Capacitive deionization utilizing Activated Biochar – Manganese Dioxide (AB - MD) nanocomposites for desalination applications

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Abstract. Faradaic electric double layer capacitor (EDLC) nanocomposites for desalination were synthesized using coconut-shell derived activated biochar (AB) and manganese dioxide (MnO2) for capacitive deionization (CDI). Three different co-precipitation methods were explored to produce the composite such as: (1) indirect liquid-phase combination (ILC) method; (2) direct liquid-phase combination (DLC) method; and (3) acid-assisted grafting oxidation combination (AGO) method. Surface characterization confirmed the presence of α-MnO2 incorporated on the mesoporous activated biochar surface (485.92 m2 g-1) for all the nanocomposites developed. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests show that the three methods yielded a quasi-rectangular and symmetric CV plot indicating good EDLC behavior and a steep EIS plot. The highest specific capacitance of 522.7 F g-1 at 5 mV s-1 was observed using AGO method. CDI tests under 1.2 V at varying NaCl concentrations show high capacitive performance of the synthesized electrodes. The ILC method nanocomposite exhibited superior electrosorptive performance with an electrosorption capacity of 114.11 mg g-1 at 500 ppm NaCl concentration. Due to the synergistic effects of the pseudocapacitive redox reaction of MnO2 and the outstanding double-layer charging of AB on the composite, it serves as a suitable CDI electrode for desalination.

Keywords: Capacitive deionization, activated biochar, manganese dioxide, nanocomposite

1. Introduction

Recently, there is an accelerated rise in the global demand for potable water due to several factors, namely: the ever-growing human population, pollution of groundwater streams due to leaching, and effects of climate change and drought. Capacitive deionization (CDI), a separation process for removing ionic elements or salt ions from aqueous solutions through electrosorption, is now considered as an alternative to the more conventional membrane desalination technologies like reverse osmosis and electrodialysis. CDI has several advantages over the recent available desalination technologies, such as low manpower costs, high effluent recovery, ease of electrode regeneration, ecologically friendly, energy efficient and unlikely to have fouling problems. The electrosorptive process can be likened to an electrochemical capacitor which makes use of the capacitance (energy storage) of materials, attracting ions using an induced low voltage. Cations and anions that are in the influent will move towards the respective oppositely charged electrode under an external electric field. Several studies showed that the physicochemical properties of the nanomaterials used in CDI highly contributes to its electrosorptive performance. However, the electrosorptive capacity of present materials lacks the capacitive charge storage and electrosorption capacity needed for high concentration desalination applications. The improvement on the electrochemical properties of existing nanomaterials is one of the challenges of CDI technology on becoming a more effective desalination method.

Activated biochar (AB) is a promising electrode for CDI because of its low cost, abundance, high stability to electrochemical stress, high specific surface area and high conductivity. Biochar is synthesized from the pyrolysis of biomass, like coconut shells, which are one of the highly unutilized agricultural wastes globally. Its utilization most certainly brings great environmental benefits. However, studies showed that activated biochar and similar non-Faradaic electric double layer capacitor
(EDLC) materials have low electrochemical performance, with specific capacitance values as high as 150-250 F g\(^{-1}\) [19-21]. Recent studies have focused on synthesizing carbonaceous material – transition metal oxide (CM - TMO) nanocomposites, since the pseudocapacitive property of TMOs derived from reversible and fast Faradaic reactions, when combined with CMs, produces synergistic effects [7-13,19-27].

Among all of the TMOs studied, manganese dioxide (MnO\(_2\)) has gained significant interest as an electrode material due to its low cost, high abundance, ease of synthesis, environmentally benign nature and a high theoretical pseudocapacitance value of 1370 F g\(^{-1}\) [13, 21]. However, the utilization of bulk MnO\(_2\) is hindered due to its poor electronic conductivity, with values of 0.009 and 5.8x10\(^{-6}\) S cm\(^{-1}\) for cryptomelane and birnessite, respectively [28]. Also, several polymorphic forms of MnO\(_2\) are present which significantly contribute to the electrochemical properties of the material [7,11, 13,21, 27-29]. A study by Yin et. al. [29] found that α-MnO\(_2\) has approximately three times better specific capacitance than that of β-MnO\(_2\), which is due to the large tunnel structure provided by the MnO\(_6\) octahedra of α-MnO\(_2\). This morphology is suitable for the insertion or extraction of ions. Taking this into account, the integration of manganese dioxide (preferably in α polymorph) to the activated biochar surface will counteract any drawbacks and produce a synergistically enhanced Faradaic EDLC nanomaterial for CDI applications.

