Environment and Water Engineering

Homepage: www.jewe.ir

Improving performance of nanocrystalline cellulose adsorbent in carbon dioxide adsorption process by amine modification method

Omid Mohammadi Moinalzoafa[1], and Maryam Tahmasebpoor[1]

[1]Department of Chemical Engineering, Faculty of Chemical and Petroleum Engineering, University of Tabriz, Tabriz, Iran

ARTICLE INFO	ABSTRACT
	An increase in the concentration of carbon dioxide in the atmosphere endangers the lives of all living organisms. This research was conducted to investigate the efficiency of nanocrystalline cellulose in adsorbing CO_2 and to improve its performance by modifying it with amine. For this purpose, nanocrystalline cellulose adsorbent was synthesized by acid hydrolysis method, and two types of amine monoethanolamine and diethanolamine were used to improve its performance in CO_2 absorption. To investigate the formation of chemical groups, the morphology of the samples, and their adsorption capacity, FTIR, SEM and TGA were employed. The adsorption study was utilized at temperatures of 25 and 50 °C, and CO_2 concentrations of 10 and 90 vol.%. The results demonstrated that at 25 °C and 90 vol.% CO_2, the nanocrystalline cellulose modified with 20 wt% monoethanolamine exhibited an adsorption capacity of 1.52 *mmol/g*. Under the same conditions, the adsorption capacity of pure nanocrystalline cellulose was 0.25 mmol/g. This clearly demonstrates the positive effect of amine modification on nanocrystalline cellulose, leading to a significant increase in its adsorption capacity. According to investigations and comparisons with similar research works, nanocrystalline cellulose, especially in its modified type, can be used as a novel and biodegradable adsorbent in the field of CO_2 adsorption.

1. Introduction

Among greenhouse gases (GHG), carbon dioxide (CO_2) is considered one of the most important greenhouse gases, as it accounts for approximately 70% of total greenhouse gas emissions (Imani et al., 2023; Nobarzad et al., 2021). The elevation of CO_2 concentrations in the atmosphere is strongly correlated with climate change and associated climatic phenomena, leading to an increase in Earth's temperature (Nunes, 2023; Yang et al., 2022). Research conducted by scientists suggests that, without appropriate measures to mitigate the effects of rising CO_2 levels, atmospheric concentrations of this gas could reach 500 ppm by the year 2050, presenting a significant threat to life on Earth (Bains et al,. 2017).

Carbon capture and storage (CCS) represents a viable strategy for mitigating climate change. This process entails the capture and separation of carbon dioxide emissions from power generation facilities and industrial operations. Subsequently, the captured CO_2 is transported to an appropriate controlled site for final storage, which may occur either deep underground or within oceanic environments (Salvi and Jindal, 2019). There are four primary methods utilized for CO_2 separation: solvent absorption, cryogenic distillation, membrane separation, and adsorption. Numerous factors affect the choice of separation technology implemented. In light of the various limitations associated with the aforementioned methods, including solvent loss and elevated operational costs in solvent absorption, considerable energy inefficiencies and the requirement of high pressure to mitigate CO_2 sublimation in cryogenic distillation, as well as the need for pre-treatment and low flux in membrane separation techniques, a predominant focus of current research is the advancement of adsorbents. This research prioritizes the development and utilization of adsorbents that either do not possess these drawbacks or present enhanced advantages relative to alternative methods (Das et al., 2023; Gautam and Mondal, 2023). Surface adsorption represents a highly effective technique for the separation of CO_2 from flue gas streams. In this approach, the flue gas is directed through an adsorbent

material that selectively retains CO_2, thereby facilitating the separation of other gaseous components from the flue gas.

Two primary types of adsorption are identified in solid adsorbents: physical adsorption and chemical adsorption. Physical adsorption is governed by van der Waals forces, whereas chemical adsorption occurs through the formation of chemical bonds (Kenarsari et al., 2013). Surface adsorption demonstrates significant potential for future applications, attributed to its low energy demands for regeneration, reduced operational costs, compatibility with dilute gas mixtures, high CO_2 adsorption capacity, and minimal pressure drop during CO_2 separation in comparison to alternative methods (Dziejarski et al., 2023; Lai et al., 2021). One of the adsorbents used in the adsorption method is nanocellulose-based adsorbents. Cellulose nanocrystals (CNCs) are produced through chemical treatment, and cellulose nanofibrils (CNFs) are produced through the mechanical breakdown of wood fiber pulps and plant fibers using high-pressure homogenization, grinding, cryocrushing, high-intensity ultrasonication, or microfluidization. Cellulose nanocrystals are typically produced through the hydrolysis of a strong acid with wood fibers, plant fibers, or cellulose nanofibrils. Cellulose is hydrolyzed by the attack of protons (H^+) on the beta-(1-4)-glycosidic bond, primarily reacting with amorphous regions to produce oligosaccharides and glucose. The hydrolysis process generally utilizes sulfuric acid, phosphoric acid, hydrochloric acid, and nitric acid. The main difference between cellulose nanocrystals and cellulose nanofibers is their size and level of crystallinity. CNFs consist of a combination of amorphous and crystalline cellulose chains, with lengths spanning several microns, while CNCs lack amorphous regions and typically measure less than 500 nm in length (Grishkewich et al., 2017; Muthami et al., 2021). Given that pure nanocrystalline cellulose exhibits a low adsorption capacity, further research aimed at enhancing the performance of this adsorbent has consistently been a priority. Zhu et al. (2020) employed chemical vapor deposition to modify nanocrystalline cellulose with an aminosilane referred to as APS (3-(2-aminoethylamino)-propylmethyldimethoxy silane) for CO_2 absorption. They reported that the adsorption capacity of nanocrystalline cellulose post-modification with APS increased from 0.1929 to 1.5034 mmol/g. Doan and Chiang (2023) synthesized nanocrystalline cellulose/silica aerogel hybrid composites through the hybridization of nanocrystalline cellulose and sodium silicate employing a single-step sol-gel method, subsequently modified with polyethyleneimine (PEI). Their study demonstrated that at 90 °C, the PEI modification enhanced the adsorption capacity of this adsorbent from 0.25 to 2.61 mmol/g, indicating that amine modification of cellulose adsorbents represents a promising approach in this domain.

