

Article

Electrospun Composites Made of Reduced Graphene Oxide and Polyacrylonitrile-Based Activated Carbon Nanofibers (rGO/ACNF) for Enhanced CO₂ Adsorption

Faten Ermala Che Othman ¹, Norhaniza Yusof ¹, Javier González-Benito ^{2,*}, Xiaolei Fan ³
and Ahmad Fauzi Ismail ¹

¹ Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Johor Bahru 81310, Malaysia; fermalma2@live.utm.my (F.E.C.O.); norhaniza@petroleum.utm.my (N.Y.); afauzi@utm.my (A.F.I.)

² Department of Materials Science and Engineering and Chemical Engineering, IQMAAB, Universidad Carlos III de Madrid, Avda. Universidad 15, Leganés, 28911 Madrid, Spain

³ Department of Chemical Engineering and Analytical Science, School of Engineering, The University of Manchester, Manchester M13 9PL, UK; xiaolei.fan@manchester.ac.uk

* Correspondence: javid@ing.uc3m.es

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Abstract: In this work, we report the preparation of polyacrylonitrile (PAN)-based activated carbon nanofibers composited with different concentrations of reduced graphene oxide (rGO/ACNF) (1%, 5%, and 10% relative to PAN weight) by a simple electrospinning method. The electrospun nanofibers (NFs) were carbonized and physically activated to obtain activated carbon nanofibers (ACNFs). Texture, surface and elemental properties of the pristine ACNFs and composites were characterized using various techniques. In comparison to pristine ACNF, the incorporation of rGO led to changes in surface and textural characteristics such as specific surface area (S_{BET}), total pore volume (V_{total}), and micropore volume (V_{micro}) of 373 m²/g, 0.22 cm³/g, and 0.15 cm³/g, respectively, which is much higher than the pristine ACNFs (e.g., $S_{\text{BET}} = 139$ m²/g). The structural and morphological properties of the pristine ACNFs and their composites were studied by Raman spectroscopy and X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM) respectively. Carbon dioxide (CO₂) adsorption on the pristine ACNFs and rGO/ACNF composites was evaluated at different pressures (5, 10, and 15 bars) based on static volumetric adsorption. At 15 bar, the composite with 10% of rGO (rGO/ACNF0.1) that had the highest S_{BET} , V_{total} , and V_{micro} , as confirmed with BET model, exhibited the highest CO₂ uptake of 58 mmol/g. These results point out that both surface and texture have a strong influence on the performance of CO₂ adsorption. Interestingly, at $p < 10$ bar, the adsorption process of CO₂ was found to be quite well fitted by pseudo-second order model (i.e., the chemisorption), whilst at 15 bar, physisorption prevailed, which was explained by the pseudo-first order model.

Keywords: activated carbon nanofibers (ACNF); reduced graphene oxide (rGO); rGO/ACNF composite; CO₂ capture; electrospinning

1. Introduction

The massive emissions of anthropogenic carbon dioxide (CO₂) gas into the atmosphere are considered as the main reason for the occurrence of global warming and climate change [1,2]. Human activities such as the combustion of fossil fuels in industry, especially in the power generation

sector, are major emission sources of CO₂ into the atmosphere [3,4]. In mid-August 2020, according to the latest update from Mouna Loa Observatory [5], the increment of CO₂ concentration was recorded as 3.02 ppm from August 2019 to August 2020 and reached up to 412.97 ppm as compared to the previous year's concentration, i.e., 409.95 ppm, which is an alarming rate, since CO₂ concentration in the atmosphere at <350 ppm is considered safe [6]. There was a temporary reduction in daily global CO₂ emissions during the COVID-19 forced confinement in April 2020 reported by Le Quéré et al. (2020), but this does not really reflect structural changes in the economic, transport or energy system [7]. Various agreements have been developed among nations worldwide, including the Kyoto Protocol and Paris Agreement, to face the challenges caused by carbon emission, especially CO₂ emission. Accordingly, this has encouraged many research efforts around the world to develop advanced materials, techniques and strategies to address the problems associated with CO₂ emission. Popular strategies have been explored and adopted, including the utilization of low carbon fuels and renewable energy sources, and CO₂ capture, storage and utilization from their source points [8].

Carbon capture and storage (CCS) is a promising approach to mitigate anthropogenic CO₂ with the capacity to reduce up to 22% of CO₂ emissions in 2035 [3]. These past few decades, absorption is the common method in CCS for CO₂ capture and separation from flue gases in power plants. However, CO₂ absorption via amine scrubbing possesses apparent disadvantages, such as the release of toxic gases and chemicals, high energy requirement for regeneration, and extensive corrosion of the equipment, which limit the practical application of this technology. Although amine-scrubbing has been widely employed in industrial applications, due to their disadvantages, the development of practical yet sustainable alternatives is still highly desired [9,10]. Consequently, other alternative and effective methods, such as adsorption, have been suggested, due to its simplicity in operation [2], low energy requirement, ease of regeneration, environmental-friendly, and cost-effective [11]. Adsorption employs solid porous adsorbents such as silica [12], zeolites [13], activated carbon [11], metal organic frameworks (MOF) [14–16], carbon nanotubes (CNT) [17], metal oxides [18], and graphene [19], to adsorb adsorbate molecules, especially CO₂, onto the porous structures. Amongst the available adsorbents being investigated, porous ones such as activated carbons (ACs) were preferred due to their low cost, high surface area and porosity, high adsorption capability, high amenability to modify the pore structure and functionalize the surface, low energy requirements for regeneration, as well as hydrophobicity [20,21].

ACs in granular and powdered form are the most commonly used adsorbent [21]. Generally, ACs have relatively low micropore volume and multimodal pore size distribution, which are the main factors to limit their adsorption capabilities. Conversely, in comparison with the conventional ACs, newly developed fibrous ACs, also known as activated carbon nanofibers (ACNFs) [22], have shown the improved adsorption capacity due to the fibrous structure and presence of accessible micropores from their external surface [23], which reduce the mass transfer resistance for adsorbate diffusion to reach the adsorption sites. Polyacrylonitrile (PAN) is the most used polymer in electrospinning of NFs due to its high carbon yield and thermal-stable at high temperature treatments. Although the developed pristine PAN-based ACNFs has shown the improved adsorption performance as compared with the commercial ACs, recent study disclosed that the inclusion of nanofillers/additives could further improve the surface area and micropore volume of the modified ACNFs [24,25]. In comparison with other additives, graphene and graphene oxide with novel properties and economical carbon-based materials have been the potential candidates for adsorbent materials due to their large theoretical specific surface area (S_{BET}) and high porosity [26,27]. These excellent properties have opened up the utilization of graphene in a wide range of applications, including supercapacitors, biomedical, fuel cells, energy storage etc. [28]. Accordingly, graphene-based composites such as nitrogen-doped graphene oxide sheets (N-GOs) have been proposed by Alghamdi et al. (2018) [29] for energy storage applications related to gas adsorption and separation. They have observed that the N-GOs demonstrated a good CO₂ adsorption capacity of 1.36 mmol/g. Notably, the selection of GO in this study is also because the GO

can be mass-produced from inexpensive graphite as raw materials and a cost-effective method which made the reduced GO (rGO) composites into economical adsorbents.

Here, this work reports the preparation of novel carbonaceous composites of reduced graphene oxide (rGO) doped PAN-based activated carbon nanofibers, i.e., rGO/ACNF using a simple electrospinning method and pyrolysis process. Up to now, there is no publication that extensively discussed the utilization of PAN-based rGO/ACNFs composites for CO₂ adsorption. Therefore, the main novelty of this present work is to develop and characterize the rGO/ACNF composites (with different rGO loadings) using different techniques to understand their physicochemical properties and assess for CO₂ adsorption (using a volumetric adsorption system at 5–15 bar) to evaluate their potentials for CCS. Kinetics of CO₂ adsorption of the materials under investigation are also studied in detail to understand their adsorption mechanisms and performance.

2. Materials and Methods

2.1. Synthesis of Reduced Graphene Oxide (rGO)

The graphite powder (~325 mesh, 99%) was purchased from Alfa Aesar, and other chemicals such as sulphuric acid (H₂SO₄), sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), hydrogen chloride (HCl), and hydrogen peroxide (H₂O₂) were obtained from Merck and used without further purification. Graphene oxide (GO) was prepared from natural graphite powder using a conventional Hummer's method. Then, 150 mL of concentrated H₂SO₄ was added into the mixture of graphite powder and NaNO₃. The suspension was vigorously stirred at <20 °C in an ice bath, followed by the addition of KMnO₄ (18 g). Then, the temperature of the solution was increased slowly to 35 °C, and the mixture was stirred for another 30 min before it was quenched by adding 300 mL of deionized (DI) water. The temperature of the mixture was then raised to 98 °C and stirred overnight. Afterward, 300 mL of 30% H₂O₂ was introduced into the mixture, which was followed by the addition of 5% HCl solution to remove any metal ions left over [30]. The resulting solid was washed several times with DI water (until the neutral pH was achieved), separated by vacuum filtration and dried under vacuum (at 50 °C for 24 h) to obtain the GO. To obtain rGO, the GO sample was thermally reduced and exfoliated under thermal condition at >800 °C and inert atmosphere [31,32].

2.2. Preparation of Activated Carbon Nanofibers Nanocomposites (gACNFs)

rGO (1, 5 and 10 wt. %, respectively, relative to the weight of polymer polyacrylonitrile, PAN; 150,000 molecular weight of kDa) was dispersed in dimethylformamide (DMF; 99.999%) and sonicated under stirring for 24 h at room temperature until the homogenous solution was obtained. Both polymer and solvent were procured from Sigma-Aldrich. PAN (8 wt. % relative to the total weight) was added into the solution, and the solution was stirred again for 24 h at room temperature to obtain a homogenous solution [25]. Detailed formulation was shown in Table S1 (Supplementary Materials).