Notably, a limited number of studies has explored the usage of activated biochar – manganese dioxide nanocomposite for CDI applications. Liu et. al. [7] developed a MnO\(_2\) – activated carbon (AC) composite electrode through anodic deposition, which presented almost a two-fold increase in electrosorption capacity with that of AC alone. Yang et. al. [11] produced a nano-porous carbon – MnO\(_2\) electrode for CDI while Hu et. al [13] synthesized a MnO\(_2\) – carbon fiber composite electrode using the electrosorption process to remove copper ions from water. These studies show that the electrochemical performance of the electrode is dependent on the surface characteristics of the carbon-based material, and the synthesis and deposition characteristics of manganese dioxide. However, no previous study has been reported on co-precipitation methods of activated biochar – manganese dioxide composites for CDI applications.

In this study, synthesis of coconut shell-derived activated biochar – manganese dioxide (AB - MD) nanocomposites through several co-precipitation (indirect, direct and acid-assisted grafting oxidation) methods was done and their potential as electrodes for CDI applications were explored. Favorable results of this study will pave ways in the development of practical applications towards capacitive deionization for desalination, and removal of heavy metals from solutions.

2. Materials and Methods

2.1. Materials
The chemicals and reagents used in the experiments were the following: carbon black (CB, Uni-onward Corp., New Taipei, Taiwan), deionized (DI) water, hydrochloric acid (36.5-38% HCl, Fluka Chemie AG, WI, USA), manganese acetate tetrahydrate (99% Mn(Ac)\(_2\).4H\(_2\)O, Sigma-Aldrich, Milwaukee, WI, USA, manganese nitrate tetrahydrate (97% Mn(NO\(_3\)).4H\(_2\)O, Alfa Aesar, Ward Hill, MA, USA), N-methyl-2-pyrrolidone (>99% NMP, Riedel-de Haën, Sleeze, Germany), nitric acid (65% HNO\(_3\), Sigma-Aldrich, Milwaukee, WI, USA), polyvinylidenefluoride (PVDF, Sigma-Aldrich, Milwaukee, WI, USA), potassium hydroxide (KOH pellets, Sigma-Aldrich, Milwaukee, WI, USA), potassium permanganate (KMnO\(_4\), J.T. Baker, Phillipsburg, NJ, USA), sodium chloride (99.5% NaCl crystals, Riedel-de Haën, Sleeze, Germany), and sodium sulfate (99% Na\(_2\)SO\(_4\), 10-60 mesh, anhydrous, Macron Fine Chemicals, NJ, USA). All reagents were used as received without further purification.

2.2. Synthesis of activated biochar (AB)
Coconut shell powder was introduced in a tube furnace with argon gas influent. The furnace was run at 5°C min\(^{-1}\) to 550°C under a residence temperature of 2h. Biochar (BC) was cooled and then ground to pass through a 100-mesh sieve. BC was then impregnated with KOH solution, with a KOH to biochar mass ratio of 2:1. After mixing at room temperature for 2h, the suspension was centrifuged at 10,000 rpm for 10 min. The centrifugate was decanted, and the impregnated BC was dried in an oven at 60°C for 48h.
Carbonization was done in the tube furnace at 675°C ramping at 5°C min⁻¹, with a residence time of 4h using argon gas. After cooling, the activated biochar (AB) was mixed with 0.1 M HCl and stirred at room temperature for an hour for demineralization. AB was rinsed with DI until the pH of the wash water became neutral (through litmus paper). The resulting activated biochar was dried in an oven at 60°C.

2.3. Activated biochar – manganese dioxide (AB - MD) co-precipitation methods

The synthesis of activated biochar – manganese dioxide nanocomposites was based on modified methodologies of Wang, Chen and Chen [27], Wang, Sheng and Qiu [31], and Yin et. al [29]. For all methods, the reactant to activated biochar mass ratios were kept at a ratio of 1:2. The mixture in a 50 ml beaker was covered with aluminum foil to prevent unwanted oxidation of permanganate.

2.3.1. Indirect liquid phase combination (ILC) synthesis

Approximately 300 mg of AB was combined with 25 mL 0.2 M HNO₃ and 150 mg of Mn(NO₃)₂·4H₂O in a beaker. The suspension was moderately stirred for 24h, and then vacuum filtered using 0.6μm membrane and then washed with DI to remove unreacted Mn (II) cations on the biochar surface [31]. The impregnated AB was transferred into a beaker with 25 mL of DI and 150 mg KMnO₄. The nanocomposite was separated from the mixture through vacuum filtration and was then rinsed with DI and dried in an oven at 60°C for 24h.

2.3.2. Direct liquid phase combination (DLC) synthesis.

About 300 mg of AB was combined with 25 mL 0.2 M HNO₃ and 150 mg of Mn(NO₃)₂·4H₂O in a beaker. The mixture was stirred moderately for 1h under a water bath maintained at 60°C [27, 29]. After 1h, 5mL DI with 150 mg of KMnO₄ was added dropwise. The solution was again moderately stirred for 24h under a water bath at 60°C. The sample was then vacuum filtered, rinsed with DI and dried in an oven at 60°C for 24h.