Due to the limited application of cellulose derived from cotton linter in the production of nanocrystalline cellulose and the insufficient investigation into first and second-type amines, this study focuses on generating nanocrystalline cellulose through the acidic hydrolysis of alpha cellulose sourced from cotton linter, utilizing sulfuric acid as the hydrolyzing agent. The material was then modified with monoethanolamine and diethanolamine to improve the adsorbent's performance. The adsorption capacities of the nanocrystalline cellulose and the modified nanocrystalline cellulose were assessed. This study aims to evaluate the effectiveness of nanocrystalline cellulose derived from cotton linter in CO_2 absorption and to enhance its adsorption capacity through amine modification. To examine the structure of the synthesized adsorbents, the establishment of chemical bonds, and their adsorption capacity, Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), and thermogravimetric analysis (TGA) were utilized, respectively.

2. Materials and Methods

2.1 Raw materials

The alpha-cellulose used in this study was obtained from cotton linters and supplied by Linterpak Company, located in Mazandaran, Behshahr (Iran). For the acid hydrolysis process, sulfuric acid (H_2SO_4) was procured from Merck (Germany). Furthermore, monoethanolamine (MEA) with the chemical formula (C_2H_7NO) and diethanolamine (DEA) with the chemical formula ($C_4H_{11}NO_2$) were also sourced from Merck. Ethanol (C_2H_5OH) was purchased from Dr. Mojalali Company for the modification of nanocrystalline cellulose.

2.2 Preparation of basic and modified adsorbents

The acid hydrolysis method was employed for the synthesis of cellulose nanocrystals. For this purpose, 5 g of alpha-cellulose, whose fibers had previously been manually separated, was mixed with 50 ml of 64% (w/w) sulfuric acid at 60 °C for 30 min using a magnetic stirrer to ensure complete reaction and thorough hydrolysis of the cellulose fibers. Subsequently, the fibers obtained from the acid hydrolysis were washed with distilled water and centrifuged using a Universal-5000 centrifuge (manufactured in Iran) for 10 min at 3000 rpm to separate unhydrolyzed fibers and excess sulfuric acid from the hydrolyzed fibers. The washed fibers were placed in a dialysis bag for further purification and then immersed in deionized water at ambient conditions for 24 hr. Subsequently, the obtained fibers were subjected to ultrasonication using a Pars 7500S ultrasonic device with a frequency of 20 kHz. The process involved three consecutive cycles, each consisting of 10 min of treatment followed by 5 min of rest, to achieve a gel-like product. For the preparation of amine-modified samples, 5 ml of ethanol was added per gram of cellulose nanocrystals. Then, amine was added to the solution at 10, and 20% by weight of the total cellulose nanocrystals and ethanol. It should be noted that the synthesis conditions were identical for both MEA and DEA. The mixture was refluxed and stirred at 75 °C for 3 hr. Afterward, the solution was centrifuged and washed. Finally, the gel-like modified samples were dried using an oven or freeze-drying process for use in adsorption experiments and various analyses, yielding approximately 4.5 g of dried material.

2.3 Characterization of adsorbent properties

To investigate the surface characteristics, changes induced by surface modification, and the structural properties of the primary and amine-modified adsorbents, a MIRA3 FEG-SEM Tescan device (manufactured in the Czech Republic) was utilized. For sample preparation, a portion of the dried samples was first attached to a golden stub using double-sided adhesive tape. Subsequently, the samples were coated with gold using a gold sputtering device belonging to the FESEM laboratory at

the University of Tabriz. Additionally, to examine and analyze the functional groups and chemical bonds formed in the samples, FTIR analysis (using a Tensor 27 device manufactured in Germany) was performed. The prepared samples were initially ground using a mortar and then placed in the device. Finally, the corresponding spectra were obtained in the range of 400 to 4000 cm^{-1}.

2.4 Adsorption analysis in various cycles

In this study, a TGA/DSC1 device manufactured in Switzerland was utilized to measure the amount of CO_2 adsorbed by the samples at ambient pressure. Initially, a flow of N_2 gas at a rate of 50 ml/min was injected into the device for 60 min to remove all moisture and impurities adsorbed by the samples. In the first adsorption phase at 50 °C, the atmosphere inside the device was switched to a gas mixture consisting of 90 % CO_2 and 10 % N_2, and the adsorption process was carried out for 90 min. During the desorption phase at this temperature, the adsorbent, which had adsorbed CO_2 was subjected to a flow of N_2 gas under the same initial conditions for 60 min to complete the regeneration process. After completing the first adsorption/desorption cycle at 50 °C, the temperature of the TGA device was reduced to 25 °C, and the first adsorption/desorption cycle was repeated under the same conditions for 25 °C. This experiment was repeated

for three adsorption/desorption cycles at both temperatures, using CO_2 gas at different concentrations of 90 and 10 % by volume, balanced with N_2 gas (Chakravartula Srivatsa and Bhattacharya, 2018; Lourenço et al., 2021).

