C_0} \right) \right] ,$$

(1)

$$V_T = Q t_{rup}$$

(2)

$$q_{rem} = Q \left[ t_{sat} \left( C_0 - C(t) \right) dt \right] ,$$

(3)

where $q_{eq}$ (g·g$^{-1}$) is the concentration of ions in the electrodes at equilibrium, $Q$ (L·min$^{-1}$) is the volumetric flow rate of the saline solution, $C_0$ is the initial concentration and $m_e$ (g) is the sum of the masses of the two electrodes. Furthermore, $C(t)$ (mg·L$^{-1}$) is the final concentration of the solution at a given time after passing through the system, $V_T$ (L) is the volume of solution treated, and $t_{rup}$ (min) is the time leading to an exit concentration of 5% of feed concentration. Also, $q_{rem}$ (g) is the amount of ions removed during electrosorption kinetics and $t_{sat}$ (min) is the saturation time (Porada et al. 2013a).

The skeleton density was measured by He-pycnometry (Quantachrome, MVP 4DC, USA). The open porosity was estimated through the relationship between the skeleton and geometrical densities. The morphology and microstructure of the rattan-derived carbon samples were evaluated by scanning electron microscopy (SEM, Jeol JSM-6390LV) combined with energy dispersive X-ray spectroscopy (EDS) for elemental analysis. Electrical conductivity of the biomorphic carbons was measured using the four-probe method by using a high precision SMU (Agilent B2912A).

**RESULTS AND DISCUSSION**

Figure 2 shows SEM micrographs of the pyrolysed rattan before (Figure 2(a) and 2(b)) and after (Figure 2(c) and 2(d)) desalination.

The inserts are EDS spectra of a large region of the respective SEM image. All microarchitectural features of the original rattan template were well conserved after pyrolysis. Figure 2(a) displays the characteristic cell structure of rattan. In contrast to wood, rattan is a tropical climbing palm that exhibits no seasonal rings (Uhl & Dransfield 1971). In Figure 2(b), the porous wall of a large vessel (200–330 μm) from the metaxylem, as well as the middle-sized cells (around 90 μm) from the phloem, can be seen. It can also be observed that the channels do not exhibit large tortuosities, allowing the saline solution to flow without impediments along the channel.

Biesheuvel et al. (2011) carried out a study establishing an extended theory for capacitive deionization. In their studies, they used not only the double layers contained in the pores of the electrode but also the interparticular
spaces of the pores. They argue that the porosity of the inter-particles become available for salt storage, thus increasing the total storage capacity of the porous electrode. According to Porada et al. (2015b), salt electrosorption capacity and the total pore volume are not directly related. However, a theoretical prediction of salt electrosorption capacity can be made through analysis of the pore volume correlated with incremental pore size ranges, where pores with different sizes exhibit a different salt removal capacity.

It should be noted that the features revealed by SEM analysis are extremely important for the performance of the electrodes in this technique. The EDS insert in Figure 2(a) shows the presence of potassium and oxygen elements in the sample, which is due to the large amount originally present in the sample before processing. The presence of the chemical elements sodium, chlorine, potassium, and calcium were verified in all samples after desalination.

The porosity of the biomorphic electrode was $62.9 \pm 0.02\%$, with a pore volume equal to $2.04 \pm 0.05 \text{ cm}^3$. Therefore, the biomorphic carbon exhibits adequate porosity for use as an electrode in electrosorption technology. Moreover, the electrical resistivity of the biomorphic carbon electrodes is $0.5 \pm 0.1 \Omega \cdot \text{m}$, which is relatively low (for an electrical conducting material), an important characteristic when it comes to electrosorption. Rattan-derived carbon is analogous to pyrolyzed pinewood and other ligninocellulosic species that exhibit a strong dependence of electrical conductivity (up to four orders of magnitude) with pyrolysis temperature in the range of $500^\circ \text{C}$ to $700^\circ \text{C}$. However,
for higher temperatures, the conductivity tends to be constant (up to 1,000 °C it varies only one order of magnitude). Values of electrical conductivity may range between $10^{-5}$ and $10^{-3}$ S/cm (Liu et al. 2012).

