

# Formulation and Modification of Multi-Walled Carbon Nanotubes for Post-Combustion CO<sub>2</sub> Capture

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**Abstract** The emission of CO<sub>2</sub> from fossil fuels causes environmental degradation; hence, this noxious gas must be captured and put away for environmental sustainability. Adsorption technology shows promising characteristics for CO<sub>2</sub> capture and storage. Multi-walled carbon nanotubes have been explored for CO<sub>2</sub> capture. However, studies on their modification with deep eutectic solvents, a class of ionic liquids with the propensity for enhancing CO<sub>2</sub> capture, are scarce in the open literature. Thus, this study formulated multi-walled carbon nanotubes (MWCNT) from acetylene as a carbon source and modified it using deep eutectic solvent (DES) developed from choline chloride + glycerol. For comparison, polyethylene glycol (PEG), a similar alcohol-based solvent, was also used to modify the MWCNT. The CO<sub>2</sub> adsorption capacity of the adsorbents was evaluated at temperatures of 26, 40, and 70°C and pressures of 5, 10, and 15 psi using an experimental adsorption setup designed and fabricated for this study. Results showed that unmodified MWCNT, MWCNT+PEG, and MWCNT+DES had CO<sub>2</sub> adsorption capacities of 0.174 mmol/g, 0.220 mmol/g, and 0.226 mmol/g at 26°C and 15 psi, respectively. This trend showed that DES had a better affinity for CO<sub>2</sub> than the unmodified MWCNT. Also, the adsorption capacities of MWCNT-DES and MWCNT+PEG were relatively the same at 26°C and 15 psi. The adsorption isotherm of the MWCNT-DES followed the typical physisorption Langmuir model. Soil test results showed that disposing of the CO<sub>2</sub>-rich adsorbents to the environment improves soil nutrients. The low adsorption capacity of the MWCNT-DES adsorbent may be due to the fact that acetylene does not produce a suitable MWCNT with an appropriate internal structure for the adsorption of CO<sub>2</sub> under the process conditions studied. Therefore, MWCNT made from acetylene and modified with DES and PEG are unsuitable for CO<sub>2</sub> adsorption.

**Keywords** Carbon capture, Post-combustion, Nanoparticles, CO<sub>2</sub> adsorption

## 1. Introduction

The continuous emission of carbon (IV) oxide (CO<sub>2</sub>) into the environment through the exploitation of fossil fuels for energy generation and production in various process systems constitutes environmental challenges to the sustainability of our ecosystem [1]. Also, the increase in global carbon footprint poses a challenge to the actualization of the Paris Treaty of 2015 and the target of limiting global temperature rise to 1.5°C above the pre-industrial era. Therefore, this creates the need to seek innovative solutions that would forestall carbon emissions and safeguard the environment. Amid the diverse decarbonization technologies for carbon emission control and environmental change alleviation, carbon capture and storage (CCS) has become a highly viable option for decarbonizing carbon-intensive processes. CCS is a weighty module of most climate models as a contrivance to alleviate climate change in the coming

decades. Pieces of literature argue that without CCS, meeting climate change goals would become an uphill task [2]. CCS is a decarbonization technology that captures carbon from process systems, e.g., coal power plants, natural gas processing, hydrogen production plants, steel, and concrete manufacturing plants, and stores it underground, safe from the environment [3]. It is based on three technologies, including pre-combustion, oxy-combustion, and post-combustion technology, as shown in Figure 1. Among these technologies, the post-combustion carbon process is the most developed and widespread, process efficient, and easily retrofitted technology for CO<sub>2</sub> capture [4]; hence, it would be the focus technology in this study.

Post-combustion CCS plants have shown the propensity to diminish carbon emissions significantly. For instance, the Alberta Carbon Trunk Line Project, the biosphere's latest CCS project, which became operational on June 4<sup>th</sup>, 2020, has the capacity to capture 14.6 million tons of CO<sub>2</sub> yearly from a fertilizer plant and refinery for enhanced oil recovery. This is the equivalent of CO<sub>2</sub> emissions from about 2.6 million cars in Alberta, Canada. In addition, Global CCS Establishment explains that several millions of CO<sub>2</sub> have been captured and stockpiled by about 19 commercial CCS

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Received: Mar. 5, 2023; Accepted: Mar. 22, 2023; Published: Apr. 15, 2023

Published online at <http://journal.sapub.org/ijee>

plants in several countries [2]. This further highlights the aptness of post-combustion CCS as a suitable technology for environmental sustainability. Post-combustion capture innovation depends on various components, for example, absorption, adsorption, cryogenics, membranes, and microbial/algal, as shown in Figure 2. These different mechanisms are at different stages of technological development. Though absorption technology (amine scrubbing technology) is currently the most developed and deployed technology, it faces challenges because of its high

energy utilization and regeneration requirement [5]. Also, solvents degrade, evaporate, and result in equipment corrosion [6], which further poses a problem to the rapid deployment of amine scrubbing technology. Hence, other post-combustion carbon capture systems have recently gotten more consideration. Significantly, adsorption technology has gained attention lately because of its capacity to enhance the drawbacks of the amine scrubbing technology, such as high heat of regeneration, equipment corrosion, solvent degradation, and evaporation [7].