2.3.3. Acid-assisted grafting oxidation (AGO) synthesis

Exactly 2.5 g of AB was added to a mixture of 25 mL HNO₃ and 10 mL DI and then stirred for 15 min before sonicating for 1h. The mixture was then poured into a 50 mL Teflon tube container and was dried in a hydrothermal oven at 120°C for 9h [27]. The mixture was cooled and was then diluted with at least 500 mL of DI prior to vacuum filtration. The filtered sample was washed with DI repeatedly to remove nitric acid and was again dried in an oven.

Approximately 300 mg of dried sample was mixed with 25 mL of 0.2 M HNO₃ and 150 mg of Mn (Ac)₂·4H₂O. The mixture was moderately stirred for 1h under a water bath maintained at 60°C [27, 29]. After 1h, 5mL DI with 150 mg of KMnO₄ was added dropwise. The mixture was again stirred moderately for 24h at 60°C. The sample was then vacuum filtered, rinsed with DI and dried in an oven at 60°C for 24h.

2.4. Manganese dioxide (MD) synthesis

Manganese dioxide was prepared using two methods. The first batch (MD) was prepared using the bulk MnO₂ gathered directly from source (Alfa Aesar, Ward Hill, MA, USA), and was then sieved through a 140-mesh (0.105 mm) screen. The sieved sample was kept in a dry place. The second batch (MD-S) was derived from the DLC method discussed in Section 2.3.2.

Approximately 150 mg of manganese acetate tetrahydrate was mixed with 20 mL 0.2 M HNO₃ under moderate stirring for 1h under a water bath maintained at 60°C. After 1h, a 5mL dropwise mixture of 150 mg KMnO₄ solution was added. The solution again was moderate stirred for 24h at 60°C water bath. The sample was then vacuum filtered and then washed with DI. The resulting metal oxide was dried in an oven at 60°C.

2.5. Electrochemical experiments

A potentiostat/galvanostat (Autolab Metrohm PGSTAT302N) was used to understand the electrochemical behavior of the nanomaterials.
2.5.1. Electrode preparation. The electrode paste is composed of three main parts: 70 wt% active material (activated biochar), 20 wt% carbon black (CB) powder for conductivity, and 10 wt% polyvinylidene fluoride (PVDF) as binder [16]. This mixture was uniformly mixed, and ground using a ceramic mortar and pestle for 5 min and placed in an Eppendorf tube. 1mL of N-methyl-2-pyrrolidone (NMP) as solvent was added and ultrasonicated for 30 min to produce a paste-like mixture.

For cyclic voltammetry (CV) and electroimpedance spectroscopy (EIS), mechanically pressed 1 cm x 3 cm nickel foam was prepared as a current collector (CC). The nickel foam was washed with 10% HCl and rinsed with DI, and then dried in a vacuum oven for 24h. After weighing the dried CC three (3) times, a thin coating of the electrode paste was painted on one side measuring 1 cm x 1 cm. The coated CC was dried in a vacuum oven at 65°C for 24h to ensure complete removal of NMP. After drying, the electrode was weighed three (3) times. The active material loading was maintained at 1.2±0.5 mg. This was used as the working electrode for the three-electrode set-up, which was paired with a platinum wire counter electrode, and standard calomel electrode (SCE) as reference electrode.

Capacitive deionization experiments used the two-electrode set-up, with titanium (Ti) plates as CC. An even coat was painted to one side of both Ti plates covering for around 3.75 cm x 3.75 cm from the center of the plate. The coated plates are dried in a vacuum oven at 65°C for 24h. After vacuum drying, the electrode was weighed three (3) times. The electrodes were connected using silicon rubber as spacer.

The two electrodes held approximately the same weight of around 30 ± 5 mg.

2.5.2. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) experiments. For the three-electrode set-up, CV and EIS were performed. Approximately 50 mL of 1.0 M Na2SO4 was used as electrolyte. CV was done with a potential window of 0 V to 1 V at different scan rates of 5, 10, 20, 50, 100 and 200 mVs⁻¹. EIS was done immediately after CV series tests. The frequency range used to generate EIS Nyquist plot was from 10⁵ to 10⁻² Hz with an open circuit signal using a sinusoidal signal of 5 mV ac.

2.5.3. Capacitive deionization (CDI) experiments. Each capacitive deionization operation lasted for 150 min (120 min electrosorption and 30 min desorption). The CDI experiments were done under the operational mode of positive voltage electrosorption-zero voltage desorption (PVE-ZVD), 1.2 V for electrosorption and 0 V for desorption. The flow rate was kept at 25 mL min⁻¹. About 60 mL of NaCl electrolyte was used under moderate stirring. ABMD DLC and ABMD AGO were subjected to chronoamperometry (CA) at 100 ppm NaCl, while ABMD ILC were subjected to CA at 100, 500 and 1000 ppm NaCl. Figure 1 shows the capacitive deionization set-up used in this study.

