

# Evaluating Different Commercial Forms of Carbon as Cathodes in Air-cathode Assisted Iron Electrocoagulation (ACAIE) of Groundwater for Arsenic Removal

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Many people around the world rely on groundwater for drinking and sanitation, however, they are exposed to various health risks from the naturally occurring groundwater arsenic (As). Air-cathode Assisted Iron Electrocoagulation (ACAIE) using Carbon Black Pearls 2000<sup>®</sup> cathode was previously shown catalyze the removal of groundwater As by producing hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). This work explored Vulcan<sup>®</sup> XC-72, and Printex<sup>®</sup> L6 Carbon as alternative cathodes for iron electrocoagulation which are more selective towards the 2-electron oxygen reduction reaction into H<sub>2</sub>O<sub>2</sub> compared to Carbon Black Pearls<sup>®</sup>. The cathodes were tested in an ACAIE set-up to treat synthetic groundwater spiked with 1,500 µg/L of As at different charge dosage rates (CDR) from 1.56 C/L-min to 100 C/L-min with a total charge dosage of 600 C/L for all set-ups. Although the electrocoagulation energies among the cathodes were similar, the use of Printex<sup>®</sup> cathode for ACAIE remediated the groundwater for all CDR with final As levels below 10 µg/L. This is in contrast with the less selective Carbon Black Pearls<sup>®</sup> at low CDR, and the less active Vulcan<sup>®</sup> Carbon at high CDR where the treated groundwater may still have As levels above 10 µg/L. Future research would explore modifications in the carbon materials and reactor configuration to further optimize ACAIE in removing groundwater As.

## 1. Introduction

Arsenic is a toxic element that naturally occurs in groundwater, with concentrations exceeding 1,000 µg/L in many countries (Kobya et al., 2020) especially in Asia (Nidheesh and Singh, 2017), beyond the maximum contaminant level (MCL) of 10 µg/L (World Health Organization, 2011). Arsenic is present in two oxidation states, Arsenate (As (V)) and Arsenite (As (III)), where As (V) is readily removed by conventional water treatment methods, but As (III) needs pre-oxidation to facilitate its removal (Song et al., 2017).

Iron electrocoagulation (FeEC) is a process that pre-oxidizes As (III) to As (V), this involves two iron electrodes where the Fe atoms in the anode oxidizes into Fe (II) and the cathode reduces the water into hydrogen gas. The Fe (II) is further oxidized by the dissolved O<sub>2</sub> into Fe (IV), which reacts with As (III) to form Fe (III)-As(IV) flocs (Bandaru et al., 2020). The intermediate reactions and As (III) oxidation reactions occur in the bulk solution not at the electrodes with the As (III) oxidation rate directly related to its concentration (Montefalcon et al., 2020). The process is however rate limited by the reaction of the Fe (II) with the dissolved O<sub>2</sub>. This would require higher reactor volumes to increase the treatment time, which may be capital intensive.

Air Cathode Assisted FeEC (ACAIE) is an FeEC modification that replaces the cathode (Bandaru et al., 2020). Their study involved an air-cathode with Carbon Black Pearls<sup>®</sup> as the active material which generated H<sub>2</sub>O<sub>2</sub> through the 2 e<sup>-</sup> oxygen reduction reaction (ORR). The H<sub>2</sub>O<sub>2</sub> replaced dissolved O<sub>2</sub> as the Fe (II) oxidant. This improved As removal from the conventional FeEC which made electrocoagulation facile and compact (Bandaru et al., 2020).

There is a potential to further improve ACAIE performance, especially from carbon materials previously studied for  $\text{H}_2\text{O}_2$  production through ORR. Some studies have even extended to organic pollutants removal using the  $\text{H}_2\text{O}_2$  electrogenerated (Zhou et al., 2019), but there are fewer studies on the removal of toxic metals such as As. This study explored two alternative commercial carbon materials, Vulcan<sup>®</sup> XC-72R Carbon and Printex<sup>®</sup> L6 Carbon, which are widely used for ORR catalysis and are selective toward the  $\text{H}_2\text{O}_2$  generation (Assumpção et al., 2011). The carbon materials were evaluated based on the main objective of removing groundwater As.

