Arsenic removal from groundwater using low-cost carbon composite electrodes for capacitive deionization
Ju-Young Lee, Nantanee Chaimongkalayon, Jinho Lim, Heung Yong Ha and Seung-Hyeon Moon

ABSTRACT
Affordable carbon composite electrodes were developed to treat low-concentrated groundwater using capacitive deionization (CDI). A carbon slurry prepared using activated carbon powder (ACP), poly(vinylidene fluoride), and N-methyl-2-pyrrolidone was employed as a casting solution to soak in a low-cost porous substrate. The surface morphology of the carbon composite electrodes was investigated using a video microscope and scanning electron microscopy. The capacitance and electrical conductivity of the carbon composite electrodes were then examined using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), respectively. According to the CV and EIS measurements, the capacitances and electrical conductivities of the carbon composite electrodes were in the range of 8.35–63.41 F g\(^{-1}\) and 0.298–0.401 S cm\(^{-1}\), respectively, depending on ACP contents. A CDI cell was assembled with the carbon composite electrodes instead of with electrodes and current collectors. The arsenate removal test included an investigation of the optimization of several important operating parameters, such as applied voltage and solution pH, and it achieved 98.8% removal efficiency using a 1 mg L\(^{-1}\) arsenate solution at a voltage of 2 V and under a pH 9 condition.

Key words | arsenic removal, capacitive deionization, electrosorption, low-cost carbon composite electrode

INTRODUCTION
Excessive exposure to arsenic leads to skin, lung, and kidney cancers in humans (Lin et al. 2013). Several South Asian countries have reported that arsenic concentration in the groundwater is over 0.8 mg L\(^{-1}\) (The World Health Organization (WHO) provisional guideline for arsenic in drinking water is 0.01 mg L\(^{-1}\)) (Kanel et al. 2013). South Asians, who use groundwater as drinking water, are vulnerable to serious arsenic exposure. Therefore, technologies for the removal of arsenic from groundwater are required. To remove arsenic, a coagulation treatment with Fe\(_3\)O\(_4\) and FeCl\(_3\) is usually employed (Bang et al. 2005; Rao et al. 2015; Wang et al. 2015). However, the chemicals used in this process cause a secondary contaminant. In view of this problem, capacitive deionization (CDI) technology is an appealing approach to arsenic removal. CDI is a low-voltage water treatment technology that does not require the use of chemicals (Lin et al. 2009; Mossad & Zou 2013).

The construction of a typical CDI unit cell is as follows: end plate–current collector–electrode–gasket–separator–electrode–current collector–end plate (Lee et al. 2010). In this configuration, the current collectors and electrodes are crucial components in the CDI system. When an electrical potential is applied to the current collectors, it enables the conduction of the electrical charges to the electrodes. The charged electrodes contribute ion adsorption onto the electrode surfaces by forming an electrical double layer (EDL), producing the purified water (Seo et al. 2010; Lee et al. 2011).

Electrodes and current collectors are simultaneously employed in CDI processes because of their excellent capacitance and electrical conductivity, respectively. However, electrodes and current collectors account for a high percentage of the cost of producing CDI cells (Park et al. 2007). For instance, a carbon cloth for the electrode is
approximately $1,000 \text{ m}^2$, and a graphite sheet for the current collector is approximately $1,100 \text{ m}^2$ (Liu et al. 2011; Wang et al. 2012). Although those are reasonable for the removal of high-concentrated salts (seawater), the materials might not be suitable for the removal of low-concentrated groundwater. According to the Langmuir equation, an electrode with low capacitance is sufficient for use in low salt concentrations (Bang et al. 2005).

In this study, we proposed a low-cost carbon composite electrode, which was fabricated at $650 \text{ m}^2$ using low-cost materials and a simple casting process, reducing the material cost. Moreover, the carbon composite electrode carries out the roles of both the electrode and current collector. Therefore, in contrast to the typical configuration, the carbon composite electrodes were used without current collectors in the CDI cell, reducing the overall system cost. To examine the ability of the carbon composite electrode, its capacitance and electrical conductivity were characterized. The CDI cell constructed with the carbon composite electrodes was tested for the removal of arsenate from artificial groundwater, and the conditions for optimal removal efficiency are extensively discussed.