The material was evaluated based on its CA and electrosorptive performance. Exactly 1 mL of the samples were collected at time intervals of: 0, 5, 10, 20, 40, 60, 80, 100, 120, 130, 140 and 150 min. To determine the electrosorptive data, Thermo-Scientific Aquion Chromeleon 7.2 SR4 (Taipei, Taiwan) Ionic Chromatography (IC) equipment was used.

![Figure 1. Capacitive deionization set-up. A. Schematic diagram. B. Actual set-up.](image)

2.6. Material characterization

The materials were subjected to several surface characterization techniques. BET was done by nitrogen adsorption and desorption at 77K using Micromeritics ASAP 2020; scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDX, Jeol. Ltd., Tokyo, Japan and Zeiss, Oberkochen,
Germany); and X-ray photoelectron spectroscopy (XPS, Eden Prairie, Minnesota) were done to the synthesized nanomaterials. X-ray diffraction (XRD, Bruker, Bremen, Germany) were done in the 2θ range of 10° to 80°. Thermogravimetric analysis (TGA, Mettler Toledo, Colombus, Ohio) was done using nitrogen influent at 5°C/min up to 1000°C.

2.7. Experimental calculations
For all the electrochemical tests performed, three (3) important parameters require calculation: specific capacitance, electrosorptive capacity and charge efficiency.

Using the data from CV, the area was calculated to get the specific capacitance (SC) of each nanomaterial. SC is the measure of ability of a material to charge itself and attract ions under a certain voltage. From the CV, SC (in F g⁻¹) was calculated by analyzing the graph and using Eq (1):

\[
SC = \frac{\int I dV}{\omega m}
\]

where \(I\) is the response current density (A cm⁻²), \(V\) is the potential window (V), \(\omega\) is the potential scan rate (V s⁻¹), and \(m\) is the mass of the active material in the electrodes (g cm⁻²). Achieving for a rectangular or quasi-rectangular CV plot will give a desired high value of SC.

Capacitive deionization is measured by an important parameter called electrosorptive performance. Electrosorptive capacity (EC) is defined as the measurement of adhered ions to the electrode, computed as Eq (2):

\[
EC = \frac{(C_i - C_f) V m}{m}
\]

where \(C_i\) and \(C_f\) (mg L⁻¹) represent the initial and final concentration, respectively, and \(V\) is the volume of the solution (L), and \(m\) is the total mass of both electrodes (g).

Charge efficiency (CE), defined as the ratio of amount of electrosorbed ions to the equivalent total charge, is calculated using Eq (3):

\[
CE = \frac{EC n F}{I dt M}
\]

where EC is the electrosorptive capacity (mg g⁻¹), I is the specific current (A g⁻¹) at time t (s), M is molecular mass of salt (M Na = 0.002299 mg mol⁻¹), \(n\) is number of electron equivalents per mol salt (n=1) and F is the Faraday’s constant [96,485 C / mol e⁻].

3. Results and Discussion
3.1. Electrochemical Properties
In this study, the electrochemical performance of the nanomaterials using CV and EIS measurements was evaluated. The precursors BC, AB, MD and MD-S were investigated to confirm if the reference materials were successfully synthesized supported by surface characterization.
3.1.1. **CV and EIS results of Precursors.** Figure 2 show that BC and AB display symmetric and quasi-rectangular CV curves, which are proven to be characteristics of EDLC materials [7-13]. Note that the peak current (and electrochemical activity) for AB is higher than that of BC, proving the successful activation of biochar due to increased porosity. Figure 2 also show symmetric CV curves, with MD-S having significantly higher peak current values. The CV curves indicate a rapidly reversible Faradaic reaction for pseudocapacitive materials as the curves tend to transform from a quasi-rectangular shape to a leaf-like shape at higher scan rates [7,26]. Figure 2 shows that at 5 mV s⁻¹, the SC values for BC, AB, MD and MD – S are 41.9, 146.3, 56.9 and 342.0 F g⁻¹, respectively. The SC values of AB and MD – S are competitive with that of literature values [7,11,13,19-27]. It is also apparent that as the scan rate increases, the SC decreases but more significantly to the pseudocapacitive materials; the capacitance retention of BC and AB at 200 mV s⁻¹ are 60.61 and 60.7%, respectively. Meanwhile, MD and MD – S reports a capacitance retention of 35.33 and 17.47%, respectively.

![Figure 2](image_url)

**Figure 2.** CV and EIS measurements of precursors BC, AB, MD and MD-S. A. CV curves of BC. B. CV curves of AB. C. CV curves of MD. D. CV curves of MD-S. E. Summary of SC of precursor nanomaterials (Inset: CV curves at 50 mV s⁻¹). F. Nyquist plot of precursor nanomaterials.