PAN-based NFs were prepared using the optimum electrospinning conditions established by our previous research [30]. Specifically, the injection flow rate was 1.0 mL/h, voltage power was 10 kV, and the distance between the needle tip and collector was 15 cm. Furthermore, the ambient parameters inside the chamber including the humidity, temperature, and air velocity were also controlled during the operation. The obtained pristine and composite nanofibers (with 1, 5, and 10 wt. % rGO loading) were denoted as NF, rGO/NF0.01, rGO/NF0.05, and rGO/NF0.1, respectively. Activated carbon nanofibers (ACNF) were produced by subjecting the electrospun NFs to three stages of pyrolysis, including thermal stabilization (oxidation), carbonization, and activation, where the experimental details were described elsewhere [25,33]. The activated NFs were denoted as ACNF, rGO/ACNF0.01, rGO/ACNF0.05, and rGO/ACNF0.1 accordingly.

2.3. Characterization of Materials

Porous structures of the materials under investigation were characterized by using nitrogen (N₂) adsorption/desorption analysis at −196 °C on Micromeritics Tristar II 3020, and the specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method. Prior N₂ sorption analysis, the sample was degassed at 100 °C under vacuum for at least 24 h. The total pore volume (V_{total}) was measured from the adsorption amounts of N₂ gas at $p/p_0 = 0.99$ and the micropore volume (V_{micro}) was determined by density functional theory (DFT). The mesopore volumes (V_{meso}) were calculated by subtracting the V_{micro} from V_{total} . The structural transformation and degree of graphitization of the materials were analyzed using Raman spectroscopy (on Raman Xplora Plus spectrometer). To study the phase structure and crystallinity of the materials, an X-ray diffractometer (XRD, Rigaku SmartLab; Rigaku Corporation, The Woodlands, TX, United States) was used. Surface morphology and diameter, as well as the elemental composition of the materials, were analyzed using field electron scanning emission microscope coupled with elemental dispersive X-ray spectroscopy (FE-SEM-EDX, Hitachi SU8020; Hitachi High-Technologies Corporation, Tokyo, Japan). Prior to FE-SEM analysis, all samples were dried at 100 °C and stored in a desiccator overnight.

2.4. CO₂ Adsorption Experiments

Static volumetric CO₂ adsorption measurements were performed on the same rig as the one shown in Figure 1. Prior to CO₂ adsorption, the sample (~0.5 g) was dried under vacuum at 150 °C for 12 h to remove the moisture. In each test, the ACNFs and CO₂ were loaded into adsorption cell (AC) and loading cell (LC), respectively, until the pressure achieved the required levels. The gas adsorption test was started once the pressure reached the desired level (5, 10 and 15 bar), by introducing the CO₂ (adsorbates) with the ACNFs (adsorbent) in the AC by turning the valve between the AC and LC. The selection of these three pressures is to determine the adsorption capacity of both pristine and composite ACNFs at low and moderate pressures. The pressure and temperature in both AC and LC were recorded every 5 min until the pressure reached equilibrium. The adsorption equilibrium was achieved when both pressure and temperature were constant for approximately 10 min. The amount of CO₂ adsorbed was calculated by using Equation (1):

$$q = \frac{1}{m} \left[\frac{Vv}{R} \left(\left. \frac{P}{ZT} \right|_i - \left. \frac{P}{ZT} \right|_{eq,a} \right) + \left(\left. \frac{P}{ZT} \right|_i - \left. \frac{P}{ZT} \right|_{eq,l} \right) \right] \quad (1)$$

where m is the adsorbent mass (g), q is the amount of gas adsorbed (mmol/g), P is pressure (bar), T is temperature (K), V is volume (cm³), R is the gas constant, while the subscripts a , l , i , and eq refer to adsorption cell, loading cell, the initial state and adsorption final equilibrium state, respectively. Z is the compressibility factor [34].

The CO₂ adsorption performance of pristine ACNF and composite were evaluated as a function of time, until equilibrium is reached at room temperature and different adsorption pressures of 5, 10, and 15 bar. In this study, only a rGO/ACNF0.1 composite was used for further assessment (kinetic studies) to compare with the pristine ACNFs, due its comparatively high N₂ and CO₂ adsorption performance and the associated high S_{BET} value.

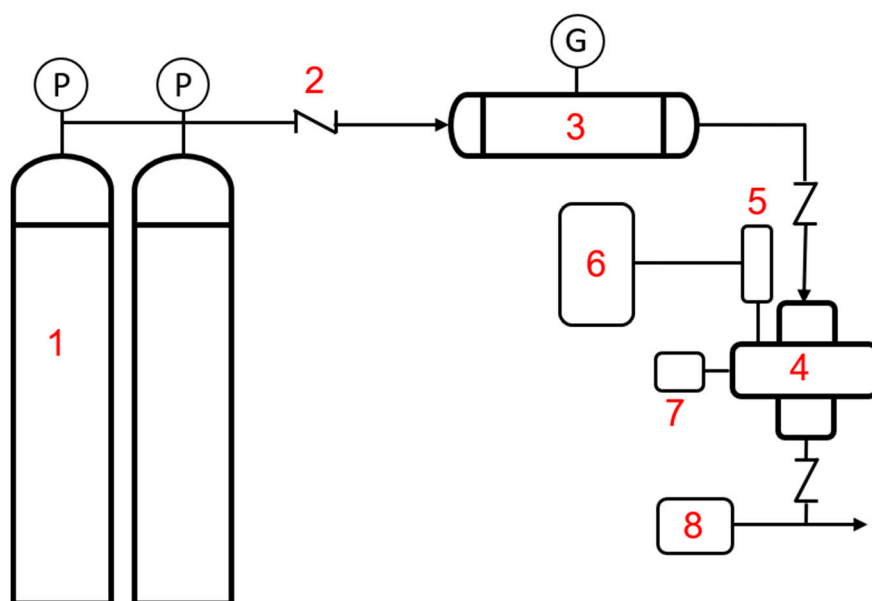


Figure 1. Schematic diagram of the volumetric set-up for CO₂ adsorption. 1. Feed gas 2. Check valve 3. Loading column 4. Adsorption column 5. High pressure transducer 6. Pressure meter 7. Thermocouple 8. Vacuum pump; P: pressure regulator; G: pressure gauge.

2.5. Kinetic Studies

Apart from the study of adsorption capacity, when a new system is evaluated in terms of its potentiality for industrial applications, an understanding of adsorption kinetics is also necessary. In principle, kinetic parameters should provide information about mass transfer rates of the adsorbates through the external adsorbed layer or layers, macropores and micropores of the adsorbent. Up to now, literature provides several kinetic models [11,35,36]. In general, experimental data obtained are fitted with the functions associated to those models to finally select the best fitting to choose the model describing the kinetics of the adsorption process.

Lagergren's pseudo-first order and pseudo-second order of kinetic models were used to study the experimental data of CO₂ adsorption on the materials at different times. The pseudo-first order assumes that the adsorption rate is proportional to the number of free adsorption sites on the surface of the adsorbent. The linear equation of this model is shown as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_t is the weight-specific adsorbed amount of the adsorbate at time t (s) during the adsorption process (mmol/g), q_e is the weight-specific adsorbed amount of the adsorbate at the end of equilibrium (mmol/g), and k_1 is the adsorption rate constant of the pseudo-first order model.

Therefore, if the representation of $\ln(q_e - q_t)$ versus time can be well fitted to a straight line, then it can be said that adsorption of CO₂ obeys the pseudo-first order model. In general, this pseudo-first order model explains reversible interactions between adsorbent and adsorbate and therefore accounts for physisorption processes [11].

On the other hand, the pseudo-second order considers that the adsorption rate is proportional to the square of vacant adsorption sites on the adsorbent surface and the linear equation, as shown in Equation (3).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 (mmol/g) is the adsorption rate constant for the pseudo-second order equation. Therefore, if the representation of t/q_t versus time can be well fitted to a straight line, then it can be said that

adsorption of CO₂ obeys the pseudo-second order model. This pseudo-second order model explains relatively strong interactions, chemical interactions, between the gas molecules and the adsorbent, therefore the process would be represented by a chemisorption as the rate controlling step [37]. Both k_1 and k_2 values can be obtained from the slopes of the corresponding fitted straight lines.

3. Results and Discussion

3.1. Properties of Materials

The microstructure and textural properties of nanofibers and composites before (NF and rGO/NF) and after activation (ACNF and rGO/ACNF) were studied by N₂ adsorption/desorption analysis at −196 °C, and the plotted results are shown in Figure 2 and Table 1. Figure 2a shows the N₂ adsorption/desorption isotherms of the NF samples before activation, showing profiles which point out type II isotherms, indicating the presence of macroporous or non-porous structures according to International Union of Pure Chemical and Applied Chemistry (IUPAC) [38,39]. This type of isotherm is believed to have single layer to multilayer adsorption, which is reflected by the shape of the isotherms in Figure 2a, i.e., linear at $p/p_0 < 0.8$ and convex at $p/p_0 > 0.85-1.0$. As shown in Table 2, all NF and rGO/NF materials are not microporous, i.e., $V_{\text{micro}} = 0 \text{ cm}^3/\text{g}$ and the addition of rGO did not alter the textural property of the NFs, since the relevant property of rGO/NF materials does not correlate with the loading of rGO. The activation procedure was able to improve the textural property of the ACNFs. The development of meso- and micropores and increment in surface area were measured in all activated samples. The microporous properties in all samples are reflected by the Type I(b) isotherms measured by N₂ adsorption [38,40]. As shown in Figure 2b, the sorption curves for the activated samples appear above the curves obtained in the case of non-activated materials, at least at $p/p_0 < 0.9$. Besides, they show a very long plateau from $p/p_0 = 0.05-0.95$, showing the typical adsorption behaviour of microporous materials. Meanwhile, at $p/p_0 > 0.95$, the adsorption curve is further increased without any significant halted observed. The adsorption-desorption isotherms of ACNFs also show the presence of H3 type of hysteresis loop [38] in the p/p_0 range of 0.4–1.0, which suggests the presence of capillary condensation in mesoporous features [41,42]. It is worth mentioning that the values of $V_{\text{micro}}/V_{\text{total}}$ confirmed that all activated samples were primarily microporous, with a relatively high proportion of V_{micro} to the V_{total} . Contributions by the mesopores to the porous structure were also measured, as shown by the V_{meso} values.