### MATERIALS AND METHODS

#### Fabrication of the carbon composite electrodes

The carbon composite electrodes were fabricated with a casting technique using a porous substrate and carbon slurry. To prepare the carbon slurry, activated carbon powder (ACP; specific area = 1000–1600 m$^2$ g$^{-1}$, Dong-il Carbon) and poly(vinylidene fluoride) (PVDF; MW = 530,000, Aldrich) were simultaneously dissolved in an N-methyl-2-pyrrolidone (Fluka) solvent. The compositions of the carbon composite electrodes are listed in Table 1.

After the carbon slurry was agitated for 6 h to ensure homogeneity, it was cast onto the porous substrate (DONA-CARBO S-253 Paper, Osaka Gas Chemicals Co., Ltd) using a doctor blade, as illustrated in Figure 1.

#### Table 1 | Composition ratios of the ACP and PVDF for the carbon composite electrode fabrication

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Composition, wt.%</th>
</tr>
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<tbody>
<tr>
<td>AP73</td>
<td>ACP:PVDF = 7:3</td>
</tr>
<tr>
<td>AP82</td>
<td>ACP:PVDF = 8:2</td>
</tr>
<tr>
<td>AP91</td>
<td>ACP:PVDF = 9:1</td>
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The carbon composite electrode was dried at room temperature for 1 d and then at 100 °C for 10 h to remove all solvents remaining on the electrode surface.

#### Physical and electrochemical characterizations of the carbon composite electrodes

The surface morphology of the carbon composite electrode was investigated using a video microscope (EGVM 35B, EG Tech, Korea) and scanning electron microscopy (SEM; JEOL, Japan). The capacitance and electrical conductivity of the carbon composite electrode were examined using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) with a potentiostat (AutoLab PGSTAT30, Eco Chemie). The capacitance was measured using a 0.785 cm$^2$ section of the carbon composite electrode with an Ag/AgCl reference electrode and Pt wire counter electrode in a 1 M H$_2$SO$_4$ solution. The scan voltage...
ranged from -0.6 to 0.6 V at a sweep rate of 100 mV s⁻¹ (Wang & Virkar 2005). The capacitance was calculated using Equation (1) with the obtained CV results (Kim & Choi 2010).

\[
c = \frac{(I_a - I_c)}{2v \cdot w}
\]

(1)

where \(c\) is the capacitance (F g⁻¹), \(I_a\) and \(I_c\) are the anodic and cathodic currents (A), respectively, \(v\) is the scan rate (V s⁻¹), and \(w\) is the weight (g).

The electrical conductivity was calculated using Equation (2) with the resistance of the carbon composite electrodes, as measured using EIS via a four-probe system within a frequency range of 10⁵–50 Hz (Sone et al. 1996; Wang & Virkar 2005).

\[
\sigma = \frac{L}{R \cdot w \cdot d}
\]

(2)

where \(\sigma\) is the electrical conductivity (S cm⁻¹), \(L\) is the sample length (cm), \(R\) is the resistance (Ω), \(w\) is the sample width (cm), and \(d\) is the sample thickness (cm).

Salt removal test

As illustrated in Figure 2(a), the typical CDI unit cell consists of the following construction: endplate–current collector–electrode–gasket–separator–electrode–current collector–endplate. Here, the cell components were reduced by using only carbon composite electrodes instead of both electrodes and current collectors. The configuration of the CDI cell proposed in this study is depicted in Figure 2(b).