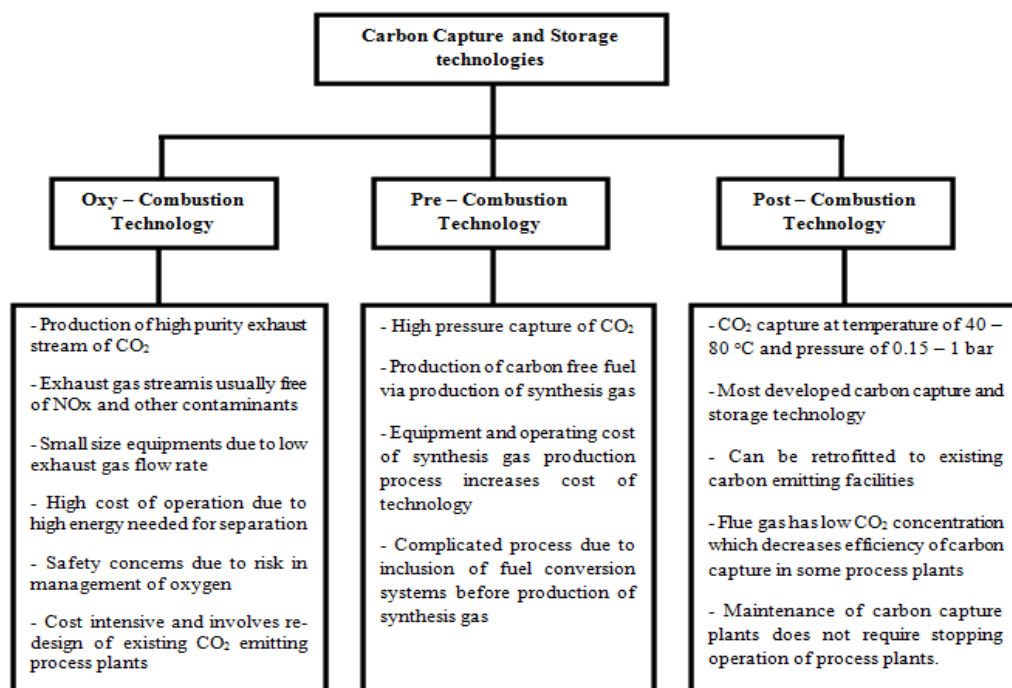


Figure 1. Different types of CCS Technologies

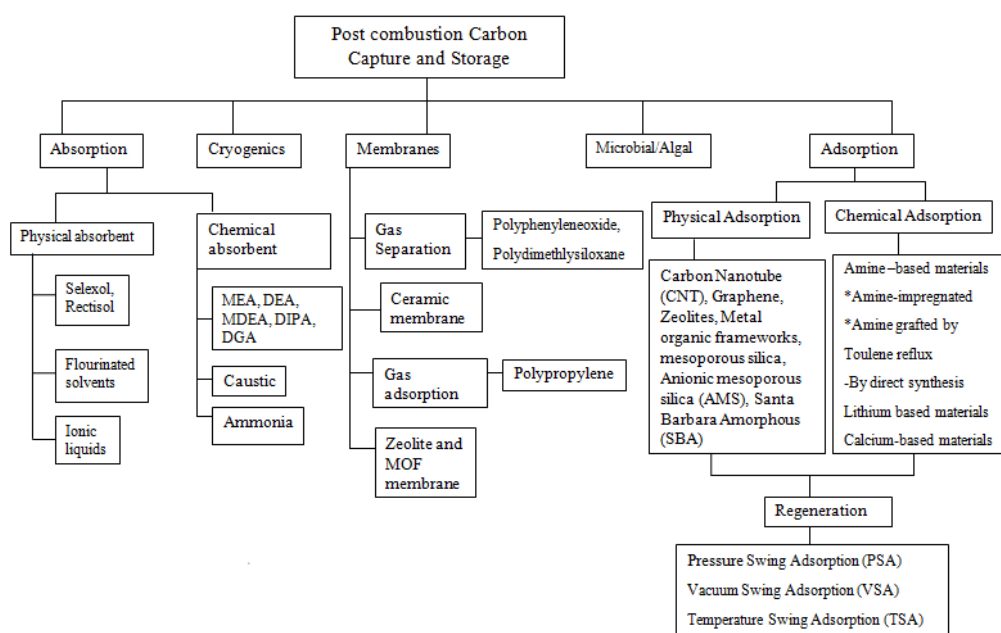


Figure 2. Different types of post-combustion carbon capture and storage mechanisms reproduced from Aimikhe and Eyankware [1]

### 1.1. Adsorbents for CCS

Adsorption technology is a molecular-driven process that involves intermolecular interactions between adsorbate ( $\text{CO}_2$ ) and adsorbent (capture media). It is divided into physisorption (driven Van der Waals force) and chemisorption (stronger intermolecular forces). Physical adsorption is a reversible process mechanism driven by the Van der Waals force involving weak intermolecular interaction in the 10– 20 KJ/mol range. On the other hand, chemical adsorption is an irreversible mechanism driven by stronger chemically induced adsorption forces within a binding energy range of 10 – 100 KJ/mol. Most of the time, adsorption technology consumes less energy because of its low heat of adsorption. Hence, this capture mechanism tends to lessen the drawbacks of popular amine scrubbing solvents. This comparative advantage prompted intensive research into using adsorbents for carbon capture at post-combustion conditions.

Various kinds of adsorbents like metal-organic frameworks [8], zeolites, [9] silica [10] activated carbon [11], and carbon nanoparticles have been reported as suitable adsorbents for  $\text{CO}_2$  scrubbing. The numerous application of adsorption technology in different process systems has prompted researchers to investigate advanced and novel adsorbents with improved functionalities. Materials with outstanding high surface areas ( $\sim 10,000 \text{ m}^2/\text{g}$ ), high porosity, selectivity, and good thermal, mechanical, and chemical stability [12]. These novel adsorbents have often outperformed traditional adsorbents. Examples include metal-organic frameworks (MOFs) [13],  $\text{Li}_4\text{S}_4\text{O}_4$  [14] peptide nanotubes [15], carbon nanosheet-based networks (GPC) [16], carbon nanotubes [17], etc. Among these different adsorbents, carbon nanoparticles produced from precursors like carbon black, activated carbon, graphite, biochar, charcoal, polymers, etc., have been demonstrated to be stable thermally and mechanically [18], [19]. In addition, the possibility of modification/functionalization of carbon nanoparticles and its consequent ability to increase the adsorption and selectivity capacity of pristine adsorbents further highlights the propensity of carbon nanoparticles as a suitable adsorbent for industrial and commercial CCS applications [20].

### 1.2. Carbon Nanoparticles

Carbon nanoparticles are nanomaterials with particle sizes  $< 100 \text{ nm}$  in two dimensions [19]. Examples of carbon nanoparticles include carbon black (CB), carbon nanotubes (CNT), and graphene derivatives. They are highly porous structures whose properties are a function of the type of carbon source from which it is derived [21]. Carbon nanoparticles possess high mechanical and thermal stability, good gas ( $\text{CO}_2$ ) adsorption capacity, high surface area, and permanent structure [18]. Among these different types of carbon nanoparticles, CNT [especially multi-walled carbon nanotube (MWCNT)] is one of the most well-known because of its favorable properties like resistance to temperature

changes, strength and thermal stability, hydrophobicity, and availability of precursors. Hence, it is the adsorbent of focus in this study.