The creation of meso-/micro-porous structures through activation at 700 °C was reflected by the significant improvement of S_{BET} in all samples, as shown in Table 2. S_{BET} of ACNFs drastically increased from 17 m²/g to 139 m²/g, which is eight times higher than the pristine NFs. For the activated composites, the highest S_{BET} of 373 m²/g was measured for rGO/ACNF0.1 and the lowest S_{BET} of 92 m²/g was determined for rGO/ACNF0.01, respectively, as rGO/ACNF0.1 exhibits the highest S_{BET} compared to other samples, indicating the possible high adsorption capacity. Interestingly, the effect of the amount of rGO loading was more noticeable after activation. This is could possibly be due to the catalytic effect of rGO that takes place at elevated temperatures [43]. S_{BET} is low in all samples before activation, showing no significant catalytic ability, but increases after being activated, indicating that rGO have good catalytic ability for developing S_{BET} at elevated temperatures. After activation, the relevant porous characteristics, such as S_{BET} and pore volumes, seem to have a good correlation with the amount of rGO loading. Typically, it is believed that adsorbent materials with high S_{BET} and V_{micro} are beneficial to adsorption of gas molecules [44].

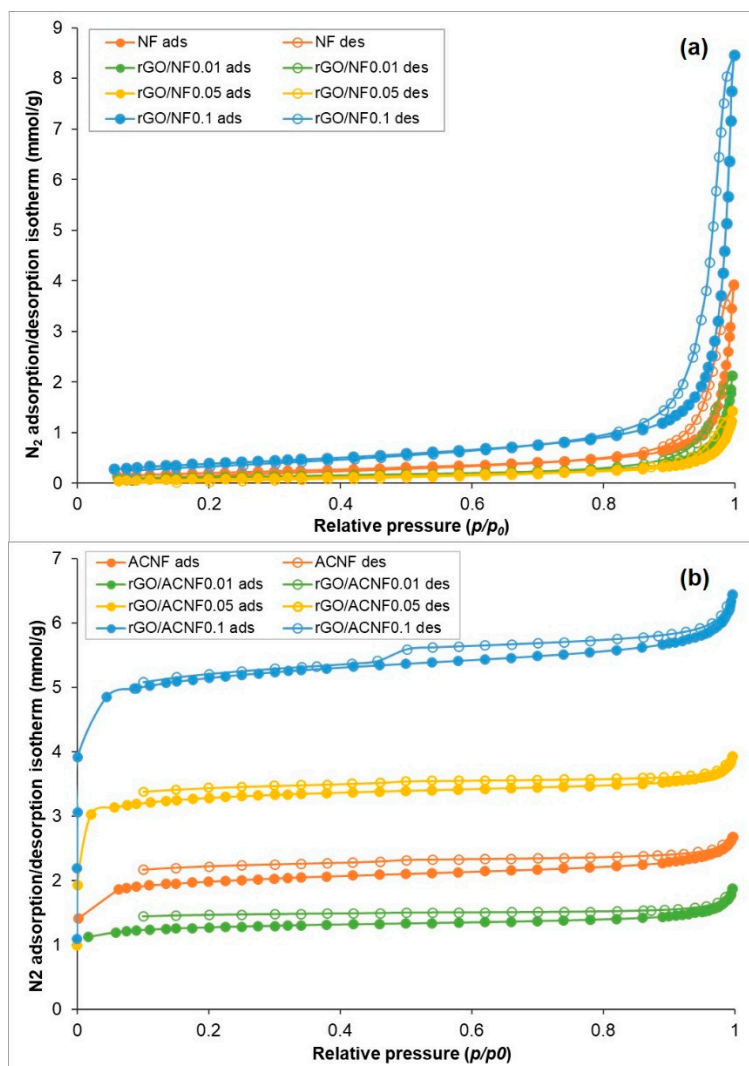


Figure 2. N₂ adsorption/desorption isotherms of the materials under investigation (a) materials before activation and (b) materials after activation.

Table 1. Porous characteristics of the pristine nanofibers (NF) and reduced graphene oxide (rGO)/NFs nanocomposites before and after activation.

	Samples	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{meso} (cm ³ /g)	V _{micro} /V _{total} (%)
Before Activation	NF	17	0.14	0	0	0
	rGO/NF0.01	10	0.07	0	0	0
	rGO/NF0.05	8	0.05	0	0	0
	rGO/NF0.1	32	0.30	0	0	0
After Activation	Activated carbon nanofibers (ACNF)	139	0.09	0.06	0.03	67
	rGO/ACNF0.01	92	0.07	0.04	0.03	57
	rGO/ACNF0.05	233	0.14	0.09	0.05	64
	rGO/ACNF0.1	373	0.22	0.15	0.07	68

S_{BET} = specific surface area; V_{total} = total pore volume; V_{micro} = micropore volume; V_{meso} = mesopore volume.

Table 2. CO₂ uptakes at different pressures at ambient temperatures.

Sample	CO ₂ Uptakes (mmol/g)		
	5 bar	10 bar	15 bar
ACNF	24	27	31
rGO/ACNF0.01	17	20	21
rGO/ACNF0.05	34	36	44
rGO/ACNF0.1	41	43	58

The degree of graphitization and structural features of the pristine rGO, NF and rGO/NF composites before and after activation was analyzed by Raman spectroscopy, as shown in Figure 3a,b, respectively. It can be seen that all samples under investigation exhibit two characteristic peaks at 1368 cm⁻¹ and 1612 cm⁻¹, which represent the D-band and G-band of graphitic materials, respectively. The presence of D-band in all samples indicates the presence of defective or disordered carbon structures [37], whilst the existence of G-band is attributed to the ordered graphitic structures with sp²-hybridized carbon atoms [26]. The only significant difference observed in Raman spectra before and after activation is the higher Raman intensity and more amorphous structure exhibited by the samples before activation. Reduction in intensity was observed when the samples underwent activation. In pristine rGO, both D-/G-bands have relatively strong intensities, with the appearance of weak 2D-band around 2700 cm⁻¹ [45], which is typical in graphene materials. The intensity of G-band is slightly higher than that of the D-band, indicating that the self-synthesised graphene-based material from graphite demonstrated the crystalline, ordered but also possessed defect structures within the carbon lattice [46]. The non-appearance of 2D-band in rGO/ACNF composites is believed to be due to the amount of rGO composited into the structures being too small. Obviously, the intensity of D-band is higher than G-band in all ACNF-based samples, indicating that the resulting composite materials possess defective structures and are highly amorphous in nature, which is in agreement with the findings by XRD analysis (to be discussed later).

The degree of graphitization of the materials was evaluated by calculating the intensity ratio of the D and G band (I_D/I_G). Obviously, rGO shows the smallest I_D/I_G ratio of 0.99 compared to other electrospun materials, which represents the high degree of graphitization and ordered carbon structures in it [31,47]. In comparison with rGO, the I_D/I_G of ACNF is comparatively higher, at 1.35, suggesting a less ordered carbon structure in the ACNF. As expected, the incorporation of rGO with ACNF gave the materials with I_D/I_G ranging from 1.2–1.4 and this ratio decrease with the increase of the rGO concentrations (Figure 3). From the results obtained, it was demonstrated that the graphitic structure of rGO/ACNF composites were improved with the increment of rGO loading, and it was found that rGO/ACNF0.1 unveiled the smallest ratio of 1.23. Regardless of its lowest I_D/I_G compared to other samples, it is believed that the carbon materials with this value are still considered to own disordered and defective structures. This is supported by a study reported by Gayathri et al. [45], as the graphene synthesized in their research still possessed a defect structure, even at very low I_D/I_G of ~0.2–0.4.