A salt removal test was performed using a 24 cm² section of the carbon composite electrode with the proposed CDI cell. Influent was supplied to the CDI cell at a rate of 2 mL min⁻¹ using a peristaltic pump (Masterflex Cole-Parmer, USA). To investigate removal efficiency with respect to various concentrations of the influent, feedwater concentrations of 10, 15, and 25 mg L⁻¹ NaCl were prepared. Voltages were applied to the carbon composite electrode using a DC power supply (6613C Agilent, USA). The variation in the ionic conductivity was measured using a conductivity meter (OAKTON, Japan) at the outlet of the cell, and the removal efficiency, \(\eta\), was then calculated using Equation (3) (Dermentzis & Ouzounis 2008). The measured ionic conductivity was automatically input into a computer through an RS232 port at 10 s intervals.

\[
\eta(\%) = \frac{C_i - C}{C_i} \times 100
\]

(3)

where \(C_i\) is the initial ionic conductivity of the influent and \(C\) is the ionic conductivity of the effluent.

Arsenic removal test

Influent prepared using Na₃HAs₄·7H₂O (Sigma) to provide 25 and 1 mg L⁻¹ arsenate solutions was supplied to the CDI cell at 4 mL min⁻¹ rate using the peristaltic pump. The various voltages were intermittently applied to the CDI cell using the DC power supply. The variations in the ionic conductivity of the effluent had been measured in real time at the outlet of the cell using a conductivity meter. The solution pH was adjusted using a 0.01 N sulfuric acid or 0.01 N sodium hydroxide solution. When the CDI
process was conducted using the 1 mg L\(^{-1}\) arsenate solution, the effluent was sampled at 15 s intervals to determine an accurate arsenate concentration using ion chromatography (IC, Dionex ICS-1600) with an AS9-HC column (Dionex).

**RESULTS AND DISCUSSION**

**Surface analysis**

Figure 3(a) and 3(b) are the magnified surfaces of the porous substrate and the carbon composite electrode, respectively, as observed using the video microscope. Vacant spaces appear in Figure 3(a) because the wires of the porous substrate were loosely interlaced. The porous substrate is made using a wet process, causing resins and slurry to soak thoroughly into the porous substrate matrix (Bleda-Martinez et al. 2005). The top and bottom of the carbon composite electrode were thereby readily formed as activated carbon surfaces without special treatment. Figure 3(b), an image of the dried carbon composite electrode, reveals that the carbon slurry was well soaked into the vacant spaces of the porous substrate. The video microscope images show the successful formation of the carbon composite electrode, which satisfies the criteria of rigid support and activated carbon surfaces.

The SEM image in Figure 3(c) shows the surface morphology of the fabricated carbon composite electrode. The image verifies the high degree of adhesion between the ACP and PVDF, which indicates that the carbon composite electrode has sufficient mechanical strength to be durable against the friction of the influent. It can be seen from Figure 3(d) and 3(e) that the flexibility is varied, along with the carbon composition. AP82 (Figure 3(d)) has a stiff appearance, but AP91 (Figure 3(e)) was a significantly flexible electrode, implying that the binder in AP91 seems to be insufficient. The insufficient amount of the binder might lead to disconnection of carbon powders, even huge carbon powders.

**Electrochemical characterization**

Capacitance indicates the electrical capacity of absorbed ions on the electrode surface. To confirm the electrical capacity of the carbon composite electrode, capacitance was measured using CV as a voltage sweep method. To examine capacitance according to the content of the ACP, the fabricated carbon composite electrodes (AP73, AP82, and AP91) were sequentially analyzed.