CNT exhibits exceptional properties making them highly suitable for process applications. The mechanical strength of CNT is viewed as one of the most established because of the development of covalent  $\text{sp}^2$  bonds between individual carbon atoms, collectively forming one of the highest elastic Young Modulus and tensile strength [22]. Furthermore, experiments have shown that the outer shell graphene layer of MWCNT withstands any stress imposed on the structure when it is dispersed in a matrix [23]. Also, MWCNT can withstand temperatures of  $750^\circ\text{C}$  and  $2800^\circ\text{C}$  in a vacuum and open space, respectively, highlighting its stability. In addition, MWCNT has a surface design that can be changed to improve its affinity for gases. This further increases the appropriateness of MWCNT for adsorption applications. Incorporation of  $\text{CO}_2$ -philic components such as *N*-compounds, amino-compounds, Lewis base, and amine solvents into structures of carbon nanoparticles have been reported to improve their adsorption properties [20], [24], [25]. Modifying the pristine structure of carbon nanoparticles creates active sites with a strong affinity for  $\text{CO}_2$ . Also, it results in the alteration of the pore sizes such that specific molecule sizes are allowed into the structure, thereby increasing selectivity. Consequently, MWCNT can be considered an appropriate material for creating adsorbents for  $\text{CO}_2$  and other harmful gas capture.

Specifically, deep eutectic solvents (DES) [26] and (PEG) [27] have been identified to have good adsorption properties. Also, glycols have been found to improve the absorption of  $\text{CO}_2$  in non-aqueous amines. Hence, this study will investigate them as modification agents for enhanced  $\text{CO}_2$  adsorption at post-combustion conditions.

### 1.3. Deep Eutectic Solvents (DES) and Polyethylene Glycol (PEG)

DES is a complex compound composed of quaternary ammonium salts (hydrogen bond acceptor) and hydrogen bond donors [28]. They are also considered a sub-class of ionic liquids. DES have lower melting points than their constituting components; hence, they are called eutectics [29]. DES is usually represented using the chemical formula shown in Equation 1.

$$\text{DES} = \text{Cat}^+ \text{X}^- z \text{Y} \quad (1)$$

Where  $\text{Cat}^+$  = sulphonium, ammonium, and phosphonium ion

$\text{X}^-$  = Halide ion

$z$  = Number of molecules of Y that interact with X

Y = Lewis Acid\--

There are four types of DES: Type I, Type II, Type III, and Type IV. Each class has distinct components (quaternary ammonium salts and HBDs) that make up the compound. These different components are highlighted in Table 1. Among these types, Type III has favorable properties such as biodegradability, simplicity in its

preparation, and non-ecotoxicity. Subsequently, it is the most utilized type of DES for modifying adsorbents. Type III DES comprises choline chloride (hydrogen bond acceptor) and alcohol, carboxylic acid, and amides (hydrogen bond donor). The usefulness of DES depends on its capacity to add –NH group to the outer layer of adsorbents expanding its basicity and affinity for CO<sub>2</sub>, which is an acidic gas. Hence, the utilization of DES in modifying adsorbents for CO<sub>2</sub> capture has been reported in the literature [26].

Polyethylene Glycol (PEG) is a hydrophilic oligomer formulated from ethylene oxide composed of repeating units of –(O – CH<sub>2</sub> – CH<sub>2</sub>) – [27]. During the synthesis of PEG, it very well may be done across a different range of molecular weights, which are alluded to as “monodispersed,” especially when the size of the PEG chain and its molecular weight are defined. In the structure of PEG, they are moieties in their chains and high segmental flexibilities [30], which highlights their ability to retain acid gases such as CO<sub>2</sub>. Furthermore, PEG polymers can receive functional groups in their reactive sites, consequently increasing their process functionality for direct applications. Some of these functional groups are heterogeneous and homogeneous bi-functional groups acting as cross-linking agents between different chemical components; hence, these functional groups can facilitate the affinity of a PEG-modified sorbent for a specific compound. Subsequently, studies have shown the incorporation of PEG into adsorbents that have

increased their capacity for improved CO<sub>2</sub> adsorption and reaction kinetics in some cases [31], [32].

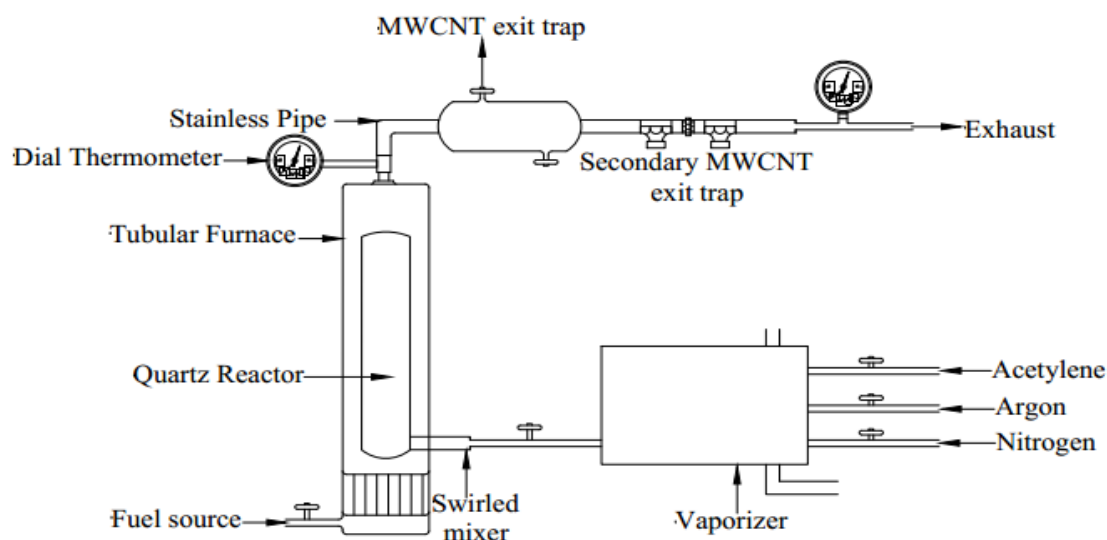
As reported by Wang et.al [33], PEG can improve adsorbents capacity for CO<sub>2</sub> capture, highlighting its suitability as a modification agent of compounds for improved process functionality. Also, PEGs are not expensive and readily accessible, making them suitable for commercial and industrial applications. In addition, they are relatively stable in acidic media [34], making them appropriate for the reception of CO<sub>2</sub>, an acidic gas. The use of PEG and DES-modified MWCNT for post-combustion capture of CO<sub>2</sub> is very scarce in the published literature. Also, experimental CO<sub>2</sub> capture studies with modified MWCNT at 40°C and beyond are rare. Due to the advantages and similarities of PEG and DES solvents as adsorbent modification agents, this study aims to investigate the effectiveness of formulated MWCNT from acetylene gas, modified with DES and PEG, for CO<sub>2</sub> capture.