The results for the kinetics of electrosorption and percentages of salt removed are shown in Figure 3(a) and 3(b), respectively.

Because during the tests performed herein only gravity was used as the driving force, a certain difficulty was found in obtaining a constant flow. During the tests flow rates varying from 0.6 to 1.0 mL·min$^{-1}$ were measured. Thus, to perform the calculations for this test we chose the mean flow over time, which was $0.8 \pm 0.2$ mL·min$^{-1}$. It can be seen in Figure 3(a) that, in the first few minutes, the greatest number of ions are adsorbed and, after 50 min, the curves begin to equilibrate and there is no further ion removal. In addition, it is noticeable that the use of a higher voltage enhances the removal of ions.

Still regarding Figure 3(a), high deviations are associated with the first points collected. It is believed that such deviations occurred due to the variable flow. Because of the low flow rate at the start of the process, the amount of solution treated is small, which results in higher measurement errors. Note that the deviations tend to decrease over time, since the flow increases and consequently also the amount of solution treated within the device per unit time.

Figure 3(b) shows the percentage of salt removed over time. Again, one can note the larger deviations at the beginning of the process, as well as at the higher concentration. It is also possible to observe that the experimental condition that resulted in higher efficiency of salt removal corresponded to a concentration of 10 g·L$^{-1}$ and a potential difference of 1.2 V. In addition, after 50 min, the system with the highest voltage continued to remove salt but in a smaller amount (below 5%). On the other hand, in the tests performed with 0.8 V, there was a decrease in the amount of salt removed (below 5%) even in the first few minutes (i.e. $t < 25$ min).

Interestingly, a higher concentration and maintaining the potential difference at 0.8 V resulted in enhanced salt removal. Thus, the combination of high voltage and high initial salt concentration is beneficial for the performance of this process (Porada et al. 2013a). It should be highlighted, though, that the minimum potential required to break water molecules into hydrogen and oxygen is 1.23 V (Shannon 2010). Therefore, since the purpose of this research was not to promote water splitting but water desalination, lower voltages are required.

The thickness of the electrodes also plays an important role since it can alter the diffusive transport in the macropores and can also affect the electrochemical activity in the porous electrode. The thicker the electrode is, the higher the volume of available macropores. An increase in macroporosity leads to a consequent increase in the access to other existing pores, resulting in higher specific salt removal as well as a higher equilibrium concentration.
In our work, we opted to fix the electrode features and evaluate processing parameters like initial salt concentration and applied tension. Additionally, it should be highlighted that relatively high salt removal efficiencies were obtained using filter paper as separator. Usually, filter paper separators yield lower desalination rates when compared to other spacers (Bian et al. 2016).

Table 1 shows the data obtained from the electrosorption kinetics. As previously mentioned, higher desalination efficiencies were obtained when a higher voltage was used. Furthermore, by setting the voltage to 1.2 V, the initial concentration of 10 g·L\(^{-1}\) maximized the performance of the system. Thus, the best results for \(q_{eq} (\text{g·g}^{-1})\) and \(q_{rem} (\text{g})\) were obtained with 10 g·L\(^{-1}\) and 1.2 V, despite having the largest deviations (see also Figure 3(b)). Average salt adsorption rates (Zhao et al. 2013) of \((4.80 \pm 2.15) \text{μmol·g}^{-1}·\text{min}^{-1}\), \((5.70 \pm 0.51) \text{μmol·g}^{-1}·\text{min}^{-1}\), \((4.00 \pm 1.04) \text{μmol·g}^{-1}·\text{min}^{-1}\) and \((5.80 \pm 0.76) \text{μmol·g}^{-1}·\text{min}^{-1}\), calculated based on the saturation time \(t_{sat}\), were obtained for the pairs of operational conditions \((5 \text{ g·L}^{-1}, 0.8 \text{ V})\), \((5 \text{ g·L}^{-1}, 1.2 \text{ V})\), \((10 \text{ g·L}^{-1}, 0.8 \text{ V})\) and \((10 \text{ g·L}^{-1}, 1.2 \text{ V})\), respectively.