3. Results and Discussion
3.1 Characterization
3.1.1 FE-SEM analysis

Fig. 1 presents the results of field-emission scanning electron microscopy analysis for alpha-cellulose, pure cellulose nanocrystals, and cellulose nanocrystals modified with amines. As shown in Fig. 1a, alpha-cellulose exhibits a striated surface resembling that of a leaf. Upon acid hydrolysis and conversion to cellulose nanocrystals (Fig. 1b), crystalline regions become evident. These rod-like crystalline regions, resembling rice grains, are the crystalline domains that remain after the breakdown of amorphous regions. They have a diameter of approximately 20 to 50 *nm* and a length of 80 to 200 nm. Fig. 1c and Fig. 1d depict cellulose nanocrystals modified with MEA and DEA, respectively. Close examination of the images reveals that modification with monoethanolamine results in the complete disappearance of crystalline regions, creating a rough and uneven surface. In contrast, modification with diethanolamine introduces minor surface irregularities while partially preserving the crystalline structure.
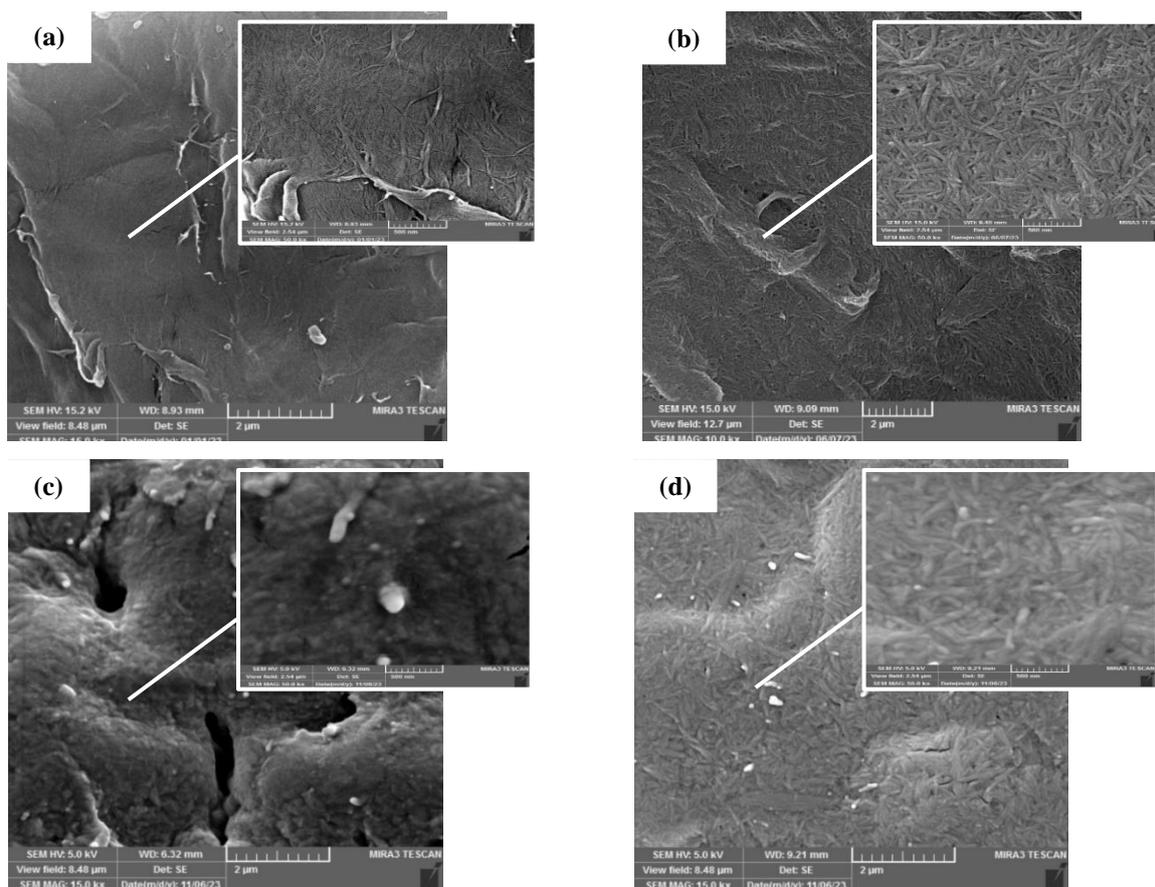

Fig. 1 FE-SEM analysis images of samples: a) Alpha cellulose, b) Pure nanocrystalline cellulose, c) Nanocrystalline cellulose modified with MEA, and d) Nanocrystalline cellulose modified with DEA

3.1.2 FTIR analysis

The results of the FTIR analysis for cellulose nanocrystals and cellulose nanocrystals modified with monoethanolamine and diethanolamine are presented in Fig. 2. Based on the obtained data, it can be concluded that the peaks observed in the regions of 3350 to 3400 cm^{-1} and 2900 cm^{-1} correspond to the stretching vibrations of O-H in the cellulose structure and the stretching vibrations of C-H, respectively, which are visible in all samples. Additionally, the peak observed at 1065 cm^{-1} is attributed to the stretching vibrations of C-O-C (Zhu et al.,

2024; Zhu et al., 2020). Considering that the absorption peaks of primary amine groups, which typically appear in the range of 3250 to 3400 cm^{-1} overlap with the stretching vibrations of O-H, it is not possible to clearly distinguish the amine groups. However, the cellulose nanocrystals modified with amines exhibit two new sharp peaks at 1470, and 1570 cm^{-1}, which correspond to the bending vibrations of C-NH_2 These results indicate the successful modification of cellulose nanocrystals with both MEA and DEA (Koshani et al., 2022; Xu et al., 2021; Zhu et al., 2024).

