



OPEN Amine-modified waste tires for CO₂ capture and resource utilization

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In this study, waste tires (WTs) were chosen to prepare an adsorbent material for carbon dioxide (CO₂) capture to reduce their huge amount of waste. To improve the CO₂ selectivity, the WT powder was amine-modified using tetraethylenepentamine (TEPA) or polyethyleneimine at different loading levels [2.5, 5, 10, and 15% (w/w)]. The optimum condition to develop a high-performance CO₂ adsorbent material was found to be the use of 10% (w/w) TEPA-modified WT (WT10T) with a CO₂ flow rate of 70 mL min⁻¹ under ambient temperature and atmospheric pressure. Based on the kinetic study of WT10T, Avrami's model fitted well with the experimental data, suggesting both physisorption and chemisorption of the CO₂. When desorbed at 60 °C under vacuum pressure, the WT10T showed a reusability of more than 10 successive adsorption cycles. Additionally, the adsorbed CO₂ in WT10T could be directly converted to value-added chemicals or fuels, such as ethylene, methane, carbon monoxide, and hydrogen, via an electrochemical reaction. Accordingly, this study shows a challenging way on how to both utilize waste materials as adsorbents and reduce the WT level from rubber industries.

Keywords Waste tire, CO₂ adsorption-desorption, Amine modification, Electrochemical CO₂ reduction reaction

The increase in greenhouse gas (GHG) emissions, especially carbon dioxide (CO₂), in the atmosphere leads to global climate change, which has become a serious issue worldwide today¹. Excessive GHGs in the atmosphere are responsible for various environmental problems, such as a rise in the sea water level, an increase in the earth's temperature, and an increasing number of ocean storms, floods, etc.². The 26th UN Climate Change Conference of the Parties (COP26) resulted in an agreement that requires countries to decrease their GHG emissions by reducing the use of fossil fuels and replacing it with clean energy by 2030^{3,4}. Currently, there are many useful methods to reduce or capture GHG emissions, such as renewable technologies^{5,6}, energy saving technologies⁷, and carbon capture, utilization, and storage (CCUS)^{8–10}. Of these, CCUS is one of the interesting technologies and is based on CO₂ adsorption by various solid adsorbents, such as activated carbon^{11–13}, zeolites^{14–16}, sepiolite¹⁷, heteroatom-doped porous carbons^{18,19}, porous organic polymers²⁰, metal-organic frameworks (MOFs)²¹, reduced graphene oxide²², and recycled waste materials^{23–26}. These strategies are also compatible with the Bio-Circular-Green Economic Model (BCG)²⁷ to create economic and environmental sustainability and to reduce the waste from many industries²⁸. However, after CO₂ adsorption in the adsorbent material, it is economically and environmentally important to make value-added products from the CO₂. The possible ways used to convert CO₂ into valuable hydrocarbon (HC) compounds include thermochemical, photocatalytic, and electrochemical conversions^{29–31}. These concepts are mainly focused on this study, as they are the part of the challenge of how to utilize waste materials as adsorbents and how to convert CO₂ to value-added chemicals.

In this study, the recycling of waste tires (WTs) was used to develop an adsorbent for CO₂ capture, since WTs are a non-biodegradable material, due to their complex structure after vulcanization, and the annual global production of WTs is currently around 1.4 billion pieces every year³². At present, WTs are mainly disposed of by the traditional methods of landfill, which requires a large space, or burning, which accumulates toxic air pollution³³. Therefore, the use of recyclable WTs as an adsorbent is beneficial for reducing the huge amount of their waste.

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Several researchers have focused on the transformation of WTs for use in various applications. For instance, WTs have been pyrolyzed and chemically modified to produce a magnetic pyrochar adsorbent for wastewater treatment^{34–37}. Pyrolytic WT products have been prepared via impregnation as a catalyst for producing hydrogen (H_2) and carbon nanotubes^{38–43}. Pyrochar from WT pyrolysis was treated by chemical activation to prepare an electrode for energy storage^{44–47}. Finally, activated carbon from WT pyrolysis was formed by physical and chemical activation as a solid adsorbent for CO_2 capture^{48–50}.

However, these techniques prepared the obtained materials through a thermal process that consumes a high amount of energy, and the process is complicated. To solve such problems, modifying or functionalizing a WT adsorbent with amines on its surface benefits the easy preparation of a solid adsorbent. Natural rubber (NR) latex foam with amine-modified silica^{51,52} or modified NR with amine-modified silica particles was found to enhance the CO_2 adsorption⁵³. Therefore, this study focused on amine-modified WTs. It is interesting to note that the WTs used in this study consisted of some additives, such as carbon black or silica, which could enhance the efficiency of CO_2 adsorption^{54,55}. In addition, the presence of vulcanization in WTs could improve the thermal properties of the material⁵⁶. Although, amine-modified WTs have been studied previously as an adsorbent in wastewater treatment⁵⁷, their application for CO_2 capture has not been demonstrated yet.

To reduce the emission level of GHGs, CO_2 can also be converted into valuable HC compounds or fuel, such as methane (CH_4), ethane (C_2H_6), carbon monoxide (CO), methanol, and ethanol. There are three possible routes for CO_2 conversion to higher value products as follows: photocatalytic conversion, electrochemical reduction, and thermochemical conversion^{58–64}. In this study, the electrochemical reduction of CO_2 was examined in the conversion of CO_2 to more reduced chemical species using electrical energy. The electrochemical reduction can support renewable energy exploitation to create an artificial carbon-neutral cycle. Also, it can be easily carried out in aqueous media at room temperature and atmospheric pressure.

Copper (II) oxide (CuO) and copper (I) oxide (Cu_2O) are both used as catalysts in the conversion of CO_2 due to their unique properties that facilitate certain chemical reactions. Their application in the CO_2 conversion processes is motivated by their redox properties, high surface area, ability to chemisorb CO_2 molecules, presence of active sites, involvement in catalytic cycles, and capability to control the selectivity^{65–68}. These catalysts play a crucial role in developing sustainable methods for utilizing CO_2 as a feedstock to produce valuable chemicals and fuels.

Accordingly, the aim of this study was to modify WT samples as an adsorbent material for CO_2 capture. The WT samples were directly impregnated with tetraethylenepentamine (TEPA) or polyethyleneimine (PEI) to enhance the CO_2 adsorption capacity. A series of adsorbents prepared with different amine types (PEI or TEPA) and amine loading levels [0–15% (w/w)] was investigated for their CO_2 capture under ambient temperature and atmospheric pressure. The adsorption kinetics were explored by fitting three adsorption kinetic models (pseudo 1st order, pseudo 2nd order, and Avramis' models). The reusability of the selected TEPA-modified WT was evaluated over 10 successive adsorption-desorption cycles, while for practical application, the CO_2 captured in the TEPA-modified WT was converted to value-added HCs via the electrochemical CO_2 reduction reaction (CO_2 RR) using a CuO: Cu_2O catalyst with a 1:2 molar ratio.