## 2. Materials and Methods

For this study, an experimental apparatus was developed to formulate MWCNT and assess its adsorption capacity at post-combustion conditions. The formulated MWCNT was then modified with PEG and DES before conducting CO<sub>2</sub> adsorption experiments using the apparatus described by Aimikhe and Eyankware [35].

**Table 1.** Types of DES and their respective components, modified from Smith et al. [28]

S/N	Type of DES	Formulae	Components
1	Type I	$Cat^+ X^- z Y$	Ammonium salt + Metal Halides / Imidazolium salt systems
2	Type II	$Cat^+ X^- z MCl_x \cdot yH_2O$	Ammonium salt + Hydrated Metal Halides
3	Type III	$Cat^+ X^- z RZ$	Choline Chloride + Amides / Carboxylic acids/Alcohols
4	Type IV	$MCl_x + RZ = MCl_{x-1}^+ RZ + MCl_{x+1}^-$	Inorganic cations + Metal Halides



**Figure 3.** Experimental setup for MWCNT Synthesis

## 2.1. Synthesis of MWCNT

MWCNT was synthesized via catalytic chemical vapor deposition (CVD) using acetylene as a carbon source, argon as the carrier, and a catalyst using a fabricated setup [36]. The fabricated apparatus is shown in figure 3. The setup was initially purged using nitrogen gas, after which acetylene and argon were flown into the vaporizer and subsequently into the swirled mixer. At this point, the gas mixer was ignited with fuel from a fuel source. Consequently, vapor decomposition occurred in the Quartz reactor situated inside the tubular reactor, whose temperature was measured using a dial thermometer. The produced MWCNT was obtained from the exit trap and secondary exit traps.

## 2.2. Modification of MWCNT

MWCNT was modified with a solution of DES prepared from choline chloride + glycerol and polyethylene glycol (PEG). These modified samples were named MWCNT-DES and MWCNT-PEG, respectively. The DES was prepared by mixing choline chloride + glycerol in 1:2 (30g: 60g) and stirring at 80°C for 2 hours using a magnetic stirrer. DES was commingled with MWCNT in the ratio of 1:2 in a vacuum at 150°C for 4 hours, after which samples were dried at 150°C to ensure a fine form for good adsorption. To prepare MWCNT-PEG, PEG and MWCNT were commingled in the ratio of 1:2 and blended utilizing a magnetic stirrer at 100°C for 4 hours. Finally, the commingled MWCNT-PEG was dried in an oven at 150°C for 3 hours to obtain dry samples.

## 2.3. Characterization of MWCNT-DES and MWCNT Adsorbents

The formulated MWCNT-DES and MWCNT adsorbents were characterized using the Infrared spectrometer (Varian 660 MidIR Dual MCT/DTGS Bundle with ATR) for the Fourier transform infrared spectroscopy (FTIR) analysis and the Hitachi SU 3500 scanning electron microscope for the SEM analysis. These analyses were performed to understand the surface morphology of the formulated adsorbent and to know the functional groups in the adsorbent not initially present in the MWCNT that may be responsible for the adsorption process.

## 2.4. CO<sub>2</sub> Adsorption Experiment

The CO<sub>2</sub> adsorption experiments were performed using the experimental setup by Aimikhe and Eyankware [35]. Measured amounts of MWCNT-DES adsorbent were placed in the reactor immersed in a water bath for temperature control and dosed with the CO<sub>2</sub> gas. Initial and final (equilibrium) pressures and corresponding temperatures were recorded. Initial pressure ranges were 2 and 15 psia at 26°C, 40°C, and 70°C. The corresponding adsorption capacity at each condition was also measured. Details of the experimental procedure can be found in the open literature [35].

## 2.5. Impact of CO<sub>2</sub>- Rich Adsorbent on Soil Properties

The impact of CO<sub>2</sub>-rich MWCNT-DES and MWCNT-PEG on soil properties was determined. Soil properties like pH, amount of soil nutrients, and Total Organic Content (TOC) were investigated to know the effect of disposing of the CO<sub>2</sub> -rich adsorbents into the environment. The test samples comprised the adsorbent + soil sample. The procedures for the analysis are described as follows:

- I. **pH Determination:** The pH meter of the Hanna 300 model was placed in each sample of 2g of dry sample mixed with 50 ml of distilled water and permitted to remain until stabilized. Reading was taken and recorded to determine the pH of the sample.
- II. **Cat-ion Determination:** 2g of dried sample was weighed into a 100ml beaker. 2ml HNO<sub>3</sub> was added. The mixture was digested by heating, using a heating mantle. More acid was added, and digestion continued for 30-40 mins. Digestion was stopped when a clear digest was obtained. The flask was cooled, and the content was transferred into a 50ml volumetric flask through a Whatman No. 42, 150mm diameter filter paper, and the solution was made-up to the 50ml mark with de-ionized water. The resulting solution was analyzed for heavy metals using the Atomic Absorption Spectrophotometer (BULK SCIENTIFIC, 205).
- III. **Total Organic Carbon (TOC) Determination.** 0.2g of the sample was evaporated to dryness. Potassium permanganate and sulphuric acids were added in a ratio of 1:2, respectively, and mixed with distilled water after 30 mins. Drops of ferritin solution were added and titrated to endpoint.