## 2. Materials and methods

While the carbon cathode materials were mainly evaluated based on their Arsenic removal from groundwater using an ACAIE set-up, their electrochemical characteristics were also determined to provide insights at the cathode level to verify their performance at the reactor level. This study used three types of carbon material: Vulcan<sup>®</sup> XC-72R Carbon (Fuel Cell Store), Printex<sup>®</sup> L6 Carbon (Orion Engineered Carbons), and Carbon Black Pearls<sup>®</sup> 2000 (Cabot Corporation).

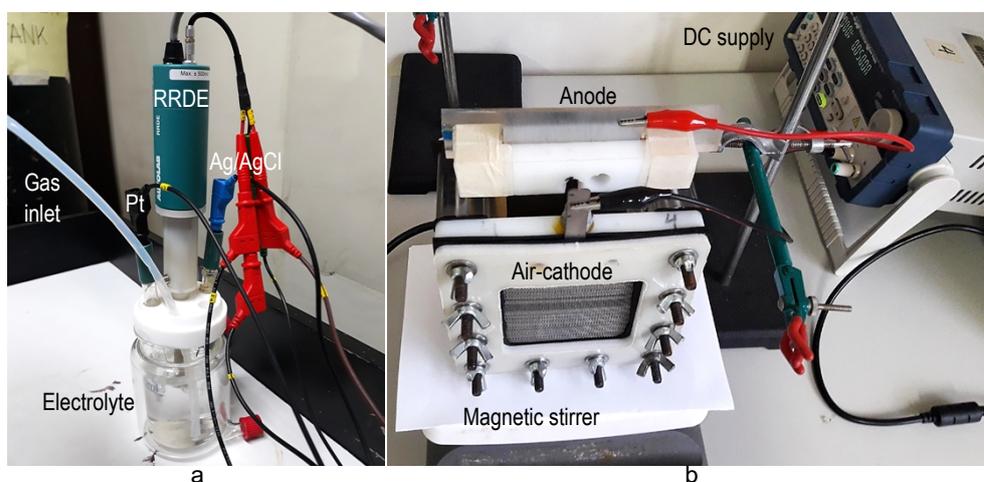


Figure 1: Electrochemical test (a) and ACAIE reactor (b) set-ups

### 2.1 Electrochemical tests

Electrochemical tests were done to determine the carbon materials' ORR activity and selectivity toward the  $2\text{e}^-$  ORR (Figure 1a). 475  $\mu\text{L}$  of ethanol was added to 3 mg of carbon catalyst (Li et al., 2019) and ultrasonicated for 30 min. Twenty-five  $\mu\text{L}$  of 5 % Nafion (Fuel Cell Store) was added to the catalyst ink and further ultrasonicated for 20 min. The working electrode was a Metrohm AG (2021) platinum ring-glassy carbon disk (5 mm diameter) rotating ring disk electrode (RRDE) tip. A 5.25  $\mu\text{L}$  catalyst ink aliquot (0.16 mg carbon/ $\text{cm}^2$ ) was dropped onto the disk and air-dried. The counter and reference electrodes used were Pt plate (Metrohm) and Ag/AgCl (Metrohm) electrodes. The electrolytes used were 200 mL of 1.0 M NaOH, and 0.5 M  $\text{Na}_2\text{SO}_4$ .

The electrochemical tests were done using an Autolab PGSTAT. The electrolyte was bubbled with  $\text{N}_2$  for 20 min before performing cyclic voltammetry (CV) between 1.0748 V vs the reversible hydrogen electrode (RHE) to -0.1460 V vs. RHE for 20 cycles. Then, linear sweep voltammetry (LSV) was done from 1.0748 V vs. RHE to -0.1460 V vs. RHE for different RRDE rotation rates from 400 to 3,600 rpm. The ring potential was fixed at 1.607 V vs. RHE to maximize  $\text{H}_2\text{O}_2$  oxidation at the ring but prevent oxygen evolution (Zhou et al., 2016). The electrolyte was then bubbled with  $\text{O}_2$  for 40 min, then CV and LSV were repeated (Valim et al., 2013).