Materials and methods

Materials

The WTs, mainly unusable tires from automobiles, were provided as a powder with an average particle size of 250 μm from the Union Commercial Development Co., Ltd, Thailand. The TEPA (189.3 g/mol), PEI (800 g/mol), Cu_2O (98% purity analytical grade), and CuO (AR grade) were purchased from Sigma-Aldrich Co., Ltd. Absolute ethanol (99.99%), potassium bicarbonate ($KHCO_3$; AR grade), and isopropyl alcohol (AR grade) were from Qrec Chemical Ltd., New Zealand. Super C65 nano carbon black conductive, used as a conductive additive in electrodes, was from MSE supplies™, USA. Ethylene glycol (AR grade) was purchased from KEMAUS Chemical, Australia. All chemicals were used as received without further purification.

Preparation of the amine-modified WT samples

The WT powders were modified by amines (TEPA or PEI) using wet impregnation. The selected amine was dissolved in 50 mL ethanol with stirring at ambient temperature (about 30 °C) for 30 min. Then, 30 g of WT powder was mixed with the amine solution by stirring at ambient temperature for 3 h. Finally, the slurry was then dried in an oven at 60 °C for 48 h. To optimize the amine loading level, amine loadings were varied at 0, 2.5, 5, 10, and 15% (w/w, based on 100 g WT). The amine-modified WT samples were coded WT_xP or WT_xT for PEI and TEPA modification, respectively, where x represents the amine % (w/w) loading level. The amine efficiency of the amine-doped composite that showed the maximum CO_2 adsorption capacity was calculated based on previous work by Sakwa-Novak et al.⁶⁹ In this study, the amine efficiency of WT10T and WT10P was approximately 0.1 and 0.08, respectively.

Characterization of the amine-modified WT samples

The WT samples before and after amine modification were characterized by nitrogen (N_2) adsorption-desorption (Micromeritics, Asap 2020, USA) to determine the Brunauer-Emmett-Teller (BET) surface area (S_{BET}) and total pore volume (V_p). The samples were degassed under a N_2 flux for 2 h at 120 °C. Scanning electron microscopy (SEM; JEOL, JSM-6480LV, USA) at an accelerating voltage of 15 kV was used to investigate the WT morphology before and after amine modification. The samples were placed on a stub and then coated with gold before testing. The elemental analysis was examined using a CHN/S analyzer (Perkin Elmer, PE-2400, USA), while the composition of the samples was evaluated using Fourier-transformed infrared spectroscopy (FTIR, Thermo Ficher, Nicolet iS5, USA). To confirm the CO_2 adsorption-desorption in the adsorbent, Raman spectroscopy (DXR Raman microscope, Thermo Scientific, USA) was examined and recorded from 100 to 4000 cm^{-1} .

The powder rubber samples (0.4 g) contained in tea bag were immersed in 100 mL of toluene for 72 h. After that the surface liquid was rapidly removed by blotting with filter paper. The samples were dried in an oven at 80 °C until at constant weight. The swelling ratio (Q), sol-gel fraction, and crosslink density were calculated according to Eqs. (1)–(4), respectively^{70,71}.

$$Q = \frac{W_2 - W_1}{W_1} \quad (1)$$

$$\text{Sol fraction (\%)} = \frac{W_1 - W_3}{W_1} \quad (2)$$

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction (\%)} \quad (3)$$

$$\text{Crosslink density} \left(\frac{\text{mol}}{\text{cm}^3} \right) = \frac{-[\ln(1 - v_r) + v_r + \chi v_r^2]}{v_0[v_r^{1/3} - \frac{v_r}{2}]} \quad (4)$$

where W_1 is the initial sample weight, W_2 is the sample weight after swelling, W_3 is the dried sample weight after swelling, v_r is the volume fraction of the rubber network in the swollen gel, v is the molar volume of the toluene (106.2 cm³/mol)⁷⁰, and χ is a rubber-solvent interaction parameter (0.393)⁷¹. The three parameters—swelling ratio, sol-gel fraction, and crosslink density—are studied to evaluate the properties of WT, specifically before and after modification. These parameters help in understanding the effects of amine incorporation on the tires' properties, providing insight into how the amine modification influences the material's structural and functional characteristics.

CO₂ adsorption-desorption

The CO₂ adsorption-desorption of the unmodified and amine-modified WT samples was performed in a stainless-steel reactor as shown in Fig. 1. The dried sample (3 g) was loaded into the reactor and then heated under vacuum pressure at 60 °C under a N₂ flow rate of 300 mL/min for 20 min to release existing bound gases. After that, the reactor was cooled down to room temperature, and then the gas was switched to CO₂ [12% and 99% (v/v)] at a flow rate of 70 mL/min at ambient temperature and atmospheric pressure. The CO₂ amount in the effluent was detected using a CO₂ sensor (CM-40401, United States of America). The CO₂ adsorption capacity was then calculated based on the difference between the CO₂ adsorption breakthrough curve areas. The CO₂ desorption of each sample was performed by the combination of vacuum and temperature swing adsorption (VTSA) process. The adsorbent after CO₂ adsorption was heated at 60 °C under reduced pressure with a N₂ flow rate of 100 mL/min and then cooled to ambience temperature. Finally, the sample was subjected to 10 sequential repeated CO₂ adsorption-desorption cycles to evaluate its reusability.

Kinetic study

The pseudo 1st order, pseudo 2nd order, and Avrami's kinetic models were used to fit the experimental adsorption kinetic data to investigate the adsorption mechanism of the adsorbent using Eqs. (5)–(7), respectively⁷²,

$$\text{Pseudo 1}^{st} \text{ order} : q_t = q_e [1 - \exp(-k_1 t)] \quad (5)$$

$$\text{Pseudo 2}^{nd} \text{ order} : q_t = \frac{k_2 q_e^2}{1 + k_2 q_e t} \quad (6)$$