Table 2 presents selected studies using capacitive deionization technology applying initial concentrations equal or above 5 g·L\(^{-1}\) for comparison with the results obtained in this work. In the study by Ryoo et al. (2005), a higher desalination of NaCl solution with initial concentration of 5 g·L\(^{-1}\) with biomorphic electrodes was observed. However, it should be emphasized that even when using a low voltage (i.e. 0.8 V), it was still possible to obtain an enhanced performance with the device reported in this work when compared with systems containing CNT-TiO\(_2\) and ZrO\(_2\)-GO nanosheets as electrodes. Furthermore, with a voltage as low as 0.8 V in the biomorphic electrodes, the desalination performance obtained herein is superior to that reached with activated carbon electrodes and commercial active carbon using 1.2 V (Zhao et al. 2010; Biesheuvel et al. 2011; Porada et al. 2012).

Overall, it should be highlighted that the combination of factors such as the mode of operation, experimental conditions, and the composition of the electrode plays an important role when analyzing the performance of devices applied to water desalination through capacitive deionization. When ZrO\(_2\) nanoparticles incorporated with graphene oxide nanosheets were used as electrodes (Yasin et al. 2016), a decrease in the removal capacity was reported in response to increasing voltage. According to Remillard et al. (2018), who compared flow-through pattern and flow-by pattern applied to capacitive deionization, the flow-by tends to have a higher capacity of salt adsorption and better efficiency of load in relation to the flow-through. However, the latter showed a higher average salt adsorption rate compared to flow-by for shorter half-cycle times. Therefore, the use of flow-through in this work is justified because, since an average flow value was used to obtain the electrosorption data of the proposed system, average adsorption rates were obtained in short periods of time.

In addition, pre-treatments can be performed on the biomorphic electrodes in order to increase their electrosorption capacity. Zhu et al. (2018) report the improvement of the performance of pyrolysed anodes, produced from residues of apricot bark, after H\(_2\) reduction treatment. Feng et al. (2018) used porous activated carbon from a lignocellulosic sponge (Luffa cylindrica) to act as a capacitive deionization electrode. They concluded that after chemical activation the total surface area and pore volume of the material increased, which resulted in an increase in the electrosorption performance.

Finally, from the material properties and kinetics of electrosorption presented herein as well as the comparisons with other works published in the literature, it is evident there is great potential for capacitive deionization using biomorphic electrodes for water desalination. Under the operational conditions adopted in this work, a significant efficiency for desalination was reached. Further improvements can be performed to increase the electrosorption capacity and to allow the application of this system in real scale through association of multiple devices in

<table>
<thead>
<tr>
<th>(C_0 (\text{g·L}^{-1}))</th>
<th>(V (\text{V}))</th>
<th>(V_r (\text{L}))</th>
<th>(q_{eq} (\text{g·L}^{-1}))</th>
<th>(q_{rem} (\text{g}))</th>
</tr>
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<tr>
<td>5</td>
<td>0.8</td>
<td>0.024</td>
<td>0.0081 ± 0.0006</td>
<td>0.016 ± 0.007</td>
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<td>1.2</td>
<td>0.048</td>
<td>0.018 ± 0.008</td>
<td>0.038 ± 0.003</td>
</tr>
<tr>
<td>10</td>
<td>0.8</td>
<td>0.036</td>
<td>0.010 ± 0.002</td>
<td>0.020 ± 0.005</td>
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<tr>
<td></td>
<td>1.2</td>
<td>0.072</td>
<td>0.027 ± 0.009</td>
<td>0.058 ± 0.007</td>
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</table>