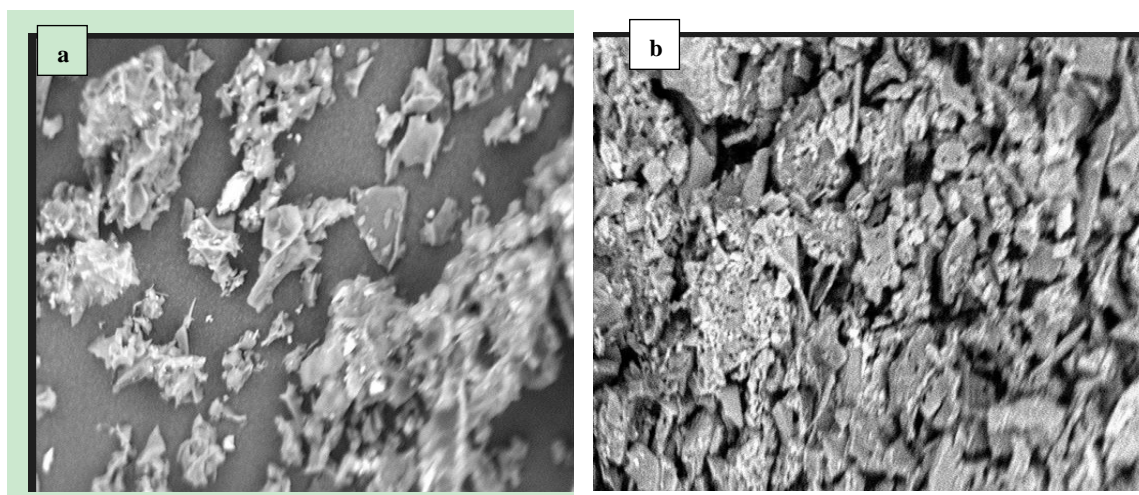
# 3. Results and Discussion

## 3.1. Characterization of MWCNT-DES and MWCNT-PEG Adsorbents

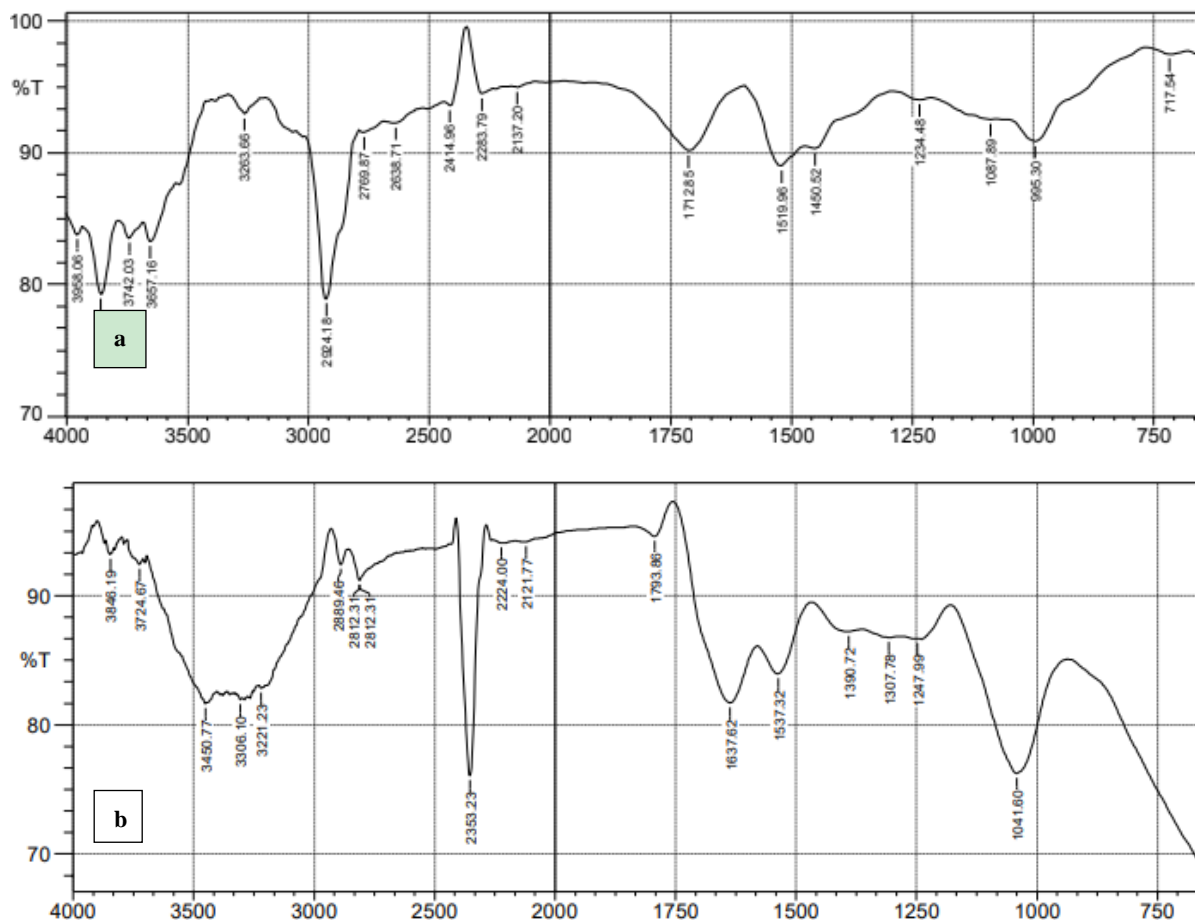
Results of the SEM images of MWCNT-DES and unmodified MWCNT using Flick through Electron Microscopy (SEM) showed that MWCNT possesses clogged pore spaces compared to the modified deep eutectic solvent. Figure 4 shows this result. Hence, the ability of MWCNT-DES to adsorb CO<sub>2</sub> gas molecules on its surface is enhanced due to pore availability. However, the unmodified MWCNTs are densely clogged, making pores less available for CO<sub>2</sub> adsorption. Figure 5 shows the FTIR spectra for the MWCNT-DES and MWCNT. For the MWCNT-DES adsorbent, the material can be described as a complex material with numerous adsorption peaks. From the spectrum, a broad adsorption band was noticed in the range of 3,250 to 3,650 cm<sup>-1</sup>, indicating the presence of the normal polymeric -OH group consistent with hydrogen bonding.

Adsorption bands consistent with primary and secondary amines, open chain Imino (C=N-) group, triple bonds, C-H stretching of the ether functional group, carbonyl group, and amides were found to exist in the adsorbent. For the unmodified MWCNT, no broad adsorption band was noticed in the range of 3,250 to 3,650 cm<sup>-1</sup>, indicating the absence of the normal polymeric -OH group consistent with hydrogen bonding.