$$\text{Avrami's model} : q_t = q_e [1 - \exp(-k_A t)^n] \quad (7)$$

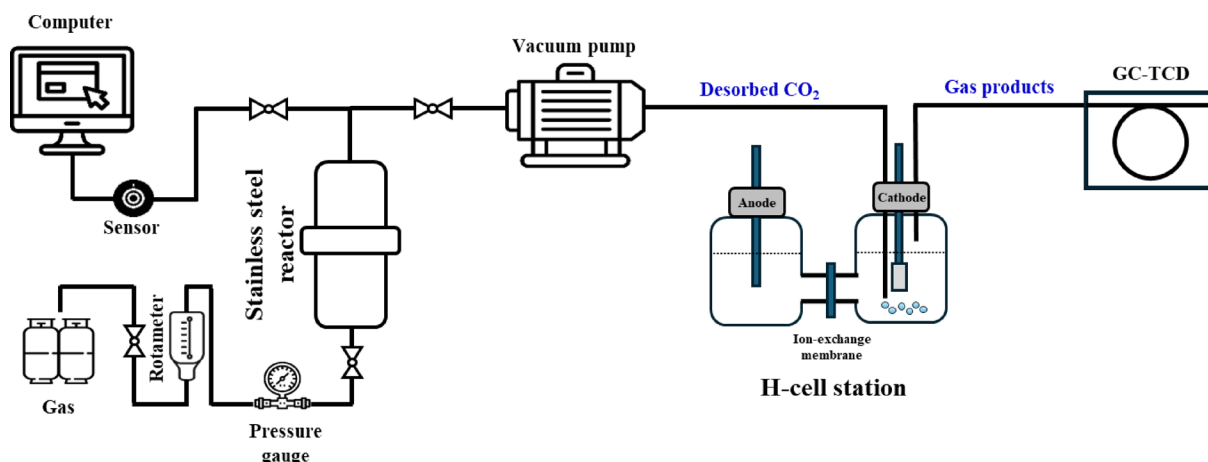


Fig. 1. Illustration of the CO₂ adsorption-desorption and CO₂ conversion equipment.

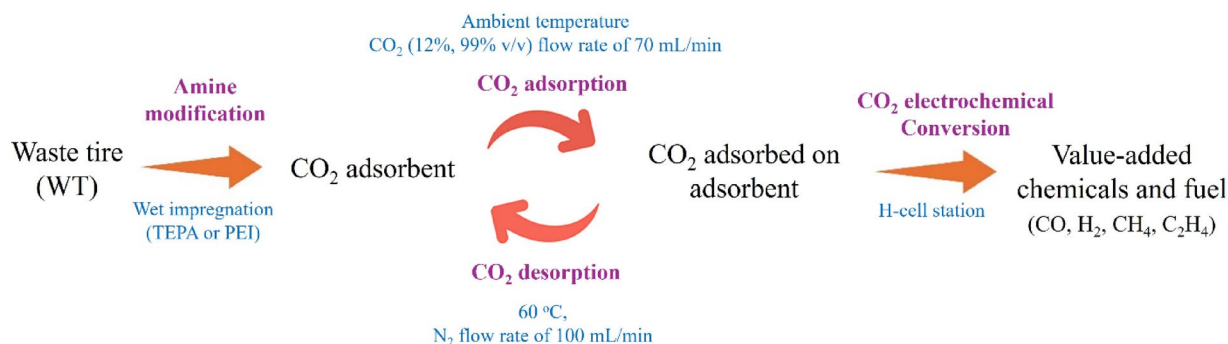


Fig. 2. The overall summary of this research.

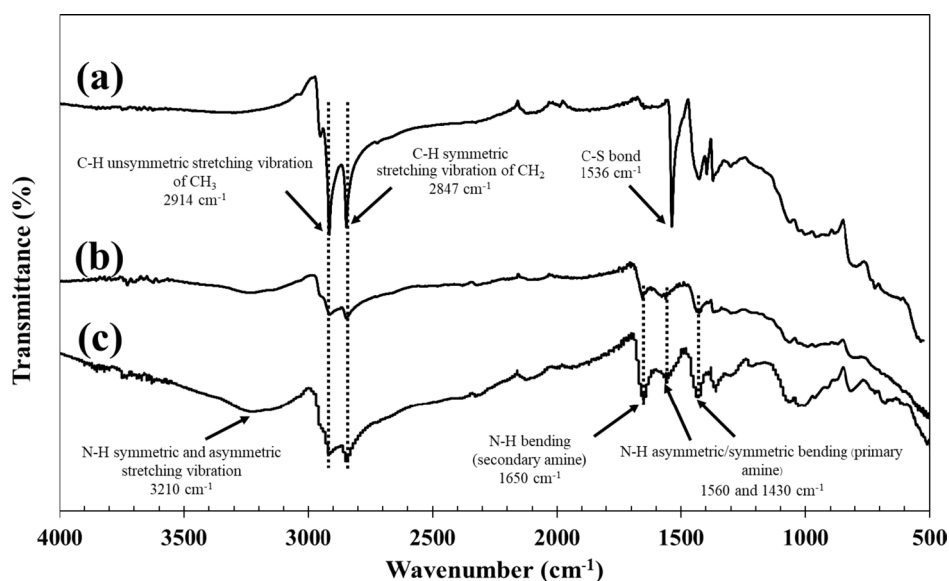


Fig. 3. Representative FTIR spectra of the (a) WT, (b) WT10T, and (c) WT10P.

where t is the adsorption time (min), q_e is the adsorption capacity at equilibrium (mg g^{-1}), q_t is the adsorption capacity at time t (min), k_1 is the pseudo 1st order rate constant (min^{-1}), k_2 is the pseudo 2nd order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), k_A (min^{-1}) is the Avrami's rate constant, and n is the order of the kinetic equation.

CO₂ conversion

The catalyst for the CO₂ electrochemical conversion by the CO₂RR was prepared as a 1:2 mol ratio of CuO: Cu₂O on carbon paper. The electrochemical test was performed using a three-electrode cell on a H-cell station. A platinum plate of 1 × 2 cm in size was employed as the counter electrode and Ag/AgCl (in 3 M sodium chloride solution) soaked in a luggin capillary was used as the reference electrode. The cathode and anode compartments were separated by a piece of proton exchange membrane (Nafion 117, Dupont) to prevent re-oxidation of the products. The 0.1 M KHCO₃ electrolyte solution was purged with CO₂ [12% and 99% (v/v)] for 10 min before applying a reduction potential of −1.7 V (vs. Ag/AgCl). The gaseous products after the chronoamperometric electrolysis were detected by gas chromatography equipped with a thermal conductivity detector (GC-TCD) using helium as the carrier gas. The overall summary of this research is shown in Fig. 2.