EIS measurements are shown in the Nyquist plot (NP) in Figure 2. NPs can be subdivided into three sections: (1) a semicircle in the 10⁴ to 10⁶ Hz region measured as the charge-transfer resistance (Rct) which is controlled by redox-active behavior, and the intersection at the real impedance axis (Z’) measured as the solution resistance (Rs); (2) a straight line with a slope greater than or equal to 45° in the medium frequency region, corresponding to semi-infinite Warburg impedance due to the frequency dependence of ion diffusion/transport in the electrolyte; and (3) a steep vertical plot at low frequencies indicating a diffusion-controlled material, characteristic of pure EDLC behavior [21]. From the previous figure, the Rs of BC, AB, MD and MD-S are 1.25, 0.51, 1.77 and 2.84 Ω, respectively. A lower value of Rs is desired, as this shows that carbon-based materials have less resistance than that of pseudocapacitive materials and depicts the relatively lower conductivity of MD and MD-S. Also, the Rct of MD and MD – S are seen to be significantly higher than that of BC and AB, and they also lack the relatively steeper plot compared to BC and AB, confirming the pseudocapacitive behavior of MnO₂. These measurements suggest competitive precursor materials which can be optimistically used for the synthesis of AB - MD nanocomposites.
3.1.2. CV and EIS results of AB-MD Nanocomposites. Figure 3 show that all three synthesis methods possess quasi-rectangular and symmetric CV curves as emphasized in Figure 3. Among the three methods, ABMD AGO has the most stable structure, keeping its shape at higher scan rates, followed by ILC and finally DLC, which is leaf shaped. This is most likely due to MnO2 being the dominant material in ABMD DLC. Figure 3 shows that at 5 mV s⁻¹, the SC values for ABMD ILC, DLC and AGO are 410.4, 479.2 and 522.7 F g⁻¹, with capacitance retention values at 200 mV s⁻¹ of 57.47, 25.60 and 36.43%, respectively. Several literatures have reported values for activated carbon – manganese dioxide composites in the range of 77.6 – 387 F g⁻¹ [7,12,21,27,28], confirming the synthesis of high-performance ABMD composites.

![Figure 3. CV and EIS measurements of AB-MD ILC, DLC and AGO. A. CV curves of ABMD ILC. B. CV curves of ABMD DLC. C. CV curves of ABMD AGO. D. CV curves of ABMD ILC, DLC and AGO at 5 mV s⁻¹ E. Summary of SC of nanocomposites. F. Nyquist plot of nanocomposites.](image)

The SC results show that the incorporation of MnO2 to the activated biochar surface has significantly improved electrochemical properties. The charge storage mechanism of MnO2 in the activated biochar surface is defined as the adsorption and desorption of proton and alkali cations through electrolysis, as cited by several authors [27,32,33], expressed as:

\[
\text{MnO}_2 + X^+ (X = \text{H, Li, Na or K}) + e^- \leftrightarrow \text{MnOOX}
\]

This shows that at high scan rates, the reduced diffusion time and the low electronic conductivity of the high MnO2 loading in ABMD DLC and AGO causes a smaller available specific capacitance.

Figure 3 confirms the nanocomposite’s identity further. ABMD DLC is dominated with MnO2 evidenced by its high Rₛ value with the following order: ILC<AGO<DLC. The Rₛ values of ABMD ILC, DLC and AGO are 0.13, 2.31 and 2.81 Ω, respectively. The Rₛ values of DLC and AGO are comparable to that of the synthesized MnO2. The superior electrochemical performance of ABMD nanocomposites serve as a potential material for CDI applications.

3.2. Surface Morphology Characterization.

The formation mechanism of the nanocomposites is proposed as follows:

\[
2\text{AB/ABGO} - \text{COOH} + \text{Mn}^{2+} \leftrightarrow (\text{AB/ABGO} - \text{COO})_2\text{Mn} + 2\text{H}^+ + \text{MnO}_4^- \rightarrow \text{AB/ABGO} - \text{COOH} + \text{ABMD}
\]

Assuming every reaction is done in the activated biochar surface, the Mn²⁺ ions from the first step (manganese nitrate or acetate impregnation) might form a complex with the carboxylic acid groups in the AB surface. This creates massive active sites for reaction via chemically oxidation with the MnO₄⁻ ions introduced in the second step, effectively forming MnO2 in the activated biochar surface. From 3.1, it was shown that the nanocomposites possess high electrochemical performance. This is due to their physicochemical properties, which is measured using several characterization techniques as follows:
3.2.1. **SEM – EDX Results.** Figure 4 show highly irregular and porous surfaces with an average particle size of 10-50 μm, confirming the availability of adsorption sites. Furthermore, the surface of ABGO is seen to be rougher than AB. Figure 4 shows the synthesized MnO₂, which possess nanorods in a pine-like formation has an average diameter of 50 nm. This crystal formation is shown to be the α-polymorph, as previous studies have discussed [29,30]. Figure 4 show the SEM images for ABMD ILC, DLC and AGO. For ABMD ILC, the formation of MnO₂ is not clearly shown, while ABMD DLC and AGO are well coated with MnO₂ due to visible loss of pores characteristic of AB. From the images, it is also observed that DLC has a larger coating than AGO.