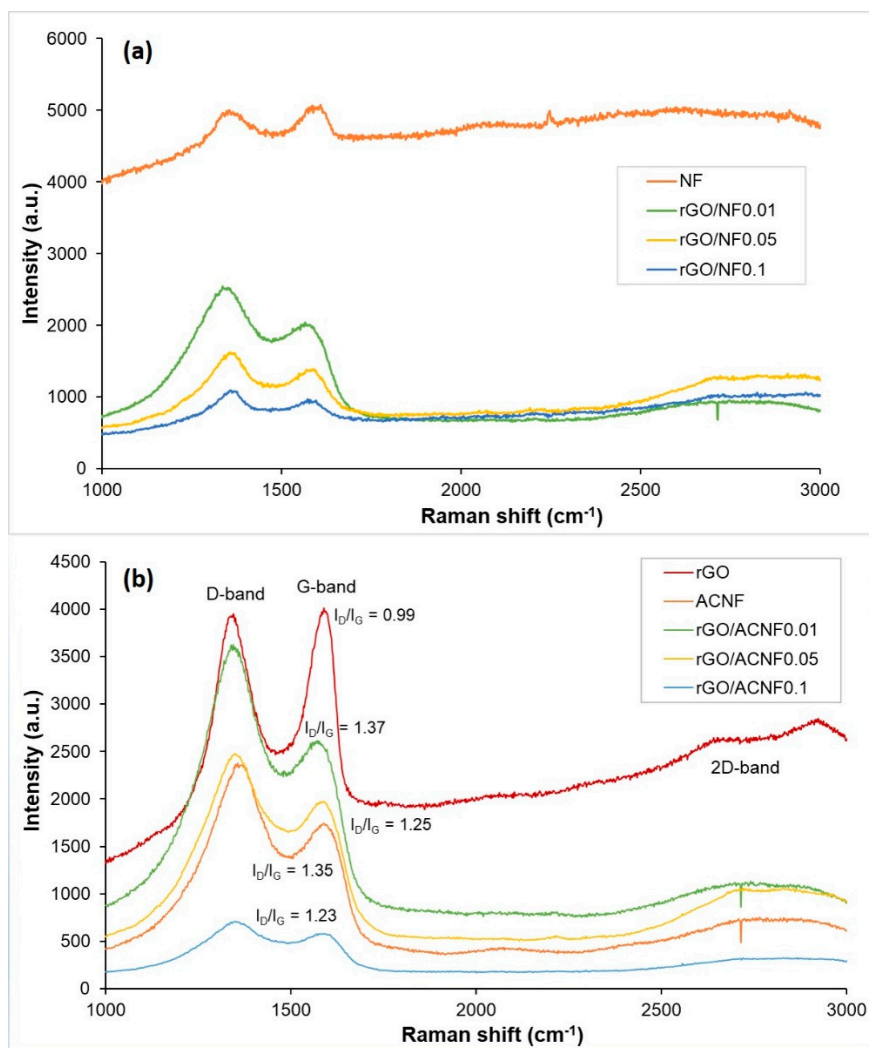


Figure 3. Raman spectra of rGO, ACNF and rGO/ACNF. (a) materials before activation and (b) materials after activation.

Figure 4a shows the comparative XRD patterns of NF and ACNF. XRD spectrum of NF shows a peak at 17.1° , which can be attributed to the diffraction feature of PAN as polymer precursor [48,49]. After activation at 700°C , the presence of broad peak at 26.3° at high intensity in ACNF corresponds to the 002 plane of the carbon skeleton [50]. This means that carbon-based materials with ladder structures such as ACNFs have been successfully developed through the cyclization of PAN during activation. Activation has also improved the crystallinity of the ACNFs. However, the ACNFs obtained in this study still remain amorphous (absence of sharp peak) due to the destruction of the in-plane aromatic lattices [51], leaving highly defect structures in the ACNFs [2,26]. Meanwhile, Figure 4b shows the comparative XRD patterns of rGO, ACNFs, and rGO/ACNF composites, which were used to investigate the effect of rGO loading on the graphitization degree and their crystallinity. All materials under investigation, including the rGO, show one intense broad diffraction peak in a range of 17° – 31° (hexagonal graphite), and another characteristic peak at 41° – 43° (rhombohedral graphite) [40], with variation only in their intensities. XRD analysis of carbonaceous phase in the materials can tell the feature of the crystallographic (100) and amorphous (110) planes. As previously mentioned, the appearance of the low and broad peaks at 41° – 43° represents the amorphous structure with a very low graphitization degree. This result corresponds well to the finding by Raman spectroscopy. According to a study conducted by Guo et al. [52], carbon materials with amorphous and defective structures are believed to have more potential in altering the textural properties of the ACNFs, which can

improve their adsorption capacity. Therefore, the ACNFs with the defective nature developed by this study were believed to have high CO₂ adsorption capacity.

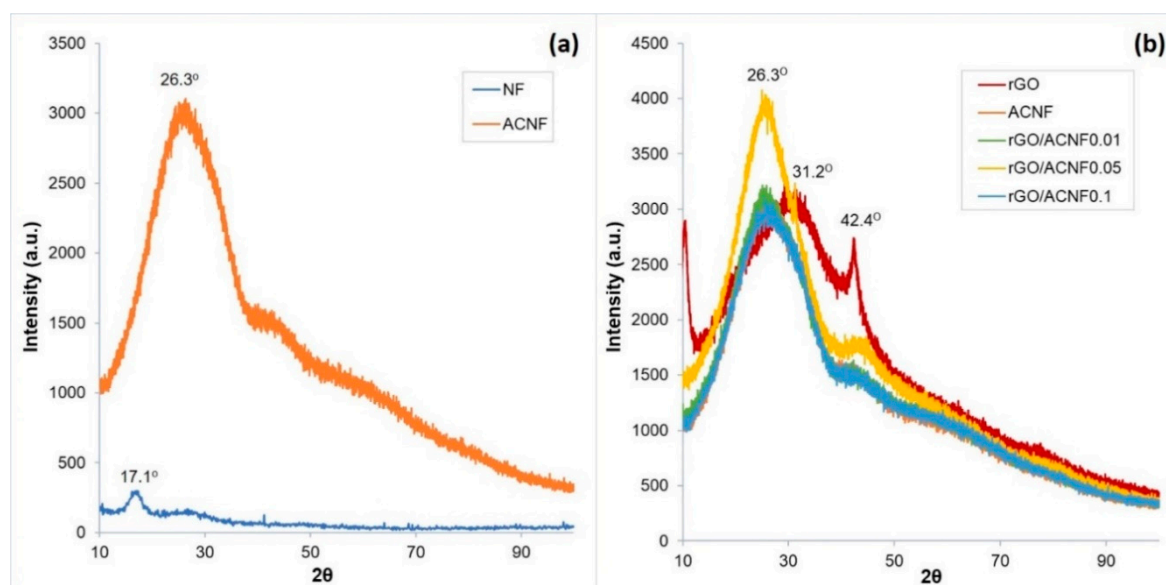


Figure 4. XRD spectra of (a) pristine NF and ACNF; and (b) rGO, ACNF, and rGO/ACNFs.

Figure 5 shows the morphology and structure of NF, rGO/NF0.1, and rGO/ACNF0.1 composites at two different magnifications, i.e., 1000 \times and 20,000 \times . The electrospun NF and rGO/NF0.1 exhibited smooth, thread-like and interconnected fibrous structures as shown in Figure 5a,b,d,e. In Figure 5e, the incorporation of 10% of rGO (Figure 5e) shows a reduction in their average diameter from \sim 450 nm to \sim 280 nm, as compared to their pristine NF. A few droplets were detected in some regions in NF composite, as shown in Figure 5b, and this is due to the effect of rGO, because graphene-based materials must alter the conductivity as well as viscosity of the solution to be electrospun [53]. Subsequently, these conductivity changes should affect the electrostatic repulsion among jet spray from the needle tip to the collector surface during the electrospinning process, which affecting the final diameter of the fibers. A report by Huang et al. [54] stated that the solution with high conductivity should lead to production fibers by electrospinning with smaller diameter. Since it seems that the smaller the fiber diameter, the higher the S_{BET} , it is expected that one could be able to control the S_{BET} by simply changing the conductivity of the polymer solution to be electrospun with the simple addition of rGO. In this study, the production of materials with high S_{BET} is one of the important issues, since it is one of the factors which contribute to the high adsorption capability. On the other hand, the change of morphology and the further reduction in fibers diameter were also observed after activation at 700 $^{\circ}$ C, as shown in Figure 5c,f. This result is in accordance with those obtained by Kim et al. [44]. The ACNFs become coarser, wrinkled, and shrunk when activated, but still maintain its fibrous morphology with some fracture identified. The shrinkage in the diameter is caused by the evolution of volatile species during the cyclization of the ACNFs, as well as the removal of moisture [55].

Elemental dispersive X-ray (EDX) analysis of the pristine and composite ACNFs was shown in Figure 6. Both EDX spectra revealed similar composition of three elements, which were carbon (C), nitrogen (N), and oxygen (O), but with different percentages. An insignificant difference was detected in the elemental composition between the two samples, as they were both carbon-based materials from a similar carbon precursor. The percentage of C in pristine ACNF is 92.8%, which is higher than than of rGO/ACNF, that is, 87.7%. This was probably due to the comparatively high concentration of PAN polymer (as carbon-based precursor) used in preparing the dope solution, resulting in a high C element in the structure.

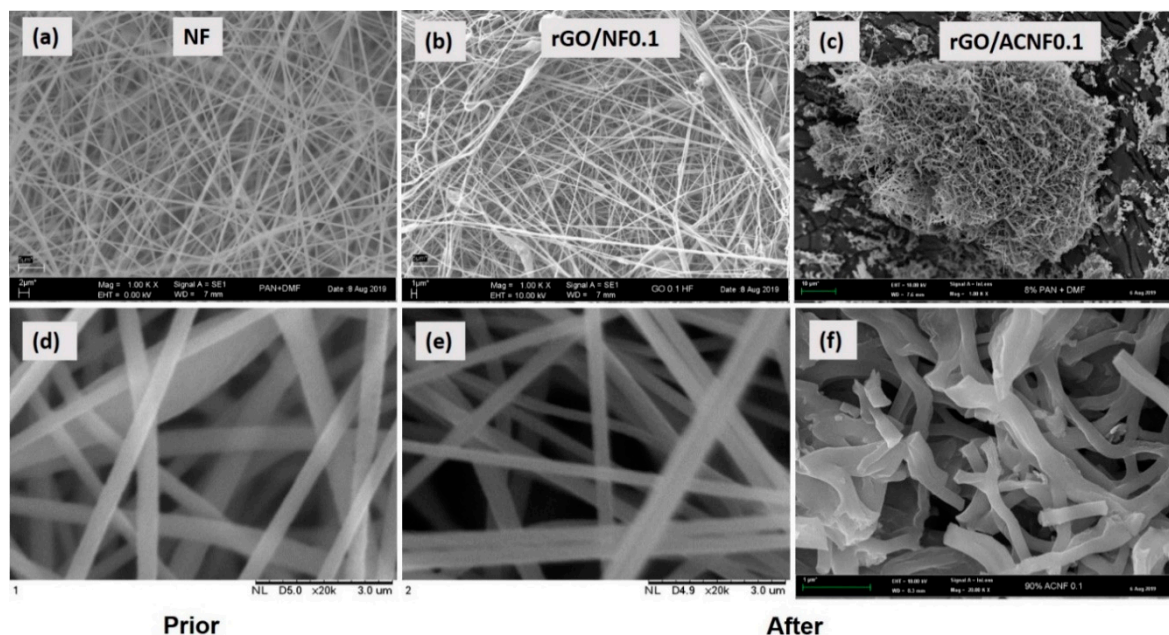


Figure 5. FESEM micrographs of NF, rGO/NF0.1 and rGO/ACNF0.1 composite at different magnifications (a–c) of 1000× magnification and (d–f) of 20,000× magnification.