Results and discussion

Characterization of the amine-modified WT

The FTIR spectra of the WT before and after amine modification are shown in Fig. 3. The peak located at 2914 cm^{-1} corresponded to the aliphatic C–H unsymmetrical stretching vibration of CH₃– groups and the peak at 2847 cm^{-1} was attributed to the aliphatic C–H symmetrical stretching vibration of –CH₂– groups^{71,73,74}. These results indicated that the WT used in this study may contain both synthetic and natural rubbers. The peak at 1536 cm^{-1} was assigned to the C–S bond from the sulfur crosslinks formed during the WT production⁷⁵. After the WT was modified by TEPA or PEI, a broad peak at 3210 cm^{-1} was evident, which represented the N–H symmetric and asymmetric stretching vibration of amine groups^{76,77}. The N–H bending of the secondary amine [–N(R)H] was represented at 1650 cm^{-1} , while the asymmetric and symmetric bending of primary amine (–NH₂)

Sample code	Elemental composition (%)								S_{BET}^a ($m^2 \cdot g^{-1}$)	Total V^b ($\times 10^4 \text{ cm}^3 \cdot g^{-1}$)
	Before regeneration				After regeneration					
	C	H	N	S	C	H	N	S		
WT	80.25	7.54	0.97	3.09	82.43	7.93	0.86	3.03	2.02	5.80
WT10T	79.97	8.10	3.33	2.72	76.41	7.86	3.26	2.78	3.69	22.4
WT10P	78.19	7.86	3.51	2.44	-	-	-	-	8.01	35.9

Table 1. Elemental analysis and textual properties of the WT without and with different amine modification. ^a BET surface area; ^b Total pore volume.

Sample	Swelling ratio (Q)	Sol fraction (%)	Gel fraction (%)	Crosslink density ($\times 10^3, \text{ mol/cm}^3$)
WT	3.56	6.32	93.68	27.32
WT10T	4.11	8.05	91.95	23.30
WT10P	3.91	7.92	92.08	23.55

Table 2. Swelling ratio, sol-gel traction, and crosslink density of the WT without and with different amine modification.

were observed at 1560 and 1430 cm^{-1} , respectively^{76,78,79}. It is interesting to note that the peak intensity of N-H stretching and bending for WT10P was clearly higher than that for WT10T due to the high numbers of amine active sites in the PEI structure. In addition, based on the elemental analysis (Table 1), the nitrogen contents of WT10P were higher than those of WT10T. According to these results, the WT was successfully modified by TEPA or PEI.

However, the peak at 1536 cm^{-1} representing the C-S bond in both the WT10T and WT10P was markedly reduced or disappeared, while the sulfur content in WT10T (2.72%) and WT10P (2.44%) was decreased compared to that in the WT (3.09%) due to the devulcanization by amines^{80,81}. Table 2 displays the swelling ratio, sol-gel fraction, and crosslink density of WT without and with various amine modifications. The swelling ratio of WT10T (4.11) and WT10P (3.91) was higher than that of unmodified WT (3.56). The sol fraction of WT10T and WT10P tended to be increased and the crosslink density of WT10T ($23.30 \times 10^{-3} \text{ mol/cm}^3$) and WT10P ($23.55 \times 10^{-3} \text{ mol/cm}^3$) was lower than that of WT ($27.32 \times 10^{-3} \text{ mol/cm}^3$). These results confirmed that the amines (TEPA and PEI) could break up the sulfur bonds in rubber vulcanizates, resulting in a decreased level of C-S bonds. Accordingly, TEPA and PEI serve not only as modifiers of WT but also as devulcanizing agents.

The morphology of the WT before and after amine modification is shown as SEM images in Fig. 4. The WT surface contained some small pores and had a S_{BET} and total V_p of 2.02 $\text{m}^2 \cdot \text{g}^{-1}$ and

$5.80 \times 10^{-4} \text{ cm}^3 \cdot \text{g}^{-1}$, respectively (Table 1). After amine modification, the modified WT surface became rougher and lost its elasticity, resulting in an increased S_{BET} and total V_p . Although, the total V_p of WT10T and WT10P was increased after amine modification, their values seemed to be low when compared to those previously reported for other solid adsorbent materials, i.e., MOFs, carbon materials, silica, and zeolite^{82–85}. Accordingly, the adsorbent materials prepared in this study exhibited the characteristics of a non-porous material.

Effect of the amine type, amine loading level, and CO₂ concentration on the CO₂ adsorption

The WT powder was modified by two amine types (TEPA and PEI) at varying amine loading levels [2.5–15% (w/w)] to form the CO₂ adsorbents, which were then compared under the same operating condition of an ambient temperature and atmospheric pressure. The breakthrough curve of the adsorbents (Fig. 5) reveals distinct adsorption behaviors. When comparing amine types, the TEPA-modified WTs showed a low sensitivity of breakthrough behavior with the amine loading level, while the PEI-modified WTs exhibited a high sensitivity in their breakthrough capacity with the amine loading level. This can be explained by the structural effects of amine polymers on adsorbent performance. Branched amine polymers may obstruct CO₂ adsorption compared to that of linear amine polymers. The breakthrough curves of WTs with different amine loadings (Fig. 5a and b) corresponded with the CO₂ adsorption capacity of the amine-modified WT with various amine loadings (Fig. 5c). The CO₂ adsorption capacity of the unmodified WT was about 7.10 mg/g of adsorbent, while the CO₂ adsorption capacity of the WT modified with TEPA or PEI increased with increasing amine loading levels up to 5% or 10% (w/w) for PEI and TEPA, respectively. With an amine loading in the range of 2.5–5% (w/w), the CO₂ adsorption capacity of the PEI-modified WT increased more than that for the TEPA-modified WT. This is presumably due to the difference in chemical structure of both amines, where PEI is an organic polyamine polymer with a network structure, while TEPA is a linear structure. Therefore, there are more basic sites in PEI than in TEPA to bind the CO₂ molecules⁸⁶.

Increasing the amine loading level to 10% (w/w) decreased the CO₂ adsorption capacity of WT10P slightly, while that for WT10T was still increased compared to that with a 5% (w/w) loading level. This suggested that a high concentration of the high molecular weight PEI made the PEI-modified WT sample stickier, resulting in a decreased surface area and high CO₂ diffusion resistance, whilst this behavior was not observed in the case