### 2.2 ACAIE reactor tests

A custom built 500 mL batch reactor (Figure 1b) was used for the ACAIE reactor tests (Bandaru et al. 2020). The air-facing side of the 10 cm x 10 cm cathode was coated with 600 mg graphite (200 mesh, Alfa Aesar) in 2 mL 60 % polytetrafluoroethylene, dried for 20 min, and sintered at 350  $^\circ\text{C}$  for 40 min. The electrolyte-facing side of the cathode was coated with 150 mg of carbon catalyst in 83  $\mu\text{L}$  polytetrafluoroethylene and 2.917 mL 2-propanol, dried for 20 min, and sintered at 350  $^\circ\text{C}$  for 40 min. The submerged area of the cathode was 64  $\text{cm}^2$ . A low-carbon steel anode (1006–1026 steel grade, McMaster-Carr) with a submerged area of 42  $\text{cm}^2$  was placed 1.5 cm parallel to the air-cathode.

The reactor was filled with 500 mL of synthetic groundwater (containing 2.76 mg/L  $\text{PO}_4^{3-}$ , 108 mg/L  $\text{HCO}_3^-$ , 3 mg/L  $\text{SO}_4^{2-}$ , 101.6 mg/L silicates, 34.8 mg/L Cl<sup>-</sup>, 23.6 mg/L  $\text{Mg}^{2+}$ , and 9.8 mg/L  $\text{Ca}^{2+}$ ) spiked with 1,500  $\mu\text{g/L}$

As ( $\text{NaAsO}_2$ , Sigma-Aldrich). A set of electrolysis runs was done on the same cathode using an external DC power supply (BK Precision 9200) with 600 C/L charge dosage for each run but repeated at varying charge dosage rates (CDR): 1.56, 6, 20, 60, and 100 C/L-min. The solution was continuously stirred at 600 rpm with a magnetic stirrer during electrolysis. After each electrolysis run, samples of the treated groundwater were filtered, and 10 mL of the filtrate was acidified with 1 mL of 37 % HCl. The filtrates were analysed using Inductively Coupled Plasma-Optical Emission Spectroscopy to measure the final As concentration, the minimum detection is 5.5  $\mu\text{g/L}$  with zero measurement readings below this value.

### 3. Results and discussions

This section relates the performance of each carbon material in removing groundwater As to the material properties of the carbon catalyst.

#### 3.1 Cathode material characterization

The electrocatalytic performance of the carbon materials was assessed based on their ring (Figure 2) and disk current (Figure 3) data. The selectivity of the carbon material towards the 2  $e^-$  ORR was determined using the following equations Eq(1) and Eq(2), with the equation terms defined in the nomenclature section. The collection efficiency of the ring,  $N$ , was set to 0.249 (Metrohm AG, 2021).

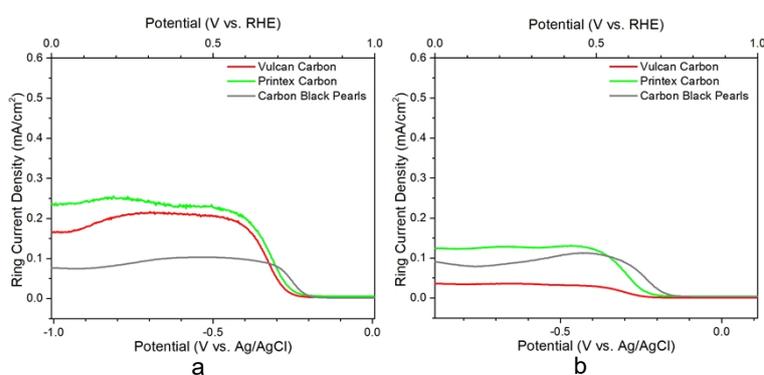


Figure 2: LSV ring current densities (normalized with respect to disk area) at 1,600 rpm for the carbon catalysts in (a) 1.0 M NaOH and (b) 0.5 M  $\text{Na}_2\text{SO}_4$