As shown in Figure 4, the widths of the current density of each carbon composite electrode gradually enlarged as the activated carbon content was increased. According to Equation (1), the capacitances of AP73, AP82, and AP91 were 8.35, 37.27, and 63.41 F g\(^{-1}\), respectively, confirming that the capacitance increased in response to increases in activated carbon content. The electrical conductivity of the...
carbon composite electrodes was then analyzed to evaluate their effectiveness as current collectors. The inherent resistance values of AP73, AP82, and AP91 were obtained using EIS. The calculated electrical conductivities were compared to determine the best ratio between the ACP and PVDF in the carbon composite electrodes. The electrical conductivity increased in response to increases in the amount of ACP content in AP73 and AP82, presenting 0.298 and 0.401 S cm\(^{-1}\), respectively. However, the electrical conductivity of AP91 decreased to 0.398 S cm\(^{-1}\). Contrary to the result of capacitance, the trends of electric conductivity was inconsistent with ACP content. It is considered that the fixation of the ACP was not stable in AP91 because the electric conductivity is attributed to connection of the carbon particles (Wang et al. 2012). Indeed, soot deposited on AP91 was separated from the electrode during examination. The amount of binder appears to be insufficient to simultaneously combine the ACP and the wires of porous substrate. Therefore, AP82 exhibited the optimal composition for use in the CDI system.

**Salt removal test**

A salt removal test was performed to confirm the desalination capacity of the fabricated carbon composite electrodes. Unlike conventional flexible carbon electrodes, the fabricated carbon composite electrodes were stiff; thus, a stable CDI stack was built without the need for current collectors. In addition, aqueous leaks were not found in the stack, because the surface of the carbon composite electrode prevented the penetration of the aqueous solution. The CDI cell was assembled with an AP82 electrode fabricated at the optimal composition. To investigate salt removal efficiency with respect to various influent concentrations, the CDI process was conducted using 25, 15, and 10 mg L\(^{-1}\) NaCl solutions.

As shown in Figure 5, a stable cycle graph was exhibited. The removal efficiencies for 25, 15, and 10 mg L\(^{-1}\) NaCl were 65.3, 68.9, and 73.0%, respectively. These results reveal that lower influent concentration results in higher salt removal efficiency because the adsorption capacity of the carbon composite electrodes is limited (Oren 2008). In this regard, higher removal efficiency is expected in an arsenic removal test, because arsenic in the groundwater is below a 1 mg L\(^{-1}\) concentration. The results showed that the carbon composite electrode removed salt successfully in the absence of the commonly used combination of carbon electrodes and current collectors. Moreover, the results demonstrated the relation between removal efficiency and influent concentrations.

**Arsenic removal test**

Arsenate species, i.e. H\(_3\)AsO\(_4\), H\(_2\)AsO\(_4\), HAsO\(_4^2\)\(^-\), and AsO\(_4^3\)\(^-\), change in response to the Eh and pH conditions of the solution (Abo-Farha et al. 2009). Because the EDL thickness on electrode surfaces varies according to the electronegativity of ion species, arsenate removal efficiency can be ascribed to the applied voltage and solution pH (Oren 2008). Thus, the optimal conditions for effective arsenate removal were investigated. First, a voltage adjustment experiment was conducted using a 25 mg L\(^{-1}\) arsenate solution. Removal efficiency was calculated using the ionic conductivity measured at the outlet of the cell.
To confirm the optimal voltage, various voltages within the range of 0.6 to 2.2 V were intermittently applied to the CDI cell. The removal test was repeatedly conducted at least three times. The average value was presented in Figure 6.

As shown in Figure 6, removal efficiency increased in response to increase in the applied voltage until 2.0 V. Although solution pH was not seriously changed under the overall voltage conditions, slightly lower solution pH was exhibited at 2.0 and 2.2 V. According to the EDL theory, higher voltages trap more ions on carbon composite electrode surfaces. However, removal efficiency was diminished at the applied voltage of 2.2 V. It seems that the main reason for this diminishment was water splitting. The hydrogen ions dissociated from water molecules produce the $\text{H}_3\text{AsO}_4$ species by reacting with existing arsenate species such as $\text{H}_2\text{AsO}_4^- \text{ and } \text{HAsO}_4^{2-}$, which leads to the weak attraction with the charged electrodes. Therefore, the voltage of 2 V was found to be optimal for CDI operation.