![Figure 4. SEM images of synthesized nanocomposites. A. Activated Biochar (AB). B. AB-Grafting Oxidation (ABGO). C. Manganese Dioxide - Synthesized. D. Activated Biochar – Manganese Dioxide Indirect Liquid-phase Combination (ABMD ILC). E. ABMD Direct Liquid-phase Combination (DLC). F. ABMD Acid-assisted Grafting Oxidation Combination (AGO).](image)

The presence of Mn in the nanocomposites are confirmed by EDX measurements, as shown in Table 1. There is obviously no Mn in AB and ABGO while the nanocomposites have, as well as MD-S. No nitrogen detected depicts no intercalation of NO₃⁻ in the surface from HNO₃. Potassium, however, is present due to K⁺ intercalation in the activated biochar surface from KOH (in activation) and from KMnO₄. Note that MD-S has 8.43% C and 6.60% K due to the intercalation of CH₃COO⁻ and K⁺ ions in the MnO₆ octahedra ‘tunnel’ of α-MnO₂. This ‘ion blockage’ phenomenon may also be the case for ABMD ILC and AGO, which is discussed in 3.2.3 (TGA results).

3.2.2. **Functional groups and crystallinity (XPS and XRD results).** XPS results show the functional groups present in the nanocomposite surface. Figure 5 shows the survey scan, with three relevant core-level regions, namely: C1s, O1s and Mn2p.

![Figure 5. XPS survey scan of synthesized nanomaterials.](image)

| Weight percent (%) | C    | O    | N    | Mn   | K    |
|--------------------|------|------|------|------|------|
| AB                 | 89.26| 10.07| 0    | 0    | 0.67 |
| MD-S               | 8.43 | 23.66| 0    | 61.30| 6.60 |
| ABMD ILC           | 71.66| 20.95| 0    | 6.19 | 1.20 |
| ABMD DLC           | 12.64| 36.44| 0    | 44.39| 6.54 |
| ABGO               | 93.45| 4.99 | 0    | 0    | 1.56 |
| ABMD AGO           | 47.06| 12.26| 0    | 39.20| 1.48 |

*does not include hydrogen, chloride and trace elements*
Figure 5 shows the C1s core-level of all three methods. All three possess the following bonds as exhibited by the spectra: C-C (~284.2 eV), C=C (~284.7 eV, weak), and O-C=O (288.5 eV) [7]. This confirms the availability of carboxylic groups in the surface which is used as reaction sites of MnO2 as discussed in the introduction of 3.2. Among the three methods, ABMD AGO has the largest peak corresponding to O-C=O. This confirms the surface modification made by reacting AB with HNO3 to form ABGO, which oxidizes the surface to generate more carboxyl groups [27]. Figure 5 shows the O1s core-level spectra of the nanocomposites, which display peaks corresponding the following oxygenated groups: Mn-O-H (~531.8 eV, weak), Mn-O-Mn (529.7) from the MnO6 octahedra, and H-O-H (532.0 eV) from interstitial water molecules. Lastly, Figure 5 show the Mn 2p core-level of the three methods. There are two main peaks observed at approximately 642.0 and 653.7 eV corresponding to the Mn 2p3/2 and Mn 2p1/2, respectively. This 11.7 eV spin-energy separation confirms that the predominant oxidation state is +4 [7,13,20,21], proving the synthesis of MnO2 in the activated biochar surface.

To further identify the structures of the nanocomposites, powder XRD analysis is done. Figure 6 are the XRD patterns of BC, AB and ABGO, showing two main peaks at 2θ of 24.0° and 43.8° corresponding to the (002) reflection from the crystal plane of graphite and (101) reflection from the higher degree of interlayer condensation of carbon [7,21]. The peaks are broad and not sharp, indicating amorphous nature of BC and AB. Figure 6 are the XRD patterns of MD and MD-S, where it was found that MD possesses the diffraction peaks indexed to β-MnO2 (JCPDS PDF# 24-735). MD-S is analyzed to possess peaks indexed to α-MnO2 as well as δ-MnO2 (JCPDS PDF#18-0802). From Figure 2, the synthesized MD (MD-S) has better superior electrochemical property than MD.

The XRD analysis results supports the study by Yin et. al. [29], where it is found that α-MnO2 possess square 2 x 2 tunnels, with dimensions of 4.6 x 4.6 Å. This effectively decreases the effective diffusion path in the crystal lattice. β-MnO2, however, only has a narrow 1 x 1 open tunnel with 1.89 Å square dimension which has great difficulty of accommodating ions. The larger tunnel size of α-MnO2 can accommodate a larger number of ions, suitable for cations (i.e. Na+, r. 1.16 Å, K+, r.1.52 Å) and anions. Due to its synthesis method, the crystal formed is similar to cryptomelane, with an empirical formula of K (Mn4+, Mn3+)4O16 [30].