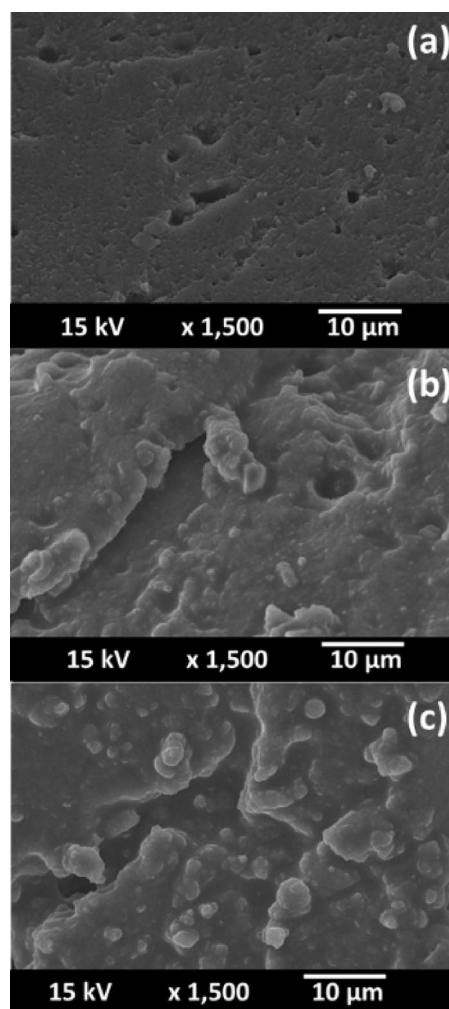


Fig. 4. Representative SEM images (1,500 x magnification) of (a) WT, (b) WT10T, and (c) WT10P.

of WT10T. At a 15% (w/w) amine loading level, the CO₂ adsorption capacities of the WT15T and, especially, WT15P decreased markedly compared to those at 10% (w/w) due to the adsorbent surface becoming sticky. The morphology of the amine-modified adsorbents with various amine loading levels are represented in supplementary information (Figs. S1 and S2).

The FTIR spectral analysis was used to ascertain the nature of WT10T and WT10P before and after CO₂ adsorption as well as CO₂ desorption (Fig. 6). Before adsorption, the peaks of each adsorbent were located at 3210 cm⁻¹, assigned to the N-H symmetric and asymmetric stretching vibration of amine groups. The peaks located at 1650 and 1560 cm⁻¹ were attributed to the N-H bending of the secondary and primary amines, respectively. After CO₂ adsorption, the peak located at 1535 cm⁻¹, which represented the asymmetric stretching vibration of the carboxylate anion (COO⁻) of ammonium carbamate, was observed in both WT10T and WT10P^{87–91}. This indicated that the CO₂ molecules could be chemisorbed on the amine-impregnated WT. However, the interaction between CO₂ molecules and amino groups was destroyed after the CO₂ desorption under regeneration using the VTSA process, resulting in the presence of N-H bending peaks at 1650 and 1560 cm⁻¹, similar to the peaks of the sorbent materials before CO₂ adsorption.

Additionally, the CO₂ capture in the adsorbent materials could be confirmed by Raman spectroscopy (Fig. 7). The two distinct bands at 1360 and 1570 cm⁻¹ represented the carbon black in WT^{92,93} and corresponded to the disordered carbon (D band) and the graphite (G band) structures, respectively⁹³. Before CO₂ adsorption (Fig. 7a), the intensity peak ratio ($I_D/I_G = I_{1360}/I_{1570}$) presented the same value (0.85) because the carbon black in all samples was the same content and did not adsorb or react with CO₂ molecules. After CO₂ adsorption (Fig. 7b), the peak intensity of the band at 1360 cm⁻¹ seemed to be increased due to a band overlap of CO₂ molecules at 1370 and 1245 cm⁻¹ and D band of carbon black as previous research^{52,94}. The I_{1360}/I_{1570} ratio of WT10P and WT10T was then increased to 0.89 and 0.91, respectively. Whilst, the I_{1360}/I_{1570} of WT did not change because the small amount of CO₂ molecules was absorbed. Accordingly, the CO₂ molecules could be adsorbed more favorably on the amine-impregnated adsorbent materials compared to the neat WT.

The CO₂ adsorption capacity of WT10T at ambient (30 °C), 45 °C, and 60 °C is summarized in Fig. 8d. When the temperature increased during the CO₂ adsorption, the CO₂ adsorption of WT10T tended to be reduced. This

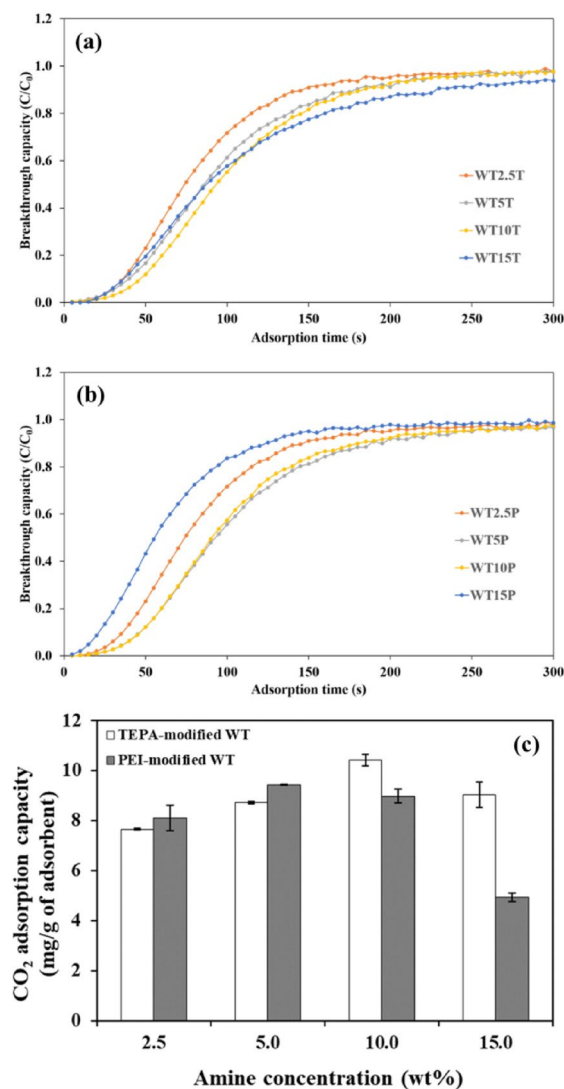


Fig. 5. Breakthrough curves of WT with different (a) TEPA and (b) PEI loading levels; and (c) the CO_2 adsorption capacity of the WT and TEPA- or PEI-modified WT at different amine loading levels [2.5–15% (w/w)] at ambient temperature and atmospheric pressure.

was due to the exothermic nature of the adsorption reaction^{95,96}, where increasing the temperature decreased the adsorption rate. As a result, the time for CO_2 to flow through the adsorbent material, and the absorption level was reduced. This behavior is different from the previous study that used NR filled with N-[(3-trimethoxysilyl)propyl]ethylenediamine and N-[(3-trimethoxysilyl)propyl]diethylenetriamine⁵². This may be due to the different amine chemical structure, rubber nature, and modified silica particles.