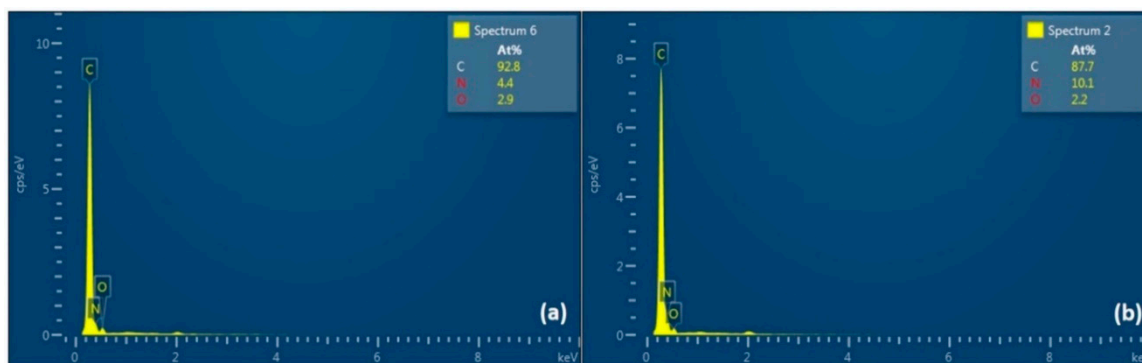


Figure 6. EDX spectra of (a) pristine ACNF and (b) rGO/ACNF composites.

3.2. CO₂ Adsorption Performance

The adsorption capacity as a function of time and detailed parameters of the CO₂ uptakes of the pristine ACNF and composites are summarized in Figure 7 and Table 2, respectively. Figure 7 shows that the shape of CO₂ adsorption curves of all materials under investigation is quite similar, with only difference in the amount adsorbed. It was found that, after the introduction of CO₂, 95% of adsorption happened within one hour, which was followed by the slow uptake until the equilibrium. This can be explained by the increased diffusion resistance during adsorption and the reduction in the unoccupied active sites in the ACNFs. Figure 8 represents the adsorption mechanism between the CO₂ molecules and the ACNFs. The CO₂ molecules were adsorbed onto the available microporous and mesoporous structures in the ACNFs by van der Waals forces of attraction, forming either monolayer or multilayers, depending on the behavior of the adsorption.

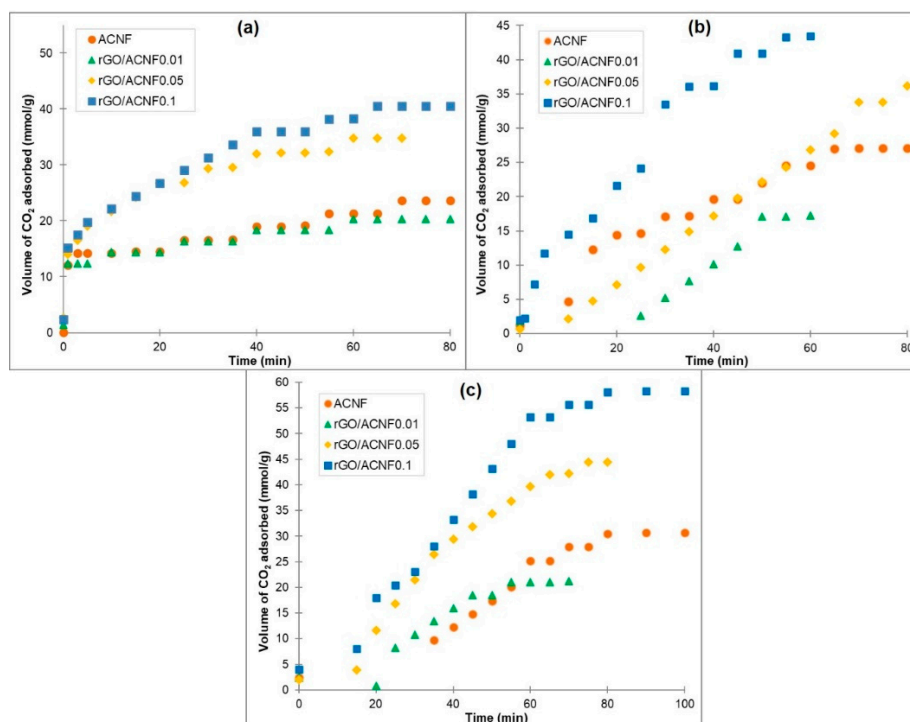


Figure 7. CO₂ uptake kinetics of the pristine ACNF and composite at different adsorption pressures (a) 5 bar, (b) 10 bar, and (c) 15 bar at 25 °C.

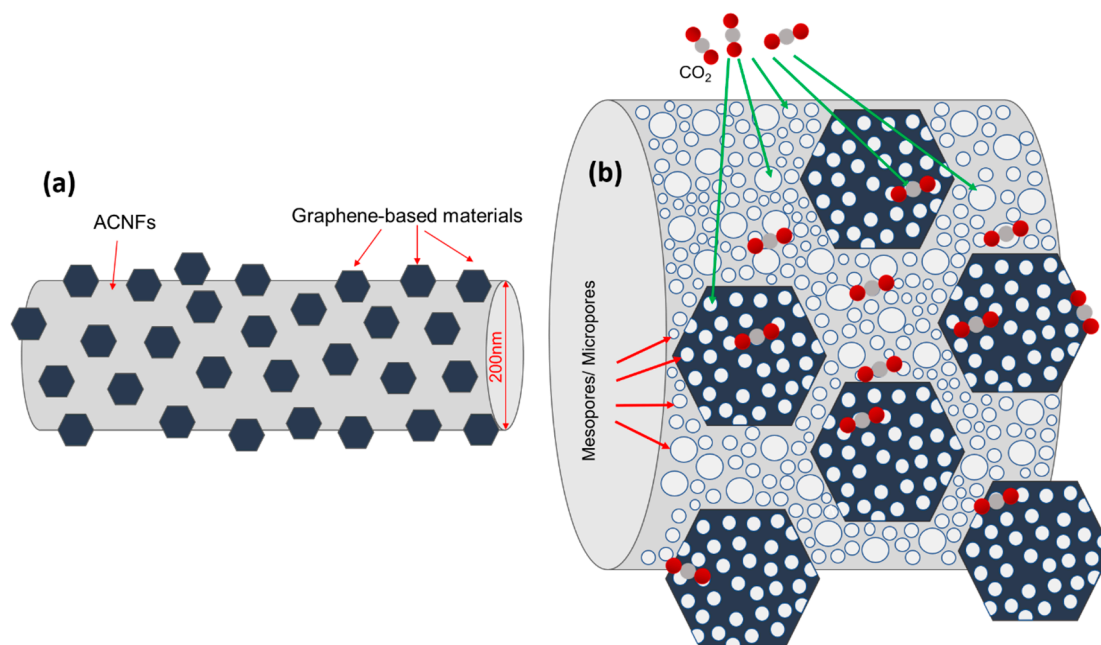


Figure 8. Illustration of (a) overview of ACNFs composite structure and (b) CO₂ adsorption mechanism on the gACNFs.

All samples exhibited similar trend at all pressures, as follows: $rGO/ACNF0.01 < ACNF < rGO/ACNF0.05 < rGO/ACNF0.1$. At 5 bar, the CO₂ uptakes of rGO/ACNF0.1 are the highest amongst the other composites, which is almost doubled the value of the uptakes of the ACNF, i.e., 41 mmol/g vs. 24 mmol/g. With an increase in the adsorption pressure, the CO₂ uptake increased as well, suggesting that the capture of CO₂ by this kind of adsorbents can be described as a physisorption phenomenon [56,57]. As shown in Table 3, the CO₂ uptakes of rGO/ACNF0.1 increases from 41 mmol/g at 5 bar to 43 and 58 mmol/g at 10 and 15 bar, respectively. Interestingly, in spite of the

moderate S_{BET} obtained, the adsorption value is comparatively higher than any previously reported on CO_2 adsorbent materials, which makes it a potentially excellent future CO_2 adsorbent. In fact, the adsorption isotherms obtained from the various pressures and specific temperature explained the equilibrium adsorption capacity of the ACNFs. The isotherms were found to be Type I, being in line with the findings based on N_2 isotherms, i.e., the microporous features that were induced to achieve the high adsorption of CO_2 [58].

Table 3. Comparison of CO_2 adsorption capacity on various types of carbon fibers and their composite-based adsorbents.

Materials	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	Vol. of CO_2 Adsorbed (mmol/g)	Temp; Pressure	Ref.
rGO/ACNF0.1	373	0.22	41	25 °C; 5 bar	This work
			43	25 °C; 10 bar	
			58	25 °C; 15 bar	
PVDF-CNFs	1065	0.61	3.1	30 °C; 1 atm	Hong et al., 2014 [58]
CNF-SnO ₂	434	0.20	2.6	25 °C; 1 atm	Ali et al., 2020 [54]
CNF-MIL-53	140	-	1.35	25 °C; 1 bar	Ullah et al., 2014 [59]
PAN-CMFs	966	-	2.9	25 °C; 1 bar	Ojeda-Lopez et al., 2019 [60]
Graphite NFs	567	0.27	59.2 mg/g	25 °C; 1 atm	Meng and Park, 2010 [61]
Graphite NFs	966	0.25	70.8 mg/g	25 °C; 1 atm	Yuan et al., 2016 [62]

Table 3 summarized the comparison between CO_2 uptakes by different carbon fibers-based adsorbents and their composites from previous literature with the rGO/ACNF composites produced in this study. As shown, the resultant S_{BET} of the rGO/ACNF0.1 is the lowest among the other reported adsorbents. Regardless, its low S_{BET} value, the volume of the CO_2 uptakes is the highest. This excellent adsorption performance is highly believed due to its well-distributed porous structures, which is the V_{micro} occupied up to 68% of the V_{total} and another 32% was occupied by mesoporous. Both micropores and mesopores play vital role in the adsorbates-adsorbent interaction.