The functional groups present in the adsorbent include the oxygen-related group consistent with saturated aliphatic methylene C-H stretching, aldehydes, primary amine, alkyl esters, and amides. From the analysis of the FTIR spectra, the MWCNT-DES adsorbent contains the -OH and more N-related groups, which typically have a high affinity for acid gases. It thus will enhance the adsorption of CO<sub>2</sub> more than the unmodified MWCNT.



**Figure 4.** SEM image of (a) MWCNT-DES and (b) unmodified MWCNT



**Figure 5.** FTIR spectra of (a) Unmodified MWCNT and (b) MWCNT-DES



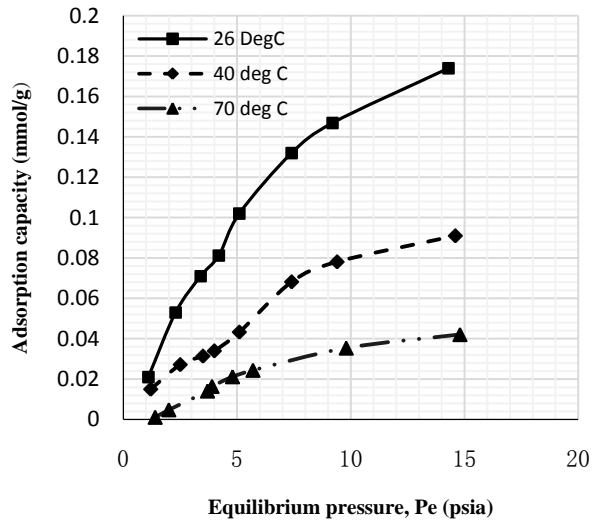


Figure 6. CO<sub>2</sub> adsorption capacity of unmodified MWC

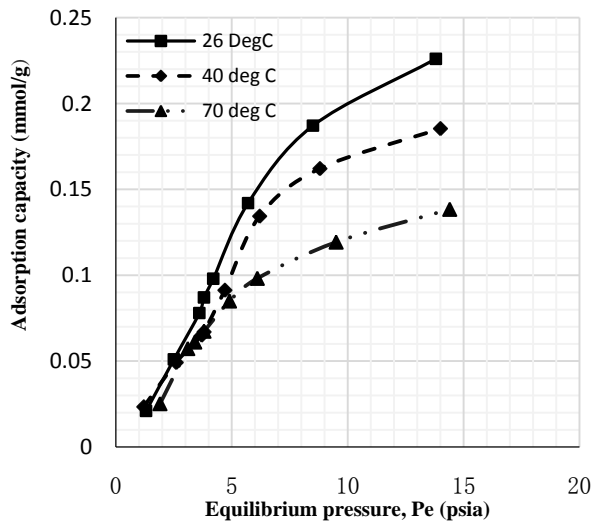


Figure 7. CO<sub>2</sub> adsorption capacity of MWCNT-DES

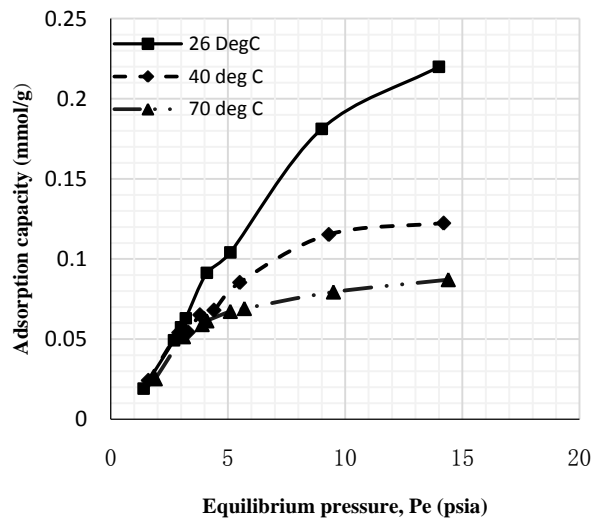


Figure 8. CO<sub>2</sub> adsorption capacity of MWCNT-PEG

### 3.2. CO<sub>2</sub> Adsorption Capacity of Adsorbents

Figures 6 to 8 showed that for CNT, MWCNT-DES, and MWCNT-PEG, CO<sub>2</sub> adsorption capacity increased as pressure increased through 2 to 15 psi at 26, 40, and 70°C, respectively. This trend was also reported by Babaei et al. [37], wherein an increase in adsorption pressure corresponded with an increase in adsorption capacity at constant temperatures. For example, the adsorption capacity of CNT at 26°C increased through 0.082, 0.149, and 0.174 mmol/g at a  $P_1$  pressure of 2 to 15 psi. The same trend was noticed for MWCNT-DES and MWCNT-PEG at 26°C, where adsorption capacities increased through 0.087, 0.187, 0.226 mmol/g, and 0.063, 0.180 and 0.22 mmol/g, respectively. The justification behind this noticed pattern is that, at increased pressures, CO<sub>2</sub> molecules are impacted with a higher force that makes them assess the adsorbent's pores, meaning higher adsorbent adsorption capacities. This result agrees with the work of Kang et al. [38], which showed that the CO<sub>2</sub> adsorption capacity of adsorbents is a component of strong gas mobility which is improved at increasing pressures.

Also, the result showed that an increase in the temperature for each adsorbent (MWCNT, MWCNT-DES, and MWCNT-PEG) through 26, 40, and 70°C reduced the adsorption capacity. For illustration, adsorption capacity at 26, 40, and 70°C at  $P_1$  pressure of 15 psi reduces through 0.174, 0.091, and 0.042 mmol/g, 0.226, 0.185, and 0.138 mmol/g and 0.220, 0.122 and 0.0871 mmol/g for MWCNT, MWCNT-DES and MWCNT-PEG, respectively.