Overall, WT10T had the highest CO_2 adsorption capacity ($10.41 \pm 0.24 \text{ mg}\cdot\text{g}^{-1}$ of adsorbent) at an ambient temperature and atmospheric pressure. Thus, this sample was then chosen for further study of kinetics, regeneration, and CO_2 RR. It is interesting to note that the effect of CO_2 concentration on Faradaic efficiency (FE) is significant. As the CO_2 concentration increased from 12% (v/v) to 99% (v/v), the CO_2 adsorption capacity of the WT10T adsorbent notably increased, from 10.41 ± 0.243 to $59.98 \pm 1.577 \text{ mg}\cdot\text{g}^{-1}$ under ambient temperature and atmospheric pressure (Table 3). This enhancement in CO_2 adsorption was accompanied by an increase in FE, with both CH_4 and C_2H_4 detected as gas products. The increase in FE with higher CO_2 concentration can be attributed to more efficient interactions between the adsorbent and CO_2 molecules at higher concentrations, leading to better electrochemical conversion. Therefore, factors such as amine type, amine loading level, and CO_2 concentration play important roles in influencing both the CO_2 adsorption capacity and the Faradaic efficiency of the amine-modified WT adsorbent.

Here in this study, the comparison of CO_2 adsorption capacity for different adsorbent materials is summarized in Table 4. The observed variation in the CO_2 adsorption capacity was due to the difference in specific properties and testing conditions of each sorbent material under a similar condition, WT10T could be considered as a potential alternative solid sorbent material for CO_2 capture. It has a high CO_2 adsorption capacity, is easy to

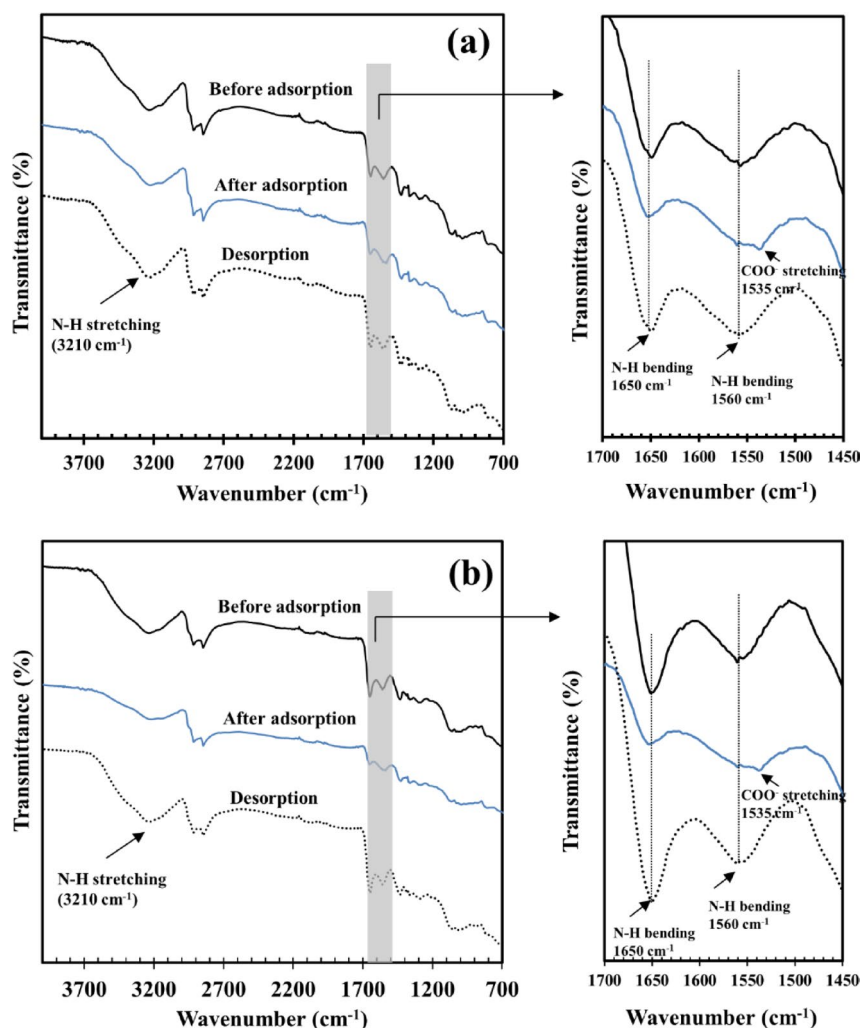


Fig. 6. Representative FTIR spectra of (a) WT10T and (b) WT10P before and after CO₂ adsorption as well as their CO₂ desorption.

prepare, low-cost, low energy requirement, and is environmentally friendly. In addition, the advantage of using WTs to make an absorbent material is that it reduces the current large-scale amount of rubber waste.

Kinetic adsorption. Kinetic modeling is an important step in evaluating the CO₂ adsorption mechanism of an adsorbent material. The experimental CO₂ adsorption capacities of the WT10T sample were fitted to each kinetic model (Fig. 8a and c), with the results summarized in Table 5. The pseudo 1st order and pseudo 2nd order models were clearly not suitable for describing the adsorption kinetics of WT10T due to their low R^2 value, whereas Avrami's model fitted well with the adsorption experimental data ($R^2 > 0.97$ with the lowest root mean square error and mean square error values). Thus, CO₂ could interact with WT10T by both physisorption with the rubbery matrix and by chemisorption with the amine groups, in agreement with the Avrami's model order (n_a) being in the range of 0.82–1.27¹⁰⁰.

Regeneration of adsorbent materials

To evaluate the stability of the amine-modified adsorbent materials, the adsorption-desorption cycle of WT and WT10T was investigated over 10 sequential cycles using the VTSA process. The relationship between the CO₂ adsorption capacity and the cycle number for both WT and WT10T are shown in Fig. 9. The CO₂ adsorption capacity of the unmodified WT decreased by 5.72% in the 2nd cycle compared to the 1st cycle. This is because the heterogeneity in sorbent's active site was treated during the first regeneration cycle. Thereafter, the CO₂ adsorption capacity then remained almost constant until the 6th cycle, which can be explained by the stability of the active component in the sorbent with the employed regeneration method. Finally, the CO₂ adsorption capacity gradually declined again by 13.55% and 16.47% at the 7th and 10th cycle (compared to the 1st cycle), respectively. This decline was due to the loss of active components in the sorbent material, as evidenced by CHNS results. Thus, the WT adsorbent material showed a poor regeneration stability. In contrast, the CO₂ adsorption capacity of WT10T seemed to be stable over all 10 cycles, decreasing by less than 3%. Accordingly, the regeneration stability of WT10T was better than that of WT, which reflected that the amine sites on WT10T are not volatile and do not show oxidative degradation during the regeneration process^{101,102}. This result was also