3.3. Adsorption Kinetics

For the adsorption of CO_2 by ACNF and rGO/ACNF0.1 at different pressures (5, 10, and 15 bar), Figure 9 shows the representation of experimental data and linear fittings associated with the kinetic models presented in the experimental part. In pseudo-first order model, a plot of $\log(q_e - q_t)$ versus t will generate a straight line using Equation (2). Meanwhile, in pseudo-second order model, the straight-line plot of t/q_t against t was generated using Equation (3). On the other hand, Table 4 gathers the kinetic parameters obtained from the linear regressions and the corresponding correlation coefficients (R^2). Based on the R^2 values collected in Table 4, the pseudo-second order model could be appropriate to describe the adsorption behavior of ACNF at 5 bar and rGO/ACNF0.1 at 5 and 10 bar, while the pseudo-first order model fitted the adsorption data best for the pristine ACNF at 10 and 15 bar and rGO/ACNF0.1 at 15 bar. The low of R^2 values found in the samples at certain pressures shown in Table 4 represents the bad quality of linearization [63] and verifies that these kinetic models do not fit well with the experimental data of the CO_2 adsorption depending on the specific pressures used. Therefore, it seems that, when the pressure of CO_2 is high enough, the CO_2 adsorption process can be better described by the pseudo-first order kinetic model, implying therefore mainly a physisorption phenomenon. On the contrary, when the pressure of CO_2 is low enough, the adsorption phenomena is better described by chemical reaction between the free sites on the ACNF and the CO_2 molecules, chemisorption [64]. It can be said that both ACNFs and rGO/ACNF0.1 are well-fitted pseudo-second order model at low pressure adsorption with higher R^2 values of 0.9645 and 0.9825, respectively,

compared to pseudo-first order model. In fact, lots of previous studies have mentioned that the CO₂ adsorption onto the sorbents' surface at higher pressure involve physisorption rather than chemisorption, which is more related to the adsorption towards the surface with higher S_{BET} , V_{total} , and V_{micro} by weak dipole interactions [65,66]. Furthermore, it also believed that this physisorption, at higher adsorption pressure, resulted in the development of multilayers of CO₂ molecules on the heterogeneous surface of both ACNFs samples. For example, a study by Belmabkhout et al. [12] reported that the adsorption of pure CO₂ (14.7 mmol/g) onto the sorbents' surface at high pressure (e.g., 45 bar) and ambient temperature involved reversible physisorption. In conclusion, it can be said that these two kinetic models are found to be suitable for fitting the present kinetic data of CO₂ adsorption at 15 bar and 25 °C, in the following order: Pseudo-first order > pseudo-second order.

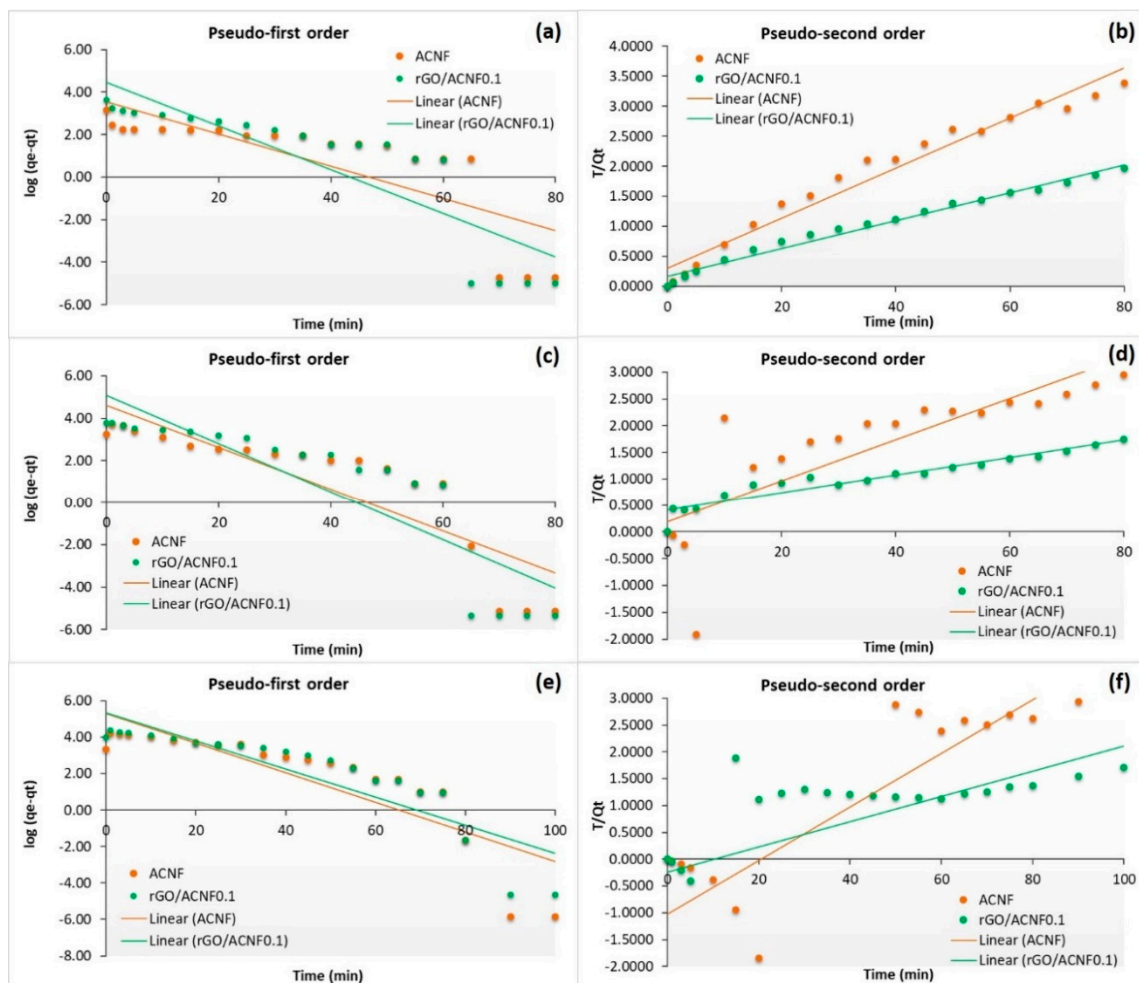


Figure 9. Pseudo-first order and pseudo-second order kinetic models of ACNF and rGO/ACNF0.1 composite at different pressures: (a,b) 5 bar, (c,d) 10 bar, and (e,f) 15 bar.

Table 4. The fitted parameters of pseudo-first order and pseudo-second order of ACNF and rGO/ACNF0.1 composite.

Sample	Pressure (bar)	$q_{e,exp}$ (mmol/g)	Pseudo-First Order		Pseudo-Second Order	
			k_1	R^2	k_2	R^2
ACNF	5	24	0.1036	0.6337	0.1397	0.9645
rGO/ACNF0.1		41	0.0865	0.7566	0.1435	0.9825
ACNF	10	27	0.1217	0.7595	0.1902	0.6563
rGO/ACNF0.1		46	0.0941	0.7667	0.0531	0.9127
ACNF	15	31	0.1114	0.7266	0.0319	0.3897
rGO/ACNF0.1		58	0.0716	0.7861	0.0697	0.2493

4. Conclusions

The excellent CO₂ adsorbent was successfully fabricated by incorporating reduced graphene oxide (rGO) into the PAN-based activated carbon nanofibers (ACNF) via the simple electrospinning and activation methods. It is noteworthy to mention that the suitable amount of rGO composited into the ACNFs is very crucial in producing rGO/ACNF composites with outstanding physicochemical properties, as well as high adsorption capacity. It worth to mention that the suitable loading of rGO is very crucial to obtain the ACNFs composites with the best properties and adsorption performance. In this study, the rGO/ACNF0.1 with 10% of rGO shows higher CO₂ uptakes of 58 mmol/g at 15 bar and 25 °C, which almost double the uptakes value compared to ACNF with a moderate S_{BET} value of 373 m²/g. At higher pressure, the CO₂ adsorption obeyed the pseudo-first order kinetic model, indicating the physisorption between the CO₂ molecules and the porous network of the adsorbents. This is the leading report on PAN-rGO/ACNF composites fabricated from self-synthesized graphene-based materials, such as rGO and porous carbon materials such as ACNFs, which is an efficient way to discover low-cost carbon adsorbents for a high CO₂ uptake.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4360/12/9/2117/s1>, Table S1: Dope formulation of gACNFs composite with different concentrations of reduced graphene oxide (rGO).