Fig. 2 FTIR spectrum of samples: a) Nanocrystalline cellulose, b) Nanocrystalline cellulose modified with MEA, and c) Nanocrystalline cellulose modified with DEA
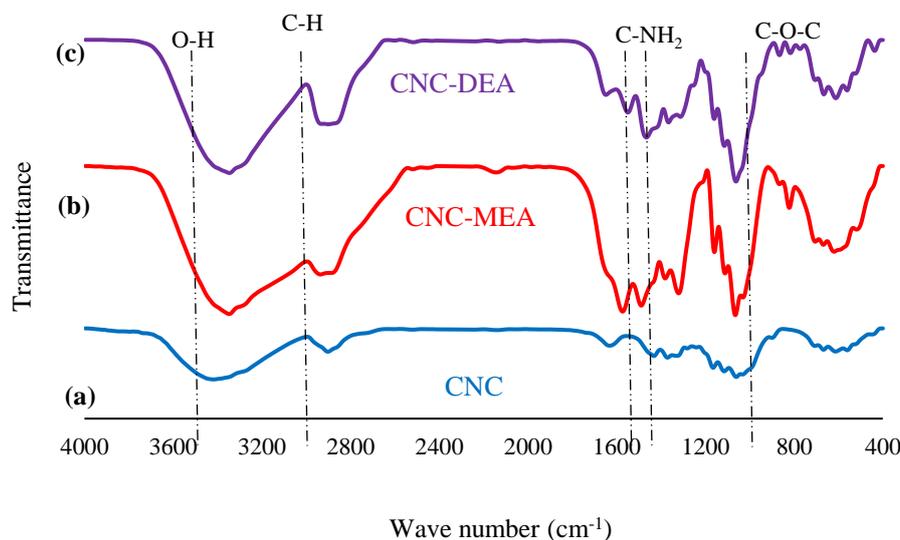
3.2 TGA analysis and adsorption capacity

Fig. 3 presents the TGA curves showing the adsorption capacity of cellulose nanocrystals and cellulose nanocrystals modified with 20 % by weight of two amines (MEA and DEA) at temperatures of 25, and 50 °C, and at CO_2 concentrations of 90% and 10%. The adsorption capacity of the samples was measured over three consecutive cycles for each temperature and concentration, and the desorption temperature for all samples under various conditions was set at 120 °C. According to the results, it is evident that as the temperature increased to 120 °C at the beginning of the TGA analysis, the weight of the samples decreased. This weight loss is attributed to the removal of moisture and any additional substances that the adsorbent had physically adsorbed prior to the analysis (Asgharizadeh et al., 2024; Tahmasebpoor et al., 2023). The analysis of the results indicates that functionalizing cellulose nanocrystals significantly enhances the adsorption capacity of the samples under all tested conditions. For example, the average adsorption capacity for pure cellulose nanocrystals at 25 °C and a CO_2 concentration of 90 % was found to be 0.25 mmol/g. In contrast, modifying the cellulose nanocrystals with 20 % by weight of MEA and DEA increased the adsorption capacity to 1.52, and 0.58 mmol/g, respectively. This demonstrates that amine modification effectively improves the CO_2 adsorption performance of cellulose nanocrystals.

### 3.2.1 Effect of carbon dioxide concentration

Based on the investigations conducted, it can be concluded that increasing the concentration of CO_2 leads to an enhancement

in the adsorption capacity across all samples. For instance, at 25 °C, increasing the CO_2 concentration from 10 to 90 % raised the adsorption capacity of pure cellulose nanocrystals from 0.16 to 0.25 mmol/g. This indicates that higher CO_2 concentrations significantly improve the adsorption performance of the samples. Similarly, at 50 °C, this value increased from 0.1 to 0.15 mmol/g. The obtained data demonstrate that, under all experimental conditions, increasing the CO_2 concentration resulted in an improved adsorption capacity for all samples. This trend highlights the direct correlation between CO_2 concentration and the adsorption performance of the materials. For example, at 25 °C, increasing the CO_2 concentration from 10 to 90 % caused the adsorption capacity of pure cellulose nanocrystals, cellulose nanocrystals modified with 20 % by weight of MEA, and cellulose nanocrystals modified with 20% by weight of DEA to increase from 0.16, 0.65, and 0.14 mmol/g to 0.25, 1.52, and 0.58 mmol/g, respectively. This significant improvement in adsorption capacity underscores the effectiveness of higher CO_2 concentrations in enhancing the performance of both unmodified and amine-modified cellulose nanocrystals. In other words, the CO_2 adsorption capacity increased by 1.5 times for pure cellulose nanocrystals, 2.3 times for cellulose nanocrystals modified with 20 wt% of MEA, and 4.1 times for cellulose nanocrystals modified with 20 wt% of DEA as the CO_2 concentration increased. This demonstrates that the enhancement in adsorption capacity due to higher CO_2 concentration is more pronounced in amine-modified samples, particularly those modified with DEA, highlighting the significant role of amine functionalization in improving CO_2

capture performance. According to Henry's Law, at a constant temperature, the amount of gas adsorbed by an adsorbent is directly proportional to the partial pressure of that gas in the gas phase. Therefore, as the concentration of CO_2 increases, its partial pressure also rises, leading to an increase in adsorption capacity. Additionally, with an increase in CO_2 concentration, the number of CO_2 molecules per unit volume also increases.

This higher density of molecules enhances the probability of collisions between CO_2 molecules and the adsorbent surface. As a result, the increased frequency of these collisions improves the contact between the adsorbent and CO_2, ultimately leading to a higher carbon dioxide adsorption capacity (Tahmasebpoor et al., 2023).