\(C_0 (\text{g·L}^{-1})\) represents the initial concentration of the solution, \(V (\text{V})\) is the voltage applied to the electrodes, \(V_r (\text{L})\) is the volume of treated solution, \(q_{eq} (\text{g·L}^{-1})\) is the concentration of ions in the electrodes at equilibrium and \(q_{rem} (\text{g})\) is the amount of salt removed.
series/parallel configurations (numbering-up strategies). Salt removal capacity could therefore be enhanced through series coupled reactors, or a system consisting of pairs of electrodes placed in series where overall efficiency would be dependent on the salt concentration after passing through the previous reactor or electrodes.

CONCLUSIONS

Water desalination using capacitive deionization can be satisfactorily accomplished applying biomorphic electrodes, resulting in high salt removal rates. This morphological characterization of rattan-derived carbon electrodes allowed us to elucidate their functionality and behavior in the desalination process. Furthermore, the constructed system proved to be feasible for operation in all of the electrosorption tests conducted. Finally, the kinetic tests of electrosorption by this system presented excellent results when compared with other studies, in addition to efficiently performing desalination of solutions with high concentrations of salt while only using low voltages.

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REFERENCES

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All experiments used NaCl solutions.
SP ¼ single pass; B ¼ batch; q ¼ specific removal or concentration in the solid; m_c ¼ carbon content contained in the material; AC ¼ activated carbon; CNT ¼ carbon nanotubes; GO ¼ graphene oxide.

<table>
<thead>
<tr>
<th>Carbon material</th>
<th>C_0 (mg·L⁻¹)</th>
<th>V_{eq} (V)</th>
<th>m_c (%)</th>
<th>Oper. mode</th>
<th>q (mg·g⁻¹)</th>
<th>Reference</th>
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<tr>
<td>TiO₂-AC cloth</td>
<td>5,844</td>
<td>1.0</td>
<td>—</td>
<td>B</td>
<td>4.3</td>
<td>Ryoo et al. (2005)</td>
</tr>
<tr>
<td>AC</td>
<td>200</td>
<td>1.5</td>
<td>—</td>
<td>SP</td>
<td>3.7</td>
<td>Kim &amp; Choi (2010)</td>
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<tr>
<td>AC</td>
<td>200</td>
<td>1.5</td>
<td>—</td>
<td>SP</td>
<td>5.3</td>
<td></td>
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<tr>
<td>Commercial AC</td>
<td>292</td>
<td>1.2</td>
<td>—</td>
<td>SP</td>
<td>10.9</td>
<td>Porada et al. (2012)</td>
</tr>
<tr>
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<td>1,170</td>
<td>1.4</td>
<td>—</td>
<td>B</td>
<td>13.0</td>
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<td>1.2</td>
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<td>SP</td>
<td>10.5</td>
<td>Biesheuvel et al. (2011)</td>
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<td>—</td>
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<td>Commercial AC</td>
<td>292</td>
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<td>85</td>
<td>SP</td>
<td>6.9</td>
<td>Zhao et al. (2010)</td>
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<td>1.2</td>
<td>85</td>
<td>SP</td>
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<tr>
<td></td>
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<td>1.4</td>
<td>85</td>
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<tr>
<td>CNT-TiO₂</td>
<td>500</td>
<td>1.2</td>
<td>—</td>
<td>B</td>
<td>4.3</td>
<td>Haibo et al. (2016)</td>
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<tr>
<td>ZrO₂-GO nanosheets</td>
<td>50</td>
<td>0.8</td>
<td>—</td>
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<tr>
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<td>Pyrolysed rattan</td>
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<td>27.5</td>
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</table>

Table 2 | Summary of the different electrode materials and their performance of electrosorption in DIC

The numbers in Table 2 refer to the following studies:
Ryoo et al. (2005)
Kim & Choi (2010)
Porada et al. (2012)
Biesheuvel et al. (2011)
Zhao et al. (2010)
Haibo et al. (2016)
Yasin et al. (2016)
This work


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