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References

1. Acevedo, E.R.; Cortés, F.B.; Franco, C.A.; Carrasco-Marín, F.; Pérez-Cadenas, A.F.; Fierro, V.; Celzard, A.; Schaefer, S.; Molina, A.C. An Enhanced Carbon Capture and Storage Process (e-CCS) Applied to Shallow Reservoirs Using Nanofluids Based on Nitrogen-Rich Carbon Nanospheres. *Materials* **2019**, *12*, 2088. [[CrossRef](#)] [[PubMed](#)]
2. Huang, G.-G.; Liu, Y.-F.; Wu, X.-X.; Cai, J. Activated carbons prepared by the KOH activation of a hydrochar from garlic peel and their CO₂ adsorption performance. *New Carbon Mater.* **2019**, *34*, 247–257. [[CrossRef](#)]

3. Bains, P.; Psarras, P.; Wilcox, J. CO₂ capture from the industry sector. *Prog. Energy Combust. Sci.* **2017**, *63*, 146–172. [[CrossRef](#)]
4. Acevedo, E.R.; Franco, C.A.; Carrasco-Marín, F.; Pérez-Cadenas, A.F.; Cortés, F.B. Biomass-Derived Carbon Molecular Sieves Applied to an Enhanced Carbon Capture and Storage Process (e-CCS) for Flue Gas Streams in Shallow Reservoirs. *Nanomaterials* **2020**, *10*, 980. [[CrossRef](#)]
5. Carbon Cycle Greenhouse Gases, Mouna Loa Observatory. 2020. Available online: <https://www.esrl.noaa.gov/gmd/ccgg/> (accessed on 17 August 2020).
6. Willard, B. CO₂—Why 450 ppm Is Dangerous and 350 ppm Is Safe. 2014. Available online: <https://sustainabilityadvantage.com/2014/01/07/co2-why-450-ppm-is-dangerous-and-350-ppm-is-safe/> (accessed on 20 July 2020).
7. Le Quéré, C.; Jackson, R.B.; Jones, M.W.; Smith, A.J.P.; Abernethy, S.; Andrew, R.; De-Gol, A.J.; Willis, D.R.; Shan, Y.; Canadell, J.G.; et al. Temporary reduction in daily global CO₂ emissions during the COVID-19 forced confinement. *Nat. Clim. Chang.* **2020**, *10*, 1–7. [[CrossRef](#)]
8. Chen, Y.P.; Bashir, S.; Liu, J. Chapter 7- Carbon Capture and Storage. In *Advanced Nanomaterials and Their Applications in Renewable Energy*; Liu, J., Bashir, S., Eds.; Elsevier Science: Amsterdam, The Netherlands, 2015; pp. 329–366.
9. Abbasi, A.; Nasef, M.M.; Babadi, F.E.; Faridi-Majidi, R.; Takeshi, M.; Abouzari-Lotf, E.; Choong, T.; Somwangthanoj, A.; Kheawhom, S. Carbon Dioxide Adsorption on Grafted Nanofibrous Adsorbents Functionalized Using Different Amines. *Front. Energy Res.* **2019**, *7*, 1–14. [[CrossRef](#)]
10. Romano, M.C.; Anantharaman, R.; Arasto, A.; Ozcan, D.C.; Ahn, H.; Dijkstra, J.; Carbo, M.; Boavida, D. Application of Advanced Technologies for CO₂ Capture From Industrial Sources. *Energy Procedia* **2013**, *37*, 7176–7185. [[CrossRef](#)]
11. Singh, V.K.; Kumar, E.A.; Emadabathuni, A.K. Measurement and analysis of adsorption isotherms of CO₂ on activated carbon. *Appl. Therm. Eng.* **2016**, *97*, 77–86. [[CrossRef](#)]
12. Belmabkhout, Y.; Serna-Guerrero, R.; Sayari, A. Adsorption of CO₂ from dry gases on MCM-41 silica at ambient temperature and high pressure. 1: Pure CO₂ adsorption. *Chem. Eng. Sci.* **2009**, *64*, 3721–3728. [[CrossRef](#)]
13. Hauchhum, L.; Mahanta, P. Carbon dioxide adsorption on zeolites and activated carbon by pressure swing adsorption in a fixed bed. *Int. J. Energy Environ. Eng.* **2014**, *5*, 349–356. [[CrossRef](#)]
14. Al-Janabi, N.; Hill, P.; Torrente-Murciano, L.; Garforth, A.; Gorgojo, P.; Siperstein, F.; Fan, X. Mapping the Cu-BTC metal—Organic framework (HKUST-1) stability envelope in the presence of water vapour for CO₂ adsorption from flue gases. *Chem. Eng. J.* **2015**, *281*, 669–677. [[CrossRef](#)]
15. Al-Janabi, N.; Deng, H.; Borges, J.; Liu, X.; Garforth, A.; Siperstein, F.R.; Fan, X. A facile post-synthetic modification method to improve hydrothermal stability and CO₂ selectivity of CyBTC metal-organic framework. *Ind. Eng. Chem. Res.* **2016**, *55*, 7941–7949. [[CrossRef](#)]
16. Olijire, A.A. Synthesis chemistry of metal-organic frameworks for CO₂ capture and conversion for sustainable energy future. *Renew. Sustain. Energy Rev.* **2018**, *92*, 570–607. [[CrossRef](#)]
17. Chiang, Y.-C.; Hsu, W.-L.; Lin, S.-Y.; Juang, R.-S. Enhanced CO₂ Adsorption on Activated Carbon Fibers Grafted with Nitrogen-Doped Carbon Nanotubes. *Materials* **2017**, *10*, 511. [[CrossRef](#)]
18. Bhatta, L.K.G.; Bhatta, U.M.; Venkatesh, K. Metal Oxides for Carbon Dioxide Capture. *Sustain. Agric. Rev.* **2019**, *38*, 63–83. [[CrossRef](#)]
19. Rodríguez-García, S.; Santiago, R.; López-Díaz, D.; Merchán, M.D.; Velázquez, M.M.; Fierro, J.L.G.; Palomar, J. Role of the Structure of Graphene Oxide Sheets on the CO₂ Adsorption Properties of Nanocomposites Based on Graphene Oxide and Polyaniline or Fe₃O₄-Nanoparticles. *ACS Sustain. Chem. Eng.* **2019**, *7*, 12464–12473. [[CrossRef](#)]
20. Pellerano, M.; Pré, P.; Kacem, M.; Delebarre, A. CO₂ capture by adsorption on activated carbons using pressure modulation. *Energy Procedia* **2009**, *1*, 647–653. [[CrossRef](#)]
21. El-Sharkawy, I.I.; Mansour, M.H.; Awad, M.M.; El-Ashry, R. Investigation of Natural Gas Storage through Activated Carbon. *J. Chem. Eng. Data* **2015**, *60*, 3215–3223. [[CrossRef](#)]
22. Othman, F.E.C.; Yusof, N.; Hasbullah, H.; Jaafar, J.; Ismail, A.F.; Nasri, N.S. Physicochemical properties and methane adsorption performance of activated carbon nanofibers with different types of metal oxides. *Carbon Lett.* **2017**, *24*, 82–89.

23. Lee, H.-M.; Kim, H.-G.; An, K.-H.; Kim, B.-J. Effects of pore structures on electrochemical behaviors of polyacrylonitrile-based activated carbon nanofibers by carbon dioxide activation. *Carbon Lett.* **2014**, *15*, 71–76. [[CrossRef](#)]
24. Tavanai, H.; Jalili, R.; Morshed, M.; Jalili, R. Effects of fiber diameter and CO₂ activation temperature on the pore characteristics of polyacrylonitrile based activated carbon nanofibers. *Surf. Interface Anal.* **2009**, *41*, 814–819. [[CrossRef](#)]
25. Othman, F.E.C.; Yusof, N.; Ismail, A.F.; Jaafar, J.; Salleh, W.N.W.; Aziz, F. Preparation and characterization of polyacrylonitrile-based activated carbon nanofibers/graphene (gACNFs) composite synthesized by electrospinning. *AIP Adv.* **2020**, *10*, 055117. [[CrossRef](#)]
26. Mishra, A.K.; Ramaprabhu, S. Carbon dioxide adsorption in graphene sheets. *AIP Adv.* **2011**, *1*, 32152. [[CrossRef](#)]
27. Takeuchi, K.; Yamamoto, S.; Hamamoto, Y.; Shiozawa, Y.; Tashima, K.; Fukidome, H.; Koitaya, T.; Mukai, K.; Yoshimoto, S.; Suemitsu, M.; et al. Adsorption of CO₂ on Graphene: A Combined TPD, XPS, and vdW-DF Study. *J. Phys. Chem. C* **2017**, *121*, 2807–2814. [[CrossRef](#)]
28. Wang, Z.; Ciacchi, L.C.; Wei, G. Recent Advances in the Synthesis of Graphene-Based Nanomaterials for Controlled Drug Delivery. *Appl. Sci.* **2017**, *7*, 1175. [[CrossRef](#)]
29. Alghamdi, A.A.; Alshahrani, A.F.; Khadry, N.H.; Alharthi, F.A.; Alattas, H.A.; Adil, S.F. Enhanced CO₂ Adsorption by Nitrogen-Doped Graphene Oxide Sheets (N-GOs) Prepared by Employing Polymeric Precursors. *Materials* **2018**, *11*, 578. [[CrossRef](#)]
30. Yoo, M.J.; Park, H. Effect of hydrogen peroxide on properties of graphene oxide in Hummers method. *Carbon* **2019**, *141*, 515–522. [[CrossRef](#)]
31. Pei, S.; Cheng, H.-M. The reduction of graphene oxide. *Carbon* **2012**, *50*, 3210–3228. [[CrossRef](#)]
32. Alam, S.N.; Sharma, N.; Kumar, L. Synthesis of Graphene Oxide (GO) by Modified Hummers Method and Its Thermal Reduction to Obtain Reduced Graphene Oxide (rGO)*. *Graphene* **2017**, *6*, 1–18. [[CrossRef](#)]
33. Othman, F.E.C.; Yusof, N.; Hasbullah, H.; Othman, M.H.D.; Ismail, A.F.; Abdullah, N.; Nordin, N.A.H.M.; Aziz, F.; Salleh, W.N.W. Polyacrylonitrile/magnesium oxide-based activated carbon nanofibers with well-developed microporous structure and their adsorption performance for methane. *J. Ind. Eng. Chem.* **2017**, *51*, 281–287. [[CrossRef](#)]
34. Nasri, N.S.; Hamza, U.D.; Ismail, S.N.; Ahmed, M.M.; Mohsin, R. Assessment of porous carbons derived from sustainable palm solid waste for carbon dioxide capture. *J. Clean. Prod.* **2014**, *71*, 148–157. [[CrossRef](#)]
35. Stevens, L.; Williams, K.; Han, W.Y.; Drage, T.C.; Snape, C.; Wood, J.; Wang, J. Preparation and CO₂ adsorption of diamine modified montmorillonite via exfoliation grafting route. *Chem. Eng. J.* **2013**, *215*, 699–708. [[CrossRef](#)]
36. Lopes, E.C.; Dos Anjos, F.S.; Vieira, E.F.; Cestari, A.R. An alternative Avrami equation to evaluate kinetic parameters of the interaction of Hg(II) with thin chitosan membranes. *J. Colloid Interface Sci.* **2003**, *263*, 542–547. [[CrossRef](#)]
37. Romero, J.R.G.; Moreno-Piraján, J.C.; Giraldo, L. Kinetic and Equilibrium Study of the Adsorption of CO₂ in Ultramicropores of Resorcinol-Formaldehyde Aerogels Obtained in Acidic and Basic Medium. *J. Carbon Res. C* **2018**, *4*, 52. [[CrossRef](#)]
38. Qi, L.; Tang, X.; Wang, Z.; Peng, X. Pore characterization of different types of coal from coal and gas outburst disaster sites using low temperature nitrogen adsorption approach. *Int. J. Min. Sci. Technol.* **2017**, *27*, 371–377. [[CrossRef](#)]
39. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodríguez-Reinoso, F.; Rouquerol, J.; Sing, K.S. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [[CrossRef](#)]
40. Lee, S.-Y.; Park, S.-J. Determination of the optimal pore size for improved CO₂ adsorption in activated carbon fibers. *J. Colloid Interface Sci.* **2013**, *389*, 230–235. [[CrossRef](#)]
41. Sing, K.S.; Williams, R.T. Physisorption Hysteresis Loops and the Characterization of Nanoporous Materials. *Adsorpt. Sci. Technol.* **2004**, *22*, 773–782. [[CrossRef](#)]
42. Liu, H.; Ding, W.; Lei, S.; Tian, X.; Zhou, F. Selective adsorption of CH₄/N₂ on Ni-based MOF/SBA-15 composite materials. *J. Nanomater.* **2019**, *9*, 149, 1–14. [[CrossRef](#)]