Figure 6 present the XRD patterns for the three methods. All patterns show the diffraction peaks for carbon (larger font), which are the same as BC, AB and ABGO but less pronounced showing the amorphous carbon. There are also subtle peaks for all patterns which can be indexed to α-MnO2 (JCPDS PDF# 44-0141). In evidence, Figure 4 show that there is no visible crystal formation for all three methods. With the confirmation of α-MnO2, this explains the nanocomposite’s improved electrochemical performance over literature values [7,11,13,21,26,27].
3.2.3. Pore properties (BET) and thermal stability (TGA) results. Figure 7 shows that the isotherms are Type-II isotherms under IUPAC classification indicating the presence of micropores with H3 hysteresis loops. Table 2 shows that the activation process significantly improved the BET surface area of AB, with a higher pore volume of 0.236 cm$^3$ g$^{-1}$. For the nanocomposites, however, it is observed that the surface area has decreased due to the MnO$_2$ mass loading blocking most of the pores. Furthermore, the usage of HNO$_3$ to modify AB reduced the surface area, which is apparent from the BET results of ABMD AGO. Fortunately, this reduced surface area is still viable for EDL formation and ion accumulation synergized with the pseudocapacitive behavior of incorporated MnO$_2$.

Also, this incorporation decreased the pore volume as an effect, mostly affecting the micropore volume. As a result, the mesopore volume ratio increased for all three methods. Some of these retained micropores may come from the tunnels of α-MnO$_2$. Liu et al [7] noted that a well-balanced ratio of mesopores and micropores is an important requirement for high electrochemical performance, as achieved in this study.

The TGA and DTG results are shown in Figure 7. The most thermally stable goes by the order: MD-S $>$ ABMD ILC $>$ AB $>$ ABMD DLC $>$ ABMD AGO. Following the TGA curve, interstitial water
molecules evaporated in the range of 100-150°C, defined by DTG peaks in the respective range. The TGA curve of MD-S compare with that of literature values, having lower than usual due to the decomposition of intercalated impurities [24].

Figure 7. A. Nitrogen adsorption-desorption isotherms of selected nanomaterials. B. Thermogravimetric analysis (TGA) results of selected nanomaterials. C. First derivative of TGA/derivative thermogravimetry (DTG) of selected nanomaterials.

Since the TGA curve of activated carbon differ from biomass used, activations methods etc., AB is the reference curve for the three methods. ABMD ILC’s TGA curve is comparable to AB, due to its low Mn value as cited in Table 1, with slightly lower end value most likely due to interstitial H2O. The end values of ABMD DLC and AGO, however, differ from AB by 19.7 and 32.3%, respectively. There are two factors that might contribute to this significant mass loss: (1) similar to MD – S, there are intercalated acetate ions in the AB – MD surface, and (2) a large amount of unreacted manganese acetate has intercalated in the activated biochar surface. In a study made by Mohamed and Halawy [34], it was found that manganese acetate decomposes at a rate of -1%/5°C after dehydration until 370°C, losing 70% of its mass in N2. This behavior is evident by the DTG results, which shows a mass loss rate of around 1%/20°C to 1%/10°C for both ABMD DLC and AGO within the specified region (200 °C – 400 °C), compared to ABMD ILC’s -1%/50°C. This could be correlatively related to the acetate composition in the nanocomposite. However, this does not account for all the mass loss represented in the graph. It is worth noting that unlike ABMD ILC, ABMD DLC and AGO did not undergo preliminary washing as the method requires direct combination, as discussed in 2.3, possibly contributing to this incompletely explained mass loss. This ‘ion blockage’ phenomenon will prove to have negative effects on the electrosorptive performance of ABMD DLC and AGO. The complex crystal formation of cryptomelane [30] and the large value of Mn in the nanocomposites may also contribute to this mass loss, if any. Further studies must explore the application of EDX on the TGA products at varying final temperatures to verify the correlations made regarding the nanocomposite’s evolution due to heat.

Table 2. Pore characteristics summary of selected synthesized nanomaterials

| Material  | SBETa (m² g⁻¹) | Smicrob (m² g⁻¹) | Vmesoc (cm³ g⁻¹) | Vmicroc (cm³ g⁻¹) | Vtotc (cm³ g⁻¹) | %Vmeso (%) |
|----------|----------------|-----------------|------------------|------------------|----------------|-------------|
| BC       | 97.36          | 35.01           | 0.06             | 0.055            | 0.115          | 52.17       |
| AB       | 485.92         | 98.5350         | 0.101            | 0.135            | 0.236          | 42.80       |
| ABMD ILC | 304.36         | 54.68           | 0.095            | 0.084            | 0.179          | 53.07       |
| ABMD DLC | 156.43         | 29.36           | 0.078            | 0.051            | 0.129          | 60.4        |
| ABMD AGO | 188.94         | 31.85           | 0.074            | 0.038            | 0.112          | 66.07       |