Fig. 3 CO_2 adsorption results for pure and modified (with 20 wt% MEA and DEA) nanocrystalline cellulose adsorbents at different temperatures of 25 and 50 °C and at the desorption temperature of 120 °C in the presence of: a) 90 vol.% CO_2 and b) 10 vol.% CO_2
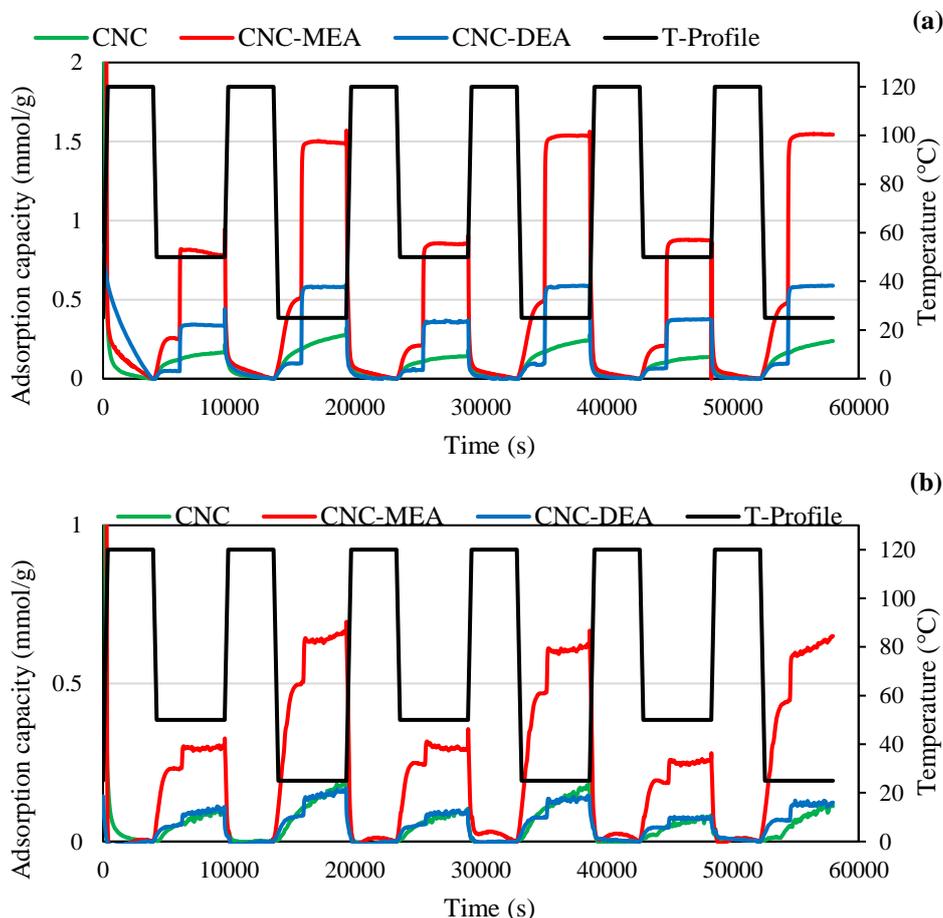
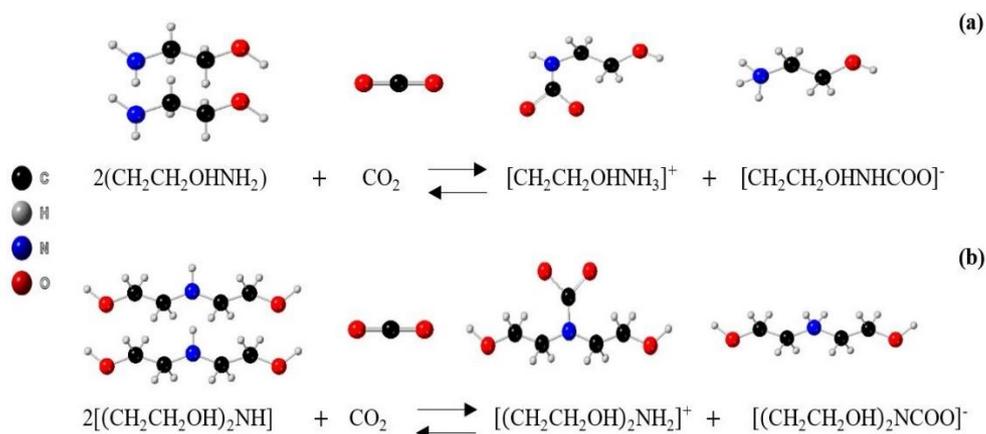### 3.2.2 Effect of modifying nanocrystalline cellulose with amine

Based on the obtained results, modifying cellulose nanocrystals with both MEA and DEA led to an increase in the adsorption capacity of the cellulose nanocrystals. However, this increase in adsorption capacity was minimal at a CO_2 concentration of 10 %. For example, at 25 °C and a CO_2 concentration of 90 %, the adsorption capacity of cellulose nanocrystals modified with 20% by weight of MEA and 20% by weight of DEA increased from 0.25 to 1.52, and 0.58 mmol/g, respectively. This demonstrates that amine modification significantly enhances CO_2 adsorption performance, particularly at higher CO_2 concentrations. The increase in adsorption capacity resulting from the modification of adsorbents with amines is due to the enhanced chemical adsorption facilitated by this modification. The reason for this is that the interactions between the basic sites of the amine groups and CO_2 molecules, which act as a Lewis acid, are stronger than the van der Waals forces responsible for the physical adsorption of CO_2 molecules onto the adsorbent. This