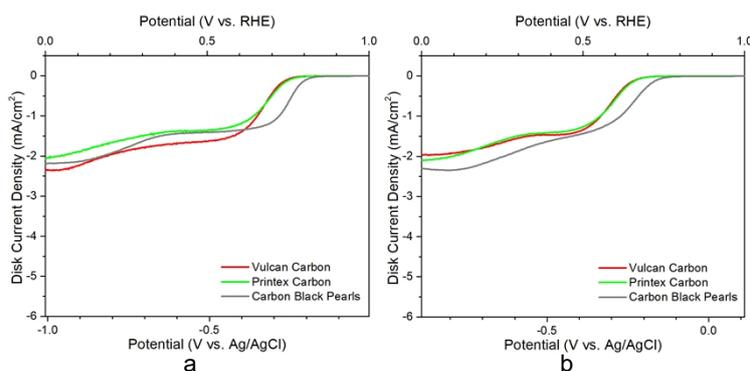


Figure 3: LSV disk current densities at 1,600 rpm for the carbon catalysts in (a) 1.0 M NaOH and (b) 0.5 M  $\text{Na}_2\text{SO}_4$

$$n_{e^-} = 4 \times \frac{-I_{\text{disk}}}{-I_{\text{disk}} + \frac{I_{\text{ring}}}{N}} \quad (1)$$

$$\%_{\text{H}_2\text{O}_2} = \frac{4 - n_{e^-}}{2} \times 100\% \quad (2)$$

For the LSV in 1.0 M NaOH, the Carbon Black Pearls<sup>®</sup> showed the highest overall ORR activity among the carbon materials with ORR onset potential at 0.8 V vs. RHE, while the Vulcan<sup>®</sup> and Printex<sup>®</sup> carbons have more

anodic onset potentials at around 0.7 V vs. RHE. The Carbon Black Pearls® had the lowest ring activity at 0.1 mA/cm<sup>2</sup> with an  $n_e$  of 3.13 or H<sub>2</sub>O<sub>2</sub> selectivity of 43.58 % at 0.4 V vs. RHE. The disk current of Vulcan® Carbon is slightly higher than that of Printex® Carbon and their ring activities were also similar but reversed. This makes the Vulcan® Carbon a more active ORR catalyst in NaOH but less selective towards the 2 e<sup>-</sup> ORR compared to Printex® Carbon. The corresponding H<sub>2</sub>O<sub>2</sub> selectivities of 66.35 % for the Vulcan® Carbon and 78.94 % for the Printex® Carbon at 0.4 V vs. RHE are similar to the findings of Moraes et al. (2016).

For the LSV in 0.5 M Na<sub>2</sub>SO<sub>4</sub>, the disk currents of Vulcan® and Printex® carbons were similar but the Printex® carbon ring current was significantly larger. The H<sub>2</sub>O<sub>2</sub> selectivities of the carbon materials are 15.87 %, 41.32 %, and 52.63 % for the Vulcan® Carbon, Carbon Black Pearls®, and Printex® Carbon, at 0.4 V vs. RHE. Comparing the catalyst performance in the two electrolytes, the Carbon Black Pearls® have a selectivity of around 40-45 %, while the Vulcan® and Printex® Carbons have uncertain selectivities. Despite the uncertainty, the Printex Carbon® maintained the highest selectivity for both electrolytes due to the oxygenated acid groups (Assumpção et al., 2011) which promote the 2 e<sup>-</sup> ORR to H<sub>2</sub>O<sub>2</sub>.

### 3.2 ACAIE reactor performance

The cathode materials were evaluated based on the energy consumption and As removal and were correlated to the catalyst properties. With the lowest energy consumption, the Carbon Black Pearls® cathode is the most active among the three carbon materials explored (Figure 4). This is consistent with the highest measured disk current from the electrochemical tests. The significantly lower energy consumption of the Carbon Black Pearls® cathode at 1.56 C/L-min CDR (0.2 mA/cm<sup>2</sup>) is due to the more positive onset potential of the Carbon Black Pearls®. With similar activities, the carbon materials show similar energy consumption especially if the uncertainties are considered.