43. Nasrollahzadeh, M.; Babaei, F.; Fakhri, P.; Jaleh, B. Synthesis, characterization, structural, optical properties and catalytic activity of reduced graphene oxide/copper nanocomposites. *RSC Adv.* **2015**, *5*, 10782–10789. [[CrossRef](#)]
44. Kim, D.W.; Jung, D.W.; Adelodun, A.A.; Jo, Y.M. Evaluation of CO₂ adsorption capacity of electrospun carbon fibers with thermal and chemical activation. *J. Appl. Polym. Sci.* **2017**, *134*, 45534. [[CrossRef](#)]
45. Gayathri, S.; Jayabal, P.; Kottaisamy, M.; Ramakrishnan, V. Synthesis of few layer graphene by direct exfoliation of graphite and a Raman spectroscopic study. *AIP Adv.* **2014**, *4*, 27116. [[CrossRef](#)]
46. Frank, O.; Mohr, M.; Maultzsch, J.; Thomsen, C.; Riaz, I.; Jalil, R.; Novoselov, K.S.; Tsoukleri, G.; Parthenios, J.; Papagelis, K.; et al. Raman 2D-Band Splitting in Graphene: Theory and Experiment. *ACS Nano* **2011**, *5*, 2231–2239. [[CrossRef](#)] [[PubMed](#)]
47. Hong, S.M.; Kim, S.H.; Jeong, B.G.; Jo, S.M.; Lee, K.B. Development of porous carbon nanofibers from electrospun polyvinylidene fluoride for CO₂ capture. *RSC Adv.* **2014**, *4*, 58956–58963. [[CrossRef](#)]
48. Badawy, S.M.; Dessouki, A.M. Cross-Linked Polyacrylonitrile Prepared by Radiation-Induced Polymerization Technique. *J. Phys. Chem. B* **2003**, *107*, 11273–11279. [[CrossRef](#)]
49. Jyothi, N.K.; Kumar, K.V.; Murthy, P.N. FTIR, XRD and DC conductivity studies of proton conducting gel polymer electrolytes based on polyacrylonitrile (PAN). *Int. J. ChemTech Res.* **2014**, *6*, 5214–5219.
50. Lee, H.-M.; Kang, H.-R.; An, K.H.; Kim, H.-G.; Kim, B.-J. Comparative studies of porous carbon nanofibers by various activation methods. *Carbon Lett.* **2013**, *14*, 180–185. [[CrossRef](#)]
51. Ouassim, B.; Fouad, G.; Arunabh, G.; Ouafae, A.; Tarik, C. Excellent CO₂ capture by ultra-high microporous activated carbon made out from Natural coal. *Chem. Eng. Technol.* **2020**, under review.
52. Guo, J.; Morris, J.R.; Ihm, Y.; Contescu, C.I.; Gallego, N.C.; Duscher, G.; Pennycook, S.J.; Chisholm, M.F. Topological Defects: Origin of Nanopores and Enhanced Adsorption Performance in Nanoporous Carbon. *Small* **2012**, *8*, 3283–3288. [[CrossRef](#)]
53. Bin Ali, A.; Renz, F.; Koch, J.; Tegenkamp, C.; Sindelar, R. Graphene Nanoplatelet (GNPs) Doped Carbon Nanofiber (CNF) System: Effect of GNPs on the Graphitic Structure of Creep Stress and Non-Creep Stress Stabilized Polyacrylonitrile (PAN). *Nanomaterials* **2020**, *10*, 351. [[CrossRef](#)]
54. Huang, Z.-M.; Zhang, Y.; Kotaki, M.; Ramakrishna, S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Compos. Sci. Technol.* **2003**, *63*, 2223–2253. [[CrossRef](#)]
55. Ahmad, M.; Wang, J.; Xu, J.; Zhang, Q.; Zhang, B. Magnetic tubular carbon nanofibers as efficient Cu(II) ion adsorbent from wastewater. *J. Clean. Prod.* **2020**, *252*, 119825. [[CrossRef](#)]
56. Wei, H.; Deng, S.; Hu, B.; Chen, Z.; Wang, B.; Huang, J.; Yu, G. Granular Bamboo-Derived Activated Carbon for High CO₂ Adsorption: The Dominant Role of Narrow Micropores. *ChemSusChem* **2012**, *5*, 2354–2360. [[CrossRef](#)]
57. Li, K.; Tian, S.; Wang, J.; Jiang, J.; Chen, X.; Yan, F. Pine cone shell-based activated carbon used for CO₂ adsorption. *J. Mater. Chem. A* **2016**, *4*, 5223–5234. [[CrossRef](#)]
58. Chen, L.; Watanabe, T.; Kanoh, H.; Hata, K.; Ohba, T. Cooperative CO₂ adsorption promotes high CO₂ adsorption density over wide optimal nanopore range. *Adsorpt. Sci. Technol.* **2017**, *36*, 625–639. [[CrossRef](#)]
59. Ullah, S.; Shariff, A.M.; Bustam, M.A.; Elkhalfah, A.E.I.; Murshid, G.; Riaz, N.; Shimekit, B. Modified MIL-53 with multi-wall carbon nanotubes and nano fibers on CO₂ adsorption. *Appl. Mech. Mater.* **2014**, *625*, 870–873. [[CrossRef](#)]
60. Ojeda-López, R.; Esparza-Schulz, M.; Pérez-Hermosillo, I.J.; Hernández-Gordillo, A.; Domínguez-Ortiz, A. Improve in CO₂ and CH₄ Adsorption Capacity on Carbon Microfibers Synthesized by Electrospinning of PAN. *Fibers* **2019**, *7*, 81. [[CrossRef](#)]
61. Meng, L.-Y.; Park, S.-J. Effect of heat treatment on CO₂ adsorption of KOH-activated graphite nanofibers. *J. Colloid Interface Sci.* **2010**, *352*, 498–503. [[CrossRef](#)]
62. Yuan, H.; Meng, L.-Y.; Park, S.-J. KOH-activated graphite nanofibers as CO₂ adsorbents. *Carbon Lett.* **2016**, *19*, 99–103. [[CrossRef](#)]
63. Hu, X.-J.; Wang, J.-S.; Liu, Y.; Li, X.; Zeng, G.-M.; Bao, Z.-L.; Zeng, X.-X.; Chen, A.; Long, F. Adsorption of chromium (VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: Isotherms, kinetics and thermodynamics. *J. Hazard. Mater.* **2011**, *185*, 306–314. [[CrossRef](#)]
64. Martín, C.; Sweatman, M.; Brandani, S.; Fan, X. Wet impregnation of a commercial low cost silica using DETA for a fast post-combustion CO₂ capture process. *Appl. Energy* **2016**, *183*, 1705–1721. [[CrossRef](#)]

65. Berger, A.H.; Bhowan, A.S. Comparing physisorption and chemisorption solid sorbents for use separating CO₂ from flue gas using temperature swing adsorption. *Energy Procedia* **2011**, *4*, 562–567. [[CrossRef](#)]
66. Culp, J.T.; Smith, M.R.; Bittner, E.; Bockrath, B. Hysteresis in the Physisorption of CO₂ and N₂ in a Flexible Pillared Layer Nickel Cyanide. *J. Am. Chem. Soc.* **2008**, *130*, 12427–12434. [[CrossRef](#)]



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