stronger chemical interaction significantly improves the overall adsorption performance of the amine-modified adsorbents (Zhang et al., 2019). The results indicate that, under all conditions, modifying cellulose nanocrystals with MEA leads to a greater improvement in CO_2 adsorption capacity compared to modification with DEA. For instance, at 25 °C and a CO_2 concentration of 90 %, the adsorption capacity increased by approximately 6 times with MEA modification, while under the same conditions, the adsorption capacity increased by about 2.3 times with DEA modification. This superiority can be attributed to the fact that MEA is a smaller molecule than DEA and exhibits less steric hindrance, which is related to its molecular structure. The smaller size and reduced steric hindrance of MEA allow for more efficient interaction with CO_2 molecules, thereby enhancing the adsorption capacity more effectively (Ahmed et al., 2016). In other words, a primary amine is attached to only one alkyl group and two hydrogen atoms, and since the MEA molecule is smaller, the steric hindrance for binding to CO_2 molecules is minimal. However, secondary and tertiary amines are attached to two and three alkyl groups, respectively, and have larger

molecular structures. Therefore, the size of the amines increases depending on the type of amine and the number of alkyl groups attached to the nitrogen atom. This difference in molecular size and steric hindrance explains why primary amines like MEA exhibit higher CO_2 adsorption efficiency compared to secondary amines like DEA. The smaller size and lower steric hindrance of MEA facilitate better access and stronger interactions with CO_2 molecules. This increase in size leads to greater steric hindrance, reducing the likelihood of CO_2 molecules approaching the nitrogen atom to form a covalent bond. As a result, primary amines exhibit a higher affinity for CO_2 molecules and, consequently, a higher

adsorption capacity. Steric hindrance occurs when the large size of the groups within a molecule prevents chemical reactions that could otherwise occur in smaller, similar molecules. Additionally, MEA has a shorter chain compared to DEA, which results in DEA having a higher molecular weight than MEA. This means that for a given weight percentage of both amines, a larger amount of MEA can cover the adsorbent surface compared to DEA, leading to a greater increase in adsorption capacity for MEA than for DEA (Ahmed et al. 2016). In Fig. 4 a schematic of the reaction between a CO_2 molecule and an amine, leading to the formation of carbamate, is presented.

Fig. 4 The reaction mechanism of: a) MEA, and b) DEA amines with CO_2

$$2(CH_2CH_2OHNH_2) \;+\; CO_2 \;\rightleftharpoons\; [CH_2CH_2OHNH_3]^+ \;+\; [CH_2CH_2OHNHCOO]^-$$

$$2[(CH_2CH_2OH)_2NH] \;+\; CO_2 \;\rightleftharpoons\; [(CH_2CH_2OH)_2NH_2]^+ \;+\; [(CH_2CH_2OH)_2NCOO]^-$$

3.2.3 Effect of amine loading

The data obtained on the effect of loading both amines on CO_2 adsorption capacity at concentrations of 10, and 90 % CO_2, as well as at temperatures of 25 and 50 °C, are presented in Fig. 5. For example, at 25 °C and a CO_2 concentration of 10 %, the CO_2 adsorption capacity for cellulose nanocrystals modified with 10 and 20 % by weight of MEA was found to be 0.57, and 0.65 mmol/g, respectively. Similarly, at 25 °C and a CO_2 concentration of 10 %, the CO_2 adsorption capacity for cellulose nanocrystals modified with 10, and 20 wt% of DEA was 0.27, and 0.14 mmol/g, respectively. These results highlight the influence of amine loading and type on the CO_2 adsorption performance of the modified cellulose nanocrystals. The investigations revealed that at a CO_2 concentration of 90 %, increasing the loading of both amines at both temperatures resulted in an increase in adsorption capacity. At a CO_2 concentration of 10%, increasing the loading of MEA at both temperatures led to an increase in adsorption capacity. However, while increasing the loading of DEA up to 10 wt% enhanced the adsorption capacity at both temperatures, further increasing the loading to 20 wt% caused a 48 % decrease in adsorption capacity at 25 °C and a 44 % decrease at 50 °C. This suggests that excessive loading of DEA may negatively impact its adsorption performance, particularly at lower CO_2 concentrations. At a CO_2 concentration of 90 %, the high level of contact between the CO_2 gas and the adsorbent means that increasing the amine

loading leads to an increase in adsorption capacity. This is because, under these conditions, the adsorption process involves a combination of chemical and physical adsorption. As the amine loading increases, the chemical adsorption component also increases, and due to the high level of interaction with CO_2, the overall adsorption capacity improves. However, at a CO_2 concentration of 10 %, the same process occurs for both amines with increasing loading, but for DEA, increasing the loading from 10 to 20 wt% results in the opposite effect. This suggests that excessive loading of DEA at lower CO_2 concentrations may hinder adsorption performance, possibly due to steric hindrance or reduced accessibility of active sites. This is because DEA, compared to MEA, has bulkier molecules. As a result, increasing the loading of DEA leads to more spaces being occupied by the amine, which reduces the physical adsorption capacity. Consequently, the overall adsorption process, which is a combination of chemical and physical adsorption, is diminished. Although chemical adsorption increases with higher amine loading, it is not sufficient to compensate for the decline in physical adsorption. This is why the adsorption capacity of cellulose nanocrystals modified with DEA decreases when the amine loading is increased from 10 to 20 %. The steric hindrance caused by the larger DEA molecules limits the accessibility of active sites, ultimately reducing the overall adsorption performance (Sepahvand et al., 2020; Wu et al., 2018).