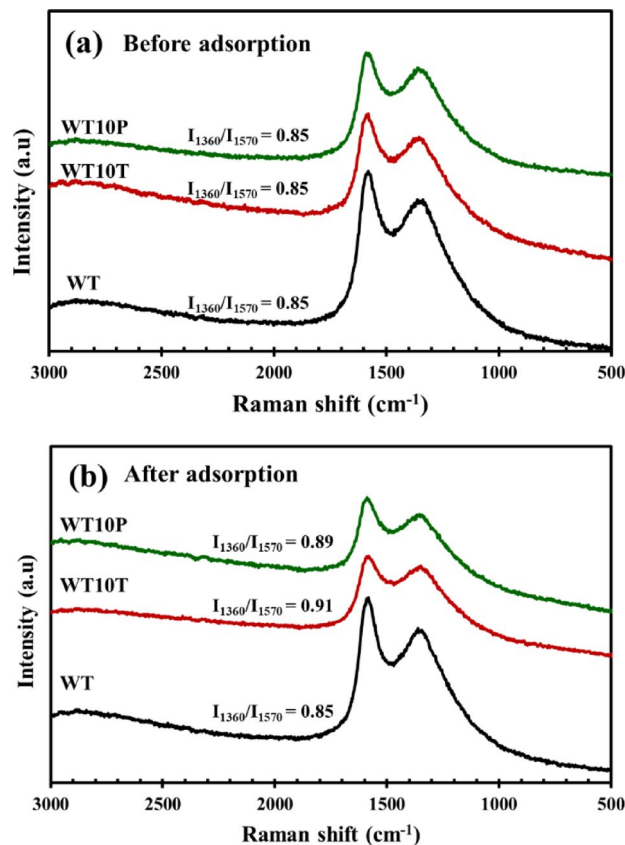


Fig. 7. Representative Raman spectra of the WT, WT10T, and WT10P (a) before and (b) after CO₂ adsorption.

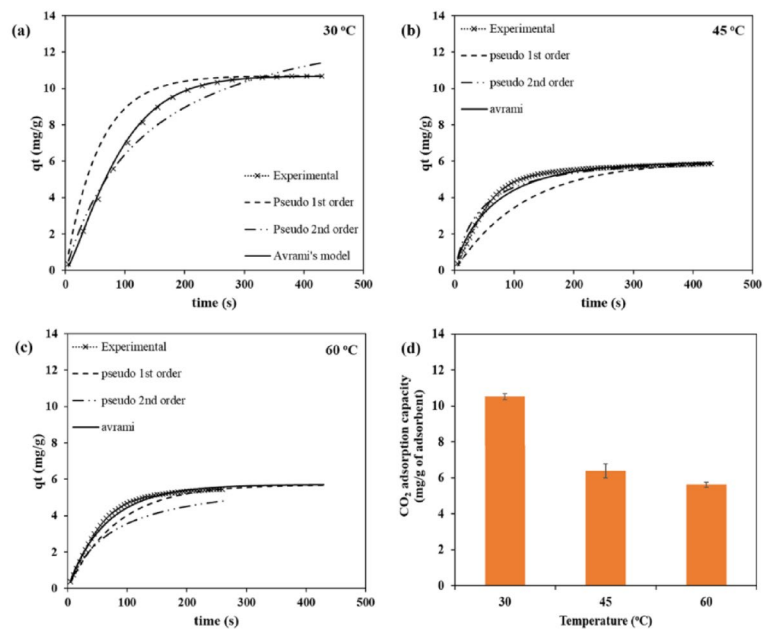


Fig. 8. Experimental CO₂ adsorption capacity of WT10T with the corresponding fits to the different kinetic models at (a) 30 °C, (b) 45 °C, and (c) 60 °C; and (d) the CO₂ adsorption capacity of WT10T at various temperatures.

CO ₂ concentration (% v/v)	CO ₂ adsorption capacity (mgCO ₂ /g _{adsorbent})	FE (%)			
		CO	H ₂	CH ₄	C ₂ H ₄
12	10.41 ± 0.243	0.15	5.99	-	-
99	59.98 ± 1.577	25.12	26.84	0.78	5.14

Table 3. The CO₂ adsorption capacity of WT10T at different CO₂ concentrations and the Faradaic efficiency (FE) of gas products from the CO₂RR^a using a 1:2 mol ratio CuO: Cu₂O catalyst. ^a Reaction time of 2 h at a potential of −1.7 V vs. Ag/AgCl in CO₂-saturated 0.1 M KHCO₃ electrolyte solution.

Sorbent materials	Temperature (°C)	CO ₂ concentration (% v/v)	CO ₂ adsorption capacity (mg/g)	Reference
CM-MSi ^a	35	12	4.08	51
NR-USi ^b	35	12	4.85	52
CHIT-HTC-48 ^c	0	99.9	19.80	97
30-ANF-TEPA ^d	0	0.3	5.24	98
30-ANF-TEPA ^d	25	99.99	42.68	98
CSAC2-600-1 ^e	25	10	30.36	99
MNR-3NMSi ^f	35	12	6.11	53
Prinstine PP	30	99.9	22.88	22
WT10T ^g	30	12	10.41	This study
WT10T ^g	30	99.9	59.98	This study

Table 4. Comparison of CO₂ adsorption capacities of various adsorbent materials. ^a Natural rubber latex foam prepared by a cake mixer filled with silica particles modified by (3-aminopropyl) triethoxysilane. ^b Natural rubber foam filled with silica. ^c Chitosan was hydrothermally treated at 180 °C for 48 h. ^d Activated carbon nanofiber prepared by carbonization of polyacrylonitrile/N, N-dimethylformamide at 800 °C for 30 min and then impregnated with 0.5 wt% TEPA solution. ^e Activated carbon prepared by activation of chestnut shell char with a KOH ratio of 2 at 600 °C for 1 h. ^f Modified natural rubber foam filled with silica particles modified with N-[(3-trimethoxysilyl) propyl]diethylenetriamine. ^g Waste tire impregnated with 10% (w/w) tetraethylenepentamine.

supported by the CHNS analysis, where the nitrogen contents of WT10T before and after regeneration seemed to be constant (Table 1).