3.3. Electrosorptive performance of synthesized nanomaterials

Figure 8 illustrates the CA curve of synthesized nanocomposites with AB as reference. As observed, when the electric field has been induced in the electrodes, an initial current sharply decreases until 20 – 30 min of the electrosorption operation and stabilizing with an almost zero current. After 120 min, the removal of the induced voltage desorbs the electrosorbed ions depicted by a negative current hastily approaching stability. Figure 8 also shows this behavior as the concentration dramatically decreases suggesting the rapid removal of salt ions from the influent. The positively charged Na⁺ ions react toward the cathode (negatively charged electrode), while the negatively charged Cl⁻ ions react on the anode (positively charged electrode). As the time increases, the change in concentration approaches pseudoequilibrium. This is noted that all final concentrations are by a small fraction lower than that of its original concentration, implying that some of the electrosorbed ions are not fully released in the desorption operation.
Electrosorptive performance of the nanomaterials are shown in Table 3. From the precursor AB, the EC increased significantly for all three methods, owing most of it to the pseudocapacitive behavior of incorporated MnO2. This same behavior of the MnO2 layer, however, is a major drawback taking into effect as the low charge efficiency of AB – MD nanocomposites. Theoretically, CE values can be increased by applying a reverse voltage polarity during desorption operation [12]. Also, the electrosorption operation can be reduced, as the results show that the operation reached pseudoequilibrium at around 60–80 min, thereby increasing the overall efficiency of the operation.

Table 3. Electrosorptive performance of AB–MD nanocomposites.

| Material                                        | C0a  | EC (mg/g) | CE (%) |
|-------------------------------------------------|------|-----------|--------|
| Activated Biochar                               | 100  | 17.73     | 31.65  |
| ABMD Indirect Liquid-phase Combination (ILC)b   | 100  | 59.71     | 19.88  |
|                                                | 500  | 114.11    | 22.86  |
|                                                | 1000 | 92.80     | 25.68  |
| ABMD Direct Liquid-phase Combination (DLC)b     | 100  | 42.86     | 10.51  |
| ABMD Acid-assisted Grafting Oxidation (AGO)b    | 100  | 48.01     | 11.85  |

Initial concentration. bActivated Biochar–Manganese Dioxide

For comparison, Table 4 shows reported values from literature. For carbon-based materials, the electrosorption capacity of the synthesized AB is within the range of 3.66 – 70.18 mg g⁻¹, with OMC having the largest value [7,35,36]. This is due to OMC’s more complicated synthesis route, making it more expensive than AB. For nanocomposites, it is evident that the performance of all three methods are outstanding compared to the literature values [7,11,13,37]. The electrosorptive performance of ABMD DLC and AGO could potentially be higher than the reported values if the ‘ion blockage’ caused by the intercalation of ions during synthesis is mitigated. Overall, all three methods of synthesizing AB – MD nanomaterials propose a high-performance material for CDI applications.

Table 4. Electrosorptive performance of AB - MD compared to other materials.

| Material | Initial concentration (ppm) | Applied voltage (V) | EC (mg g⁻¹) | Reference |
|----------|-----------------------------|---------------------|-------------|-----------|
| AB       | 100                         | 1.2                 | 17.73       | This work |
| AC       | 116.9b                      | 1.0                 | 3.66        | [7]       |
### 4. Conclusions and Recommendations

In this study, the three (3) co-precipitation methods successfully synthesized high electrochemical performance AB – MD nanocomposites with its surface chemistry explained by characterization. Among the three methods, ABMD AGO exhibited a specific capacitance of 522.7 F g⁻¹ at 5 mV s⁻¹, higher than that of its precursor standalones activated biochar and manganese dioxide. It is noteworthy that the AB – MD makes synergistic use of the mixed capacitive-Faradaic processes for improved conductivity and porosity from its precursors, with the highly accessible α-MnO₂ having a major role to ensure high electrochemical performance. Furthermore, the AB – MD nanocomposites showcased high electrosorption capacities with the highest at 114.11 mg g⁻¹ for ABMD ILC at 500 ppm initial NaCl concentration. In summary, incorporating α-MnO₂ to the activated biochar surface is successful and significant, with high potential as an electrode for desalination process. Developments in the practical use of CDI can make use of the findings of this study.

While the three methods already possess high electrochemical properties, possible future work could be done to improve the synthesis parameters of AB – MD nanocomposites to prevent the ‘ion blockage’ phenomenon from intercalated reactants during synthesis. This can be done by: (1) usage of other reactants such as manganese nitrate, manganese carbonate, etc. (2) proper stoichiometric proportions in reaction through optimization via central composite design, and (3) kinetic study optimizations. Detailed surface characterization will be needed to fully explain the properties of the nanomaterial. Optimization of CDI parameters is also a possible route to improve the charge efficiency of CDI through reversal of voltage in the desorption operation. Lastly, adsorption kinetics/isotherm studies are recommended to validate whether the desorbed ions go through physisorption or chemisorption. These following recommendations will address several issues that are not within the scope of this study.

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