This trend of reduction in CO<sub>2</sub> adsorption capacities of carbon nanotubes through increasing temperatures has been reported by Kang et. al [38] and Akpasi and Isa [39]. Herein, the decrease in adsorption capacity with an increase in temperature can be credited to the breakdown of pore structures of the adsorbents due to thermal degradation prompted by increased heat. Therefore, the quantity of pores available for CO<sub>2</sub> adsorption reduces, reducing adsorption capacity. Additionally, results showed that among the three adsorbents, – MWCNT, MWCNT-DES, and MWCNT-PEG, the MWCNT-DES material showed the most remarkable adsorption capacity through the temperatures of 26, 40, and 70°C and pressures of 2 to 15 psi. Unlike MWCNT and MWCNT-PEG, which had their highest adsorption capacities of 0.174 and 0.220 mmol/g at 26°C and 15 psi, MWCNT-DES exhibited an adsorption capacity of 0.226 mmol/g at the same conditions. Also, MWCNT, MWCNT-DES, and MWCNT-PEG were 0.091, 0.185, and 0.122 mmol/g at 40°C and 15 psi, respectively, while adsorption capacities were 0.042, 0.138, and 0.0871 mmol/g respectively at 70°C. Herein, it has been shown that although the functionalization using CO<sub>2</sub>-philic agents reduces the pore spaces, as reported by Hu et al. [24], the affinity of MWCNT-DES and MWCNT-PEG for CO<sub>2</sub> due to the presence of –N and –OH groups increase the adsorption limit of functionalized MWCNTs, thus, exceeding the CO<sub>2</sub> adsorption limit of the unmodified MWCNT material at

comparable conditions. Figure 9 shows the comparative adsorption capacities of the adsorbents at 26°C.

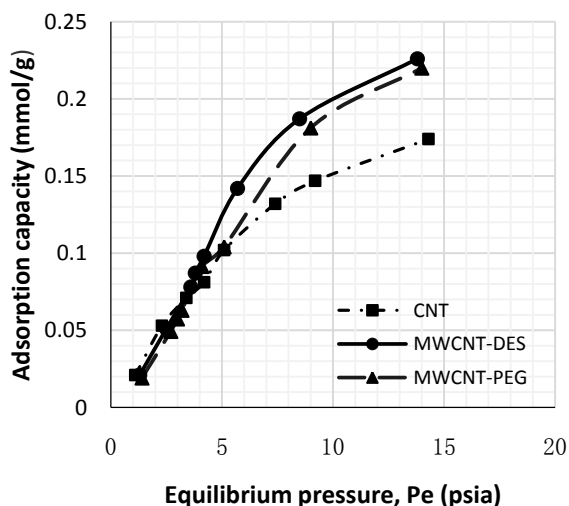


Figure 9. Adsorption capacities of adsorbents @ 26°C

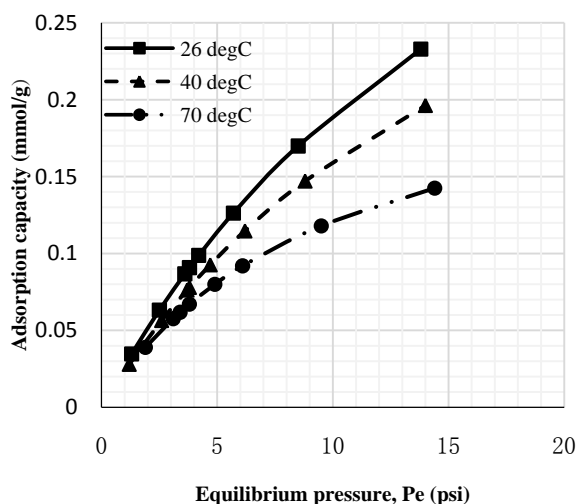


Figure 10. Langmuir adsorption isotherm

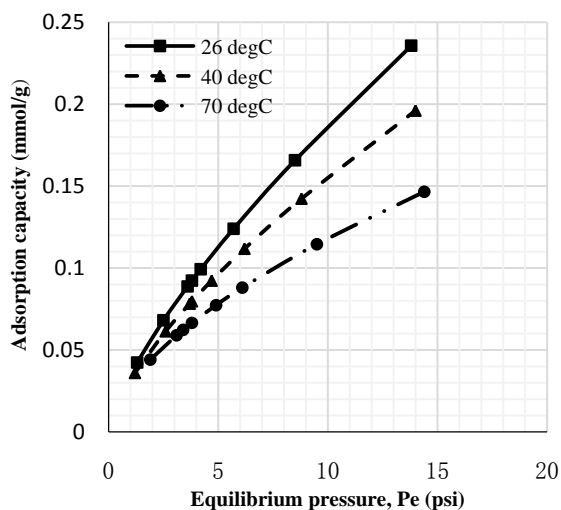


Figure 11. Freundlich adsorption isotherm

Furthermore, it is shown that MWCNT-DES displays higher CO<sub>2</sub> adsorption capacity than MWCNT-PEG (distinction of 0.006 mmol/g at 26°C and 15 psi). This slight difference in adsorption limit can be ascribed to the basicity of the functional groups. The – N functional group is more fundamental to adsorption than the alcohol – OH group. While the – N groups work with a carbamate response system collaboration between CO<sub>2</sub> particles [40], which at high amounts might have brought about a decrease in adsorption capacity. The open literature has also reported a reduced adsorption capacity at high doses of – OH functionalized adsorbents (using MOFs) [41]. The adsorption isotherm curves of the CO<sub>2</sub> adsorption process at 26, 40, and 70°C are shown in Figures 10 and 11. In addition, Langmuir & Freundlich's adsorption isotherm constants are highlighted in Table 2. The R<sup>2</sup> values for both isotherms show that Langmuir isotherms modeled the adsorption process better than Freundlich; hence, the focus was on the Langmuir adsorption isotherm. From the isotherm, adsorption capacities reduce as temperature increases due to the loss of binding strength between adsorbent and CO<sub>2</sub> molecules. This decrease in adsorption capacity reveals the process is mainly physisorption driven. The reason for this assumption is that at high temperatures, weak van der Waals are broken, unlike stronger chemical bonds (chemisorption). In addition, Langmuir constants (K<sub>L</sub>) decrease as temperature increases through 26, 40, and 70°C, indicating that it is a physisorption-based CO<sub>2</sub> adsorption process.