Fig. 5 Diagram of the influence of MEA and DEA amines loading on CO_2 adsorption capacity at two temperatures of 25 and 50 °C and concentrations of: a) 90 vol.% CO_2 and b) 10 vol.% CO_2
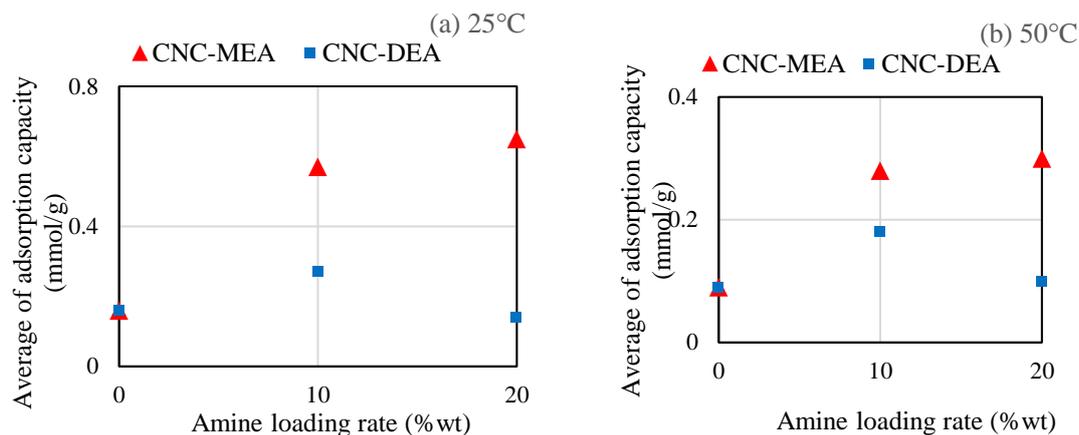
3.2.4 Effect of temperature

With an increase in temperature from 25 to 50 °C, the adsorption of CO_2 by all adsorbents decreases at both concentrations. For example, the adsorption capacity of pure cellulose nanocrystals at a CO_2 concentration of 90% decreases from 0.25 to 0.15 mmol/g. The adsorption of carbon dioxide on the adsorbent is an exothermic process. According to Le Chatelier's principle, as the temperature increases, the equilibrium shifts toward reduced adsorption to counteract the effect of the temperature rise. In other words, the system tends to release excess energy by reducing adsorption. As the temperature increases, the kinetic energy of CO_2 molecules also increases, leading to a higher rate of collisions with the adsorbent surface. Consequently, CO_2 molecules desorb more quickly from the adsorbent surface. This reduces the residence time of CO_2 molecules on the adsorbent surface, ultimately decreasing the adsorption capacity. Therefore, due to the exothermic nature of CO_2 adsorption, it is preferable to conduct this process at lower temperatures to ensure that the CO_2 adsorption capacity of the adsorbents does not significantly decrease (Sepahvand et al., 2020; Xu et al. 2021).

4. Conclusion

This study aimed to enhance the performance of cellulose nanocrystals by modifying them with amines and investigated the adsorption capacity of cellulose nanocrystals before and after amine modification. The findings of this research can be summarized as follows:

1. The adsorption capacity is positively correlated with the concentration of CO_2. Specifically, at a temperature of 25 °C, an increase in CO_2 concentration from 10 to 90 vol.% results in the adsorption capacity of the 20 wt% MEA-modified sample rising from 0.65 to 1.52 mmol/g.

2. The enhancement of the adsorbent's performance and adsorption capacity is achieved through the modification with both MEA and DEA amines.

3. An increase in the amine loading and a reduction in temperature can lead to an enhancement in adsorption capacity.

4. Under all experimental conditions, the adsorbent modified with MEA amine exhibited a superior adsorption capacity than that modified with DEA amine. Notably, at 25 °C and a CO_2 concentration of 90 vol.%, the adsorption capacity with MEA amine modification increased approximately 6-fold, whereas the DEA amine modification resulted in a 2.3-fold increase under identical conditions.

Statements and Declarations
Data availability

The data used in this research are provided in the text of the article.

Conflicts of interest

The author of this paper declared no conflict of interest regarding the authorship or publication of this paper.

Author contribution

O. Mohammadi Moinalzoafa: Methodology, Investigation, Conceptualization, Writing Original Draft; M. Tahmasebpoor: Supervision, Review-Editing.

References

Ahmed, S., Ramli, A., & Yusup, S. (2016). CO_2 adsorption study on primary, secondary and tertiary amine functionalized Si-MCM-41. *Int. J. Greenhouse Gas Control, 51*, 230-238. DOI: 10.1016/j.ijggc.2016.05.021

Asgharizadeh, K., Tahmasebpoor, M., Azimi, B., & Imani, M. (2024). Fluidity comparison of biomass-derived activated carbon and TiO(OH)$_2$ and its improving toward promoted low-temperature CO_2 capture in gaseous medium. *Chem. Eng. Res. Design, 202*, 23-37. DOI: 10.1016/j.cherd.2023.12.019

Bains, P., Psarras, P., & Wilcox, J. (2017). CO_2 capture from the industry sector. *Prog. Energy Combust. Sci., 63*, 146-172. DOI: 10.1016/j.pecs.2017.07.001

Chakravartula Srivatsa, S., & Bhattacharya, S. (2018). Amine-based CO_2 capture sorbents: A potential CO_2 hydrogenation catalyst. *J. CO_2 Util., 26*, 397-407. DOI: 10.1016/j.jcou.2018.05.028

Das, D., Agarwal, T., & Biswal, A. K. (2023). A review on different methods of CO_2 capture, separation and utilization. *Brazil. J. Chem. Eng.*, 1-19. DOI: 10.1007/s43153-023-00378-z