Comparing the reported disk current densities and the ACAIE current densities, the corresponding current density at 20 C/L-min CDR is 2.60 mA/cm<sup>2</sup> which is comparable to the 3 mA/cm<sup>2</sup> maximum disk current densities reported from LSV at 3,600 rpm. This would mean that other reduction reactions besides ORR may have prevailed at high CDR such as hydrogen evolution, especially if the cathode potential is below 0 V vs. RHE.

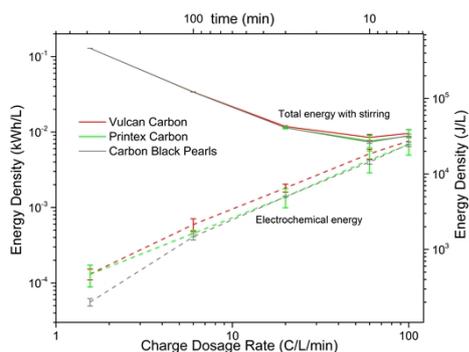


Figure 4: ACAIE energy consumption without stirring (bottom) and with stirring (top), the error bars correspond to one standard deviation of the energy consumption data

Table 1: Final groundwater As concentrations of the ACAIE runs at all charge dosage rates using the different cathode materials

Cathode Material	Charge Dosage Rate				
	1.56 C/L-min	6 C/L-min	20 C/L-min	60 C/L-min	100 C/L-min
Vulcan® Carbon	6.41 µg/L	28.84 µg/L	23.11 µg/L	24.60 µg/L	47.46 µg/L
Printex® Carbon	2.43 µg/L	0.00 µg/L	0.00 µg/L	0.30 µg/L	0.00 µg/L
Carbon Black Pearls®	23.56 µg/L	7.00 µg/L	3.87 µg/L	7.05 µg/L	3.55 µg/L

For As removal, only the Printex® Carbon cathode met the 10 µg As/L MCL for all CDR (Table 1). This means that the Printex® Carbon maintains the activity and selectivity for H<sub>2</sub>O<sub>2</sub> generation from the 2 e<sup>-</sup> ORR, allowing for smaller reactors and less energy consumption to remove groundwater As. The Carbon Black Pearls® cathode does not sufficiently remove As at low CDR, while the Vulcan® Carbon cathode does not sufficiently remove As at high CDR. While Vulcan® Carbon has better selectivity than Carbon Black Pearls®, having a better As removal at 1.56 C/L-min CDR but at higher CDR, its inferior activity affects its performance such that it had the least As removal. These imply that the cathode reaction is still the rate limiting step with the satisfactory As removal of

the Printex® Carbon at all CDR show that anode passivation does not affect the As removal which is even enhanced by the chlorides present which catalysed Fe dissolution (Song et al., 2017).

To compare this study to similar works but with different set-ups, the electrical energy per order of magnitude of As removal (EEO) is reported, Eq(3), with a 10 W stirrer power ( $P_{\text{stir}}$ ) assumed (Bandaru et al., 2020). The ACAIE EEO is less than 5 kWh/m<sup>3</sup>-log for all tests without the stirring energy, however, the stirrer increases the EEO up to 70 kWh/m<sup>3</sup>-log at 1.56 C/L-min CDR due to the long electrolysis time (Figure 5). With shorter treatment times at higher CDR, the energy consumed by the stirrer is reduced so the EEO does not exceed 6.5 kWh/m<sup>3</sup>-log even with stirring. The higher selectivity of Printex® Carbon generated more H<sub>2</sub>O<sub>2</sub> which catalysed the reaction of Fe (II) to Fe (III). The increased Fe (III) generation rate also compensated for the presence of competing ions such as phosphates, silicates and sulphates (Song et al., 2017). This enhanced As removal, allowing for an efficient electrical energy usage even at high CDR, especially if the energy consumption of the auxiliary equipment is considered which greatly depends on the reaction time.

$$\text{EEO} = \frac{(V \times I + P_{\text{stir}}) \times t}{\text{Volume} \times \log\left(\frac{C_{\text{As0}}}{C_{\text{As}}}\right)} \quad (3)$$