Electrochemical CO₂RR

To study the catalytic activity and the effect of the CO₂ concentration on the catalytic performance of the CO₂RR using a 1:2 mol ratio CuO: Cu₂O on carbon paper catalyst, the CO₂ was supplied to the CO₂RR electrochemical cell at 12% and 99% (v/v). The resulting GC-TCD chromatogram of the CO₂RR is shown in Fig. 10. With 12% (v/v) CO₂, the CO₂RR gave CO and H₂ at a 0.15% and 5.99% Faradaic efficiency (FE), respectively. The relatively low FE values might come from the low CO₂ concentration in the electrolyte solution. When the CO₂ concentration was increased to 99% (v/v), the CO₂RR produced CO, H₂, CH₄, and ethylene (C₂H₄) at a 25.12%, 26.84%, 0.78%, and 5.14% FE, respectively. These observations indicated that to obtain HC products from the electrochemical CO₂RR, a high concentration of CO₂ needs to be released from the adsorption process. It is important to know that the experiment in this study was conducted as a batch scale, which is a limitation for CO₂ conversion. Adjusting the methodology to a continuous system and increasing the CO₂ concentration will enhance the efficiency of CO₂ conversion into valuable products using CuO and Cu₂O catalysts.

Conclusion

In this study, different amine-modified WT samples were successfully prepared using TEPA and PEI, and then developed as an adsorbent for CO₂ capture. The prepared adsorbents exhibited a non-porous material nature. Based on the FTIR and CHNS analyses, the specific amine spectrum was found on the WT surface and the nitrogen content was increased after modification. The optimum condition to obtain the highest CO₂ adsorption capacity of the modified WT under a CO₂ flow rate of 70 mL min^{−1}, ambient temperature, and atmospheric pressure was modification of the WT using 10% (w/w) TEPA to give a CO₂ adsorption capacity of 10.41 mg g^{−1} of adsorbent. The kinetic adsorption of WT10T fitted well with Avrami's model, supporting both physical and chemical adsorptions. Finally, WT10T had a high stability in regeneration over at least 10 cycles. Accordingly, WT10T is an alternative CO₂ adsorbent that could potentially be used as a sorbent material for CO₂ capture. The CO₂ present in the adsorbent material could undergo direct conversion to CO, H₂, CH₄, and C₂H₄ through CO₂RR when CuO/Cu₂O on carbon paper served as the catalyst. Moreover, elevated CO₂ levels corresponded to a higher FE in HC product generation. This research can be related to the concept of BCG and CCUS and shows one way of how to potentially utilize waste materials as adsorbents and reduce the waste from rubber industries.

Model parameter		WT10T
Pseudo-1st	$R^2{}^a$	0.96
	$k_1{}^b$ (min^{-1})	0.018
	$q_{e,(Exp)}{}^c$ ($\text{mg} \cdot \text{g}^{-1}$)	10.69
	$q_{e,(Cal)}{}^d$ ($\text{mg} \cdot \text{g}^{-1}$)	10.68
	Root mean square error	0.28
	Mean square error	0.65
Pseudo-2nd	$R^2{}^a$	0.96
	$k_2{}^e$ ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	0.0005
	$q_{e,(Exp)}{}^c$ ($\text{mg} \cdot \text{g}^{-1}$)	10.68
	$q_{e,(Cal)}{}^d$ ($\text{mg} \cdot \text{g}^{-1}$)	11.43
	Root mean square error	0.57
	Mean square error	0.32
Avrami's	$R^2{}^a$	0.99
	$k_a{}^f$ (min^{-1})	0.011
	$n_a{}^g$	1.27
	$q_{e,(Exp)}{}^c$ ($\text{mg} \cdot \text{g}^{-1}$)	10.69
	$q_{e,(Cal)}{}^d$ ($\text{mg} \cdot \text{g}^{-1}$)	10.68
	Root mean square error	0.12
	Mean square error	0.02

Table 5. Kinetic model and the corresponding kinetic parameters of CO_2 adsorption for WT10T at ambient temperature and atmosphere pressure. ^a Coefficient of determination; ^b Kinetic coefficient pseudo-first (min^{-1}); ^c CO_2 adsorption capacity from experiment ($\text{mg} \cdot \text{g}^{-1}$); ^d CO_2 adsorption capacity from kinetic calculation ($\text{mg} \cdot \text{g}^{-1}$); ^e Kinetic coefficient pseudo-second ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); ^f Kinetic coefficient Avrami's (min^{-1}); and ^g Avrami's model order.

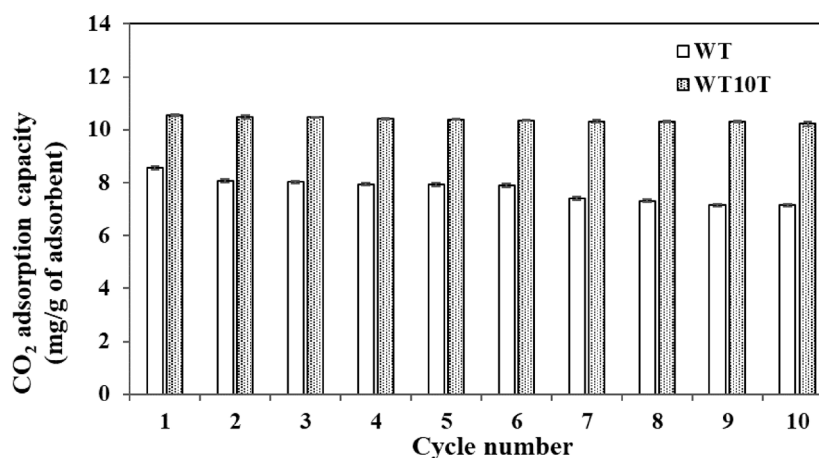


Fig. 9. Successive CO_2 adsorption-desorption cycles of WT and WT10T.

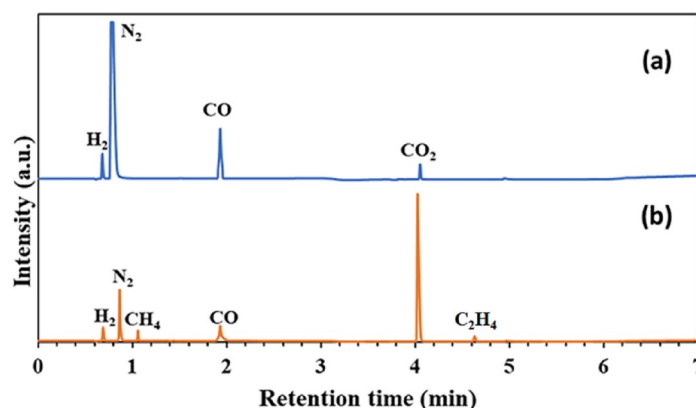


Fig. 10. Representative GC-TCD chromatogram after CO_2 RR of WT10T with a CO_2 concentration of (a) 12% (v/v) and (b) 99% (v/v).

Data availability

The dataset generated and/or analyzed during the current study are available from the corresponding authors on reasonable request.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

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