### 3.3. Impact of CO<sub>2</sub>- Rich Adsorbent on Soil Properties

An assessment of the effect of CO<sub>2</sub>-rich adsorbents on soil showed that MWCNT-PEG was soluble in water while MWCNT-DES was insoluble in water at ambient conditions. Herein, the control sample denotes the soil sample that does not contain CO<sub>2</sub>-rich adsorbents. In the results of the pH of samples, decreasing pH concentration through MWCNT-DES (7.6), MWCNT-PEG (7.5), MWCNT-PEG + control (7.5) and MWCNT-DES + control (7.2) were recorded. Although adding these CO<sub>2</sub>-rich adsorbents increased the acidity of the soil samples, their values were still within WHO limits of 6.5 – 8.5. Furthermore, it is apparent from the outcomes that the addition of MWCNT-PEG to the control did not affect the acidity of the control, unlike MWCNT-DES, highlighting its environmentally benign nature. Regarding TOC measured in mg/kg, adding MWCNT-DES (TOC Content of 3.16 mg/kg) to the control increased the TOC from 0.12 mg/kg to 3.77 mg/kg, highlighting its positive impact on soil nutrients. Similarly, adding MWCNT-PEG (TOC content of 2.92 mg/kg) to the control increased the TOC from 0.12 mg/kg to 2.90 mg/kg.

The soil's macronutrient analysis showed that the MWCNT-PEG increased the K<sup>+</sup> concentration of the control from 4.18 ppm to 29.30 ppm, and MWCNT-DES increased the K<sup>+</sup> concentration to 28.0 ppm, highlighting the positive impact of these CO<sub>2</sub>-rich adsorbents on the soil. On the



Contrary, MWCNT-DES and MWCNT-PEG decreased the  $Mg^{2+}$  concentration of the control sample. MWCNT-PEG (76.29 ppm) decreased the  $Mg^{2+}$  concentration of the control from 99.21 ppm to 98.20 ppm, while MWCNT-DES (91.96 ppm) decreased the  $Mg^{2+}$  concentration of the control sample from 99.21 ppm to 95.42 ppm. Similarly, adding MWCNT-PEG and MWCNT-DES to the control reduced the  $Ca^{2+}$  concentration of the soil. As for MWCNT-PEG, a decrease in the  $Ca^{2+}$  concentration of the control from 23.40 ppm to 22.68 ppm was observed, while for MWCNT-DES, a reduction in the  $Ca^{2+}$  concentration of the control from 23.40 ppm to 22.10 ppm was recorded accordingly. Figure 12 shows the soil test results.

### 3.4. Comparison of Modified MWCNT to Similar Adsorbents in Literature

The adsorption capacity of MWCNT-DES adsorbent at 26°C and 15 psi was compared to other published MWCNT-modified adsorbents. As emphasized in Table 3, MWCNT-DES showed limited  $CO_2$  adsorption capacity compared to similar adsorbents. In this view, MWCNT-DES is not a suitable adsorbent for  $CO_2$  capture at post-combustion conditions.

## 4. Conclusions

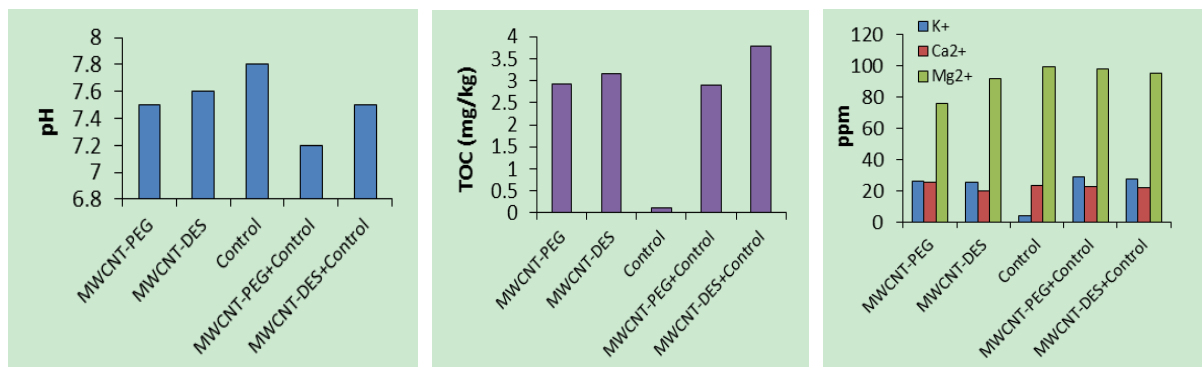
This study investigated the  $CO_2$  adsorption efficiency of MWCNT modified with choline chloride + glycerol deep eutectic solvent. A  $CO_2$  adsorption capacity of 0.226 mmol/g at 26°C and 15 psi was observed for the adsorbent. This adsorption capacity increased with pressure and decreased with increasing temperature. Compared to an MWCNT modified with polyethylene glycol (MWCNT-PEG), results showed a relatively similar adsorption capacity of 0.220 mmol/g compared to MWCNT-DES (0.226 mmol/g). The adsorption process of the MWCNT-DES was a typical physisorption process best described by the Langmuir model. In the event of disposal to the environment, soil tests revealed that the  $CO_2$ -rich MWCNT-DES adsorbent is environmentally friendly and has the propensity to improve soil properties. However, due to its low adsorption capacity (0.226 mmol/g at 26°C and 15 psi), the formulated MWCNT from acetylene via chemical vapor deposition and modified with deep eutectic solvent prepared from choline chloride and glycerol is not a suitable adsorbent for  $CO_2$  capture at post-combustion conditions.

**Table 2.** Adsorption isotherm constants

Sample		26°C		40°C		70°C	
		Langmuir.	Freundlich.	Langmuir.	Freundlich.	Langmuir.	Freundlich.
MWCNT-DES	$Q_m$ (mmol/g)	0.574	-	0.45	-	0.24	-
	$K_L$	0.049	-	0.052	-	0.102	-
	$K_F$	-	0.035	-	0.032	-	0.030
	n	-	1.38	-	1.45	-	1.69
	$R^2$	0.976	0.959	0.958	0.939	0.974	0.937

**Table 3.** Comparison of modified MWCNT to other synthesized by other authors

S/N	Modified MWCNT	Temp. (°C)	Pressure (psi)	Adsorption capacity (mmol/g)	Ref.
1	APTES modified MWCNT	25	15	2.26	[37]
2	Functionalize MWCNTs	25	14.7	0.33	[42]
3	Animated MWCNT	30	29	0.59	[43]
4	Amine modified CNTs	25	14.7	0.64	[44]
5	MWCNTs-ZnO-SiO <sub>2</sub>	0	14.7	1.32	[45]
6	DES modified MWCNT	26	15	0.23	This work



**Figure 12.** Comparison of pH, TOC, and Ion concentrations

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