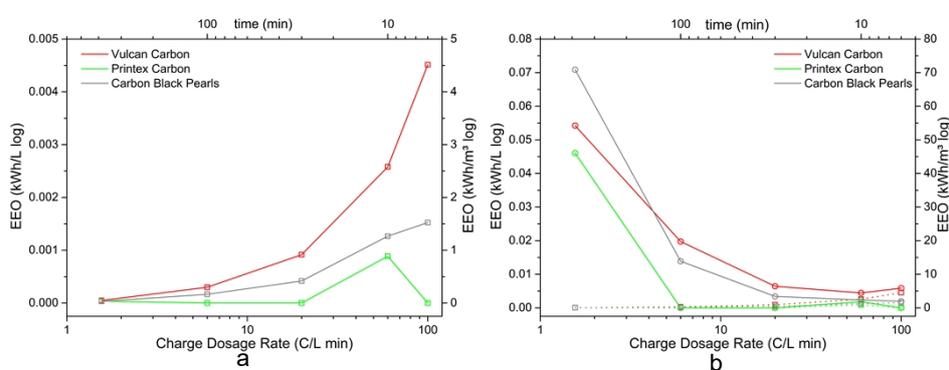


Figure 5: ACAIE EEO (a) without stirring and (b) with stirring. The dotted curves in Figure 5b are the EEO without stirring overlaid from Figure 5(a)

The use of Printex® Carbon shows that a treatment time of 360 s (6 min) at 100 C/L-min CDR is possible which is more facile compared to other cathodes that remove As via the 2 e<sup>-</sup> ORR, with the other studies needing at least 30 min to treat contaminated water (Nidheesh et al., 2020). This means that ACAIE requires less reactor volume, reducing the initial capital. The lower ACAIE EEO will also reduce the operating expenses.

The cathode catalyst can be further improved by chemical modifications such as acid and base treatment (Moraes et al., 2016). Optimisations can also be done on the electrodes, such as their mechanical stability and lifetime (Bandaru et al., 2020), and on the reactor, particularly the geometry such as the electrode spacing and electrode area with respect to the reactor volume. The effect of other chemical species in the groundwater should also be studied in greater detail given that the composition greatly varies in location and time.

#### 4. Conclusions

This work explored alternative commercial forms of carbon known to be selective towards the 2 e<sup>-</sup> ORR. The electrocatalytic activities of Vulcan® and Printex® Carbon match that of the previously demonstrated Carbon Black Pearls® air-cathode, allowing for a facile groundwater treatment via ACAIE. The oxygenated acid groups present in the Printex® L6 Carbon make it more selective to the H<sub>2</sub>O<sub>2</sub> electrogeneration from ORR. This ensures sufficient groundwater As removal by catalysing the intermediate production of Fe (IV) which oxidizes As (III) and precipitates out as Fe (III)-As(V) flocs. Even at high CDR, the performance of the ACAIE utilising Printex® Carbon cathode is not compromised, allowing for compact reactors and reducing the energy use of auxiliary equipment. Future work would further explore ACAIE by modifying the carbon material, investigating cathode stability, and optimising the reactor configuration.

#### Nomenclature

ACAIE – air-cathode assisted FeEC  
 $C_{\text{As}}$  – final As concentration  
 $C_{\text{As0}}$  – initial As concentration

CDR – charge dosage rate  
 CV – cyclic voltammetry

EEO – electrical energy per order of magnitude of As removal	$n_e$ – number of electrons transferred
FeEC – iron electrocoagulation	ORR – oxygen reduction reaction
I – total ACAIE current applied	$P_{\text{stir}}$ – stirrer power
$I_{\text{disk}}$ – disk current	RHE – reversible hydrogen electrode
$I_{\text{ring}}$ – ring current	RRDE – rotating ring disk electrode
LSV – linear sweep voltammetry	t – electrolysis time
MCL – maximum contaminant level	V – ACAIE cell voltage difference of the electrodes
N – ring collection efficiency	$\%_{\text{H}_2\text{O}_2}$ – selectivity of $\text{H}_2\text{O}_2$ generation

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