Second, the solution pH condition was optimized at an applied voltage of 1.5 V for the removal of arsenate using the 25 mg L$^{-1}$ arsenate solution. Note that the arsenate species in a solution varies with pH condition as follows (Mohan & Pittman 2007):

\[
\begin{align*}
\text{H}_3\text{AsO}_4 & \leftrightarrow \text{H}^+ + \text{H}_2\text{AsO}_4^- , \text{p}K_a1 = 2.19 \\
\text{H}_2\text{AsO}_4^- & \leftrightarrow \text{H}^+ + \text{HAsO}_4^{2-} , \text{p}K_a2 = 6.94 \\
\text{HAsO}_4^{2-} & \leftrightarrow \text{H}^+ + \text{AsO}_3^{3-} , \text{p}K_a3 = 11.50
\end{align*}
\]

Below pH 6, the dominant ion species is $\text{H}_2\text{AsO}_4$. Thus, the main target in the weak acidic region is monovalent ions. In the neutral pH region, $\text{H}_2\text{AsO}_4$ and $\text{HAsO}_4^{2-}$ coexist at almost identical concentrations. Over pH 8, $\text{HAsO}_4^{2-}$ is the dominant ion species in the solution. To investigate the optimal position of arsenate, a removal test was performed at three regions: weak acidic (pH 4 and 5), neutral (pH 7 and 8), and weak base (pH 9 and 10). This test was repeatedly performed at least three times. The average value was described in Figure 7.

As shown in Figure 7, removal efficiency improved in response to pH increases, meaning that removal efficiency increased in response to increases in the ion valence. However, the removal efficiency at pH 10 was lower than that at pH 9. The pH adjustment was carried out using a 0.01 N sulfuric acid or 0.01 N sodium hydroxide solution, which increased the initial ionic conductivity of the influent. The initial conductivity at pH 9 was 42 μS cm$^{-1}$, whereas it was 160 μS cm$^{-1}$ at pH 10. As explained in the results of the salt removal test, low removal efficiency appeared in a high-concentrated influent due to the limited capacitance of the electrode. Therefore, excessive pH control adversely influenced removal efficiency.

As a final experiment, the CDI test was conducted using the 1 mg L$^{-1}$ arsenate solution as a realistic groundwater concentration at the optimal operation condition (2 V applied voltage and pH 9 solution). Because the concentration of arsenate is very low, the arsenate concentration of the effluent was measured using IC for precise analysis. Second and third cycles of the CDI operation for AP82 proposed in this study and the commonly-used combination of carbon electrodes (carbon cloth) and current collectors (graphite) are shown in Figure 8. After the arsenate ions were removed by AP82, the remaining arsenate concentration in the effluent was 0.012 mg L$^{-1}$, which corresponds to 98.8% removal efficiency. This concentration is close to WHO standards. Similarly, the commonly-used combination of carbon electrodes and current collectors achieved 99.2% removal efficiency.
efficiency. For reference, the removal efficiency of a coagulation process is within a range of 70–99.18% using 14–0.2 mg L$^{-1}$ arsenate solution (Baig et al. 2015). These results demonstrated that the carbon composite electrode prepared in this study is capable of removing arsenic from groundwater. The coagulation process costs $2.30–5.10 per g$^{-1}$ (Baig et al. 2015). Although the cost of the carbon composite electrodes proposed in this study is three times lower than the commonly-used combination of carbon electrodes and current collectors, the preparation cost for the carbon composite electrode should be further reduced.

CONCLUSIONS

The removal of high-concentrated salts for desalination has become a global necessity. However, the removal of low-concentrated salts from groundwater must also be practiced. In this study, a carbon composite electrode was fabricated as a cost-effective means of treating low-concentrated salt. Although the capacitance and electrical conductivity of the carbon composite electrode were lower than those of the commercial carbon electrodes and current collectors, a successful desalination performance in the absence of current collectors was exhibited in the CDI operations; a successful desalination performance in the absence of current collectors was achieved. Therefore, this study demonstrated that the fabricated carbon composite electrode can be economically and successfully applied to the removal of low-concentrated salts from groundwater.

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