Doan, Q. K. T., & Chiang, K. Y. (2023). Facile synthesis of polyethyleneimine-modified cellulose nanocrystal/silica hybrid aerogel for CO_2 adsorption. *Environ. Sci. Pollut. Res.*, 1-18. DOI: 10.1007/s11356-023-28359-2

Dziejarski, B., Serafin, J., Andersson, K., & Krzyżyńska, R. (2023). CO_2 capture materials: a review of current trends and future challenges. *Mater. Today Sustain.*, 100483. DOI: 10.1016/j.mtsust.2023.100483

Gautam, A., & Mondal, M. K. (2023). Review of recent trends and various techniques for CO_2 capture: Special emphasis on biphasic amine solvents. *Fuel, 334*, 126616. DOI: 10.1016/j.fuel.2022.126616

Grishkewich, N., Mohammed, N., Tang, J., & Tam, K. C. (2017). Recent advances in the application of cellulose nanocrystals. *Current Opinion Colloid Inter. Sci., 29*, 32-45. DOI: 10.1016/j.cocis.2017.01.005

Imani, M., Tahmasebpoor, M., & Sánchez-Jiménez, P. E. (2023). Metal-based eggshell particles prepared via successive incipient wetness impregnation method as a promoted sorbent for CO_2 capturing in the calcium looping process. *J. Environ. Chem. Eng., 11*(5), 110584. DOI: 10.1016/j.jece.2023.110584

Kenarsari, S. D., Yang, D., Jiang, G., Zhang, S., Wang, J., Russell, A. G., & Fan, M. (2013). Review of recent advances in carbon dioxide separation and capture. *RSC Adv., 3*(45), 22739-22773. DOI: 10.1039/C3RA43965H

Koshani, R., Eiyegbenin, J. E., Wang, Y., & van de Ven, T. G. (2022). Synthesis and characterization of hairy aminated nanocrystalline cellulose. *J. Colloid Inter. Sci., 607*, 134-144. DOI: 10.1016/j.jcis.2021.08.172

Lai, J. Y., Ngu, L. H., & Hashim, S. S. (2021). A review of CO_2 adsorbents performance for different carbon capture technology processes conditions. *Greenhouse Gases: Sci. Technol., 11*(5), 1076-1117. DOI: 10.1002/ghg.2112

Lourenço, M. A. O., Fontana, M., Jagdale, P., Pirri, C. F., & Bocchini, S. (2021). Improved CO_2 adsorption properties through amine functionalization of multi-walled carbon nanotubes. *Chem. Eng. J., 414*, 128763. DOI: 10.1016/j.cej.2021.128763

Muthami, J., Wamea, P., Pitcher, M., Sakib, M. N., Liu, Z., Arora, S., Sheikhi, A. (2021). Hairy cellulose nanocrystals: from synthesis to advanced applications in the water–energy–health–food nexus. in Cellulose nanoparticles: synthesis and manufacturing. *Royal Soc. Chem., 1*, 1-37. DOI: 10.1039/9781788019545-00001

Nobarzad, M. J., Tahmasebpoor, M., Imani, M., Pevida, C., & Heris, S. Z. (2021). Improved CO_2 adsorption capacity and fluidization behavior of silica-coated amine-functionalized multi-walled carbon nanotubes. *J. Environ. Chem. Eng., 9*(4), 105786. DOI: 10.1016/j.jece.2021.105786

Nunes, L. J. (2023). The rising threat of atmospheric CO_2: a review on the causes, impacts, and mitigation strategies. *Environ., 10*(4), 66. DOI: 10.3390/environments10040066

Salvi, B. L., & Jindal, S. (2019). Recent developments and challenges ahead in carbon capture and sequestration technologies. *SN Appl. Sci., 1*(8), 885. DOI: 10.1007/s42452-019-0909-2

Sepahvand, S., Jonoobi, M., Ashori, A., Gauvin, F., Brouwers, H., Oksman, K., & Yu, Q. (2020). A promising process to modify cellulose nanofibers for carbon dioxide (CO_2) adsorption. *Carbohyd. Polymer., 230*, 115571. DOI: 10.1016/j.carbpol.2019.115571

Tahmasebpoor, M., Iranvandi, M., Heidari, M., Azimi, B., & Pevida, C. (2023). Development of novel waste tea-derived activated carbon promoted with SiO_2 nanoparticles as highly robust and easily fluidizable sorbent for low-temperature CO_2 capture. *J. Environ. Chem. Eng., 11*(5), 110437. DOI: 10.1016/j.jece.2023.110437

Wu, Y., Zhang, Y., Chen, N., Dai, S., Jiang, H., & Wang, S. (2018). Effects of amine loading on the properties of cellulose nanofibrils aerogel and its CO_2 capturing performance. *Carbohyd. Polymer., 194*, 252-259. DOI: 10.1016/j.carbpol.2018.04.017

Xu, J., Jia, P., Wang, X., Xie, Z., Chen, Z., & Jiang, H. (2021). The aminosilane functionalization of cellulose nanocrystal aerogel via vapor-phase reaction and its CO_2 adsorption characteristics. *J. Appl. Polymer Sci., 138*(35), 50891. DOI: 10.1002/app.50891

Yang, D., Zhang, H., Wang, Z., Zhao, S., & Li, J. (2022). Changes in anthropogenic particulate matters and resulting global climate effects since the Industrial Revolution. *Int. J. Climatol., 42*(1), 315-330. DOI: 10.1002/joc.7245

Zhang, T., Zhang, Y., Jiang, H., & Wang, X. (2019). Aminosilane-grafted spherical cellulose nanocrystal aerogel with high CO_2 adsorption capacity. *Environ. Sci. Pollut. Res., 26*, 16716-16726. DOI: 10.1007/s11356-019-05068-3

Zhu, W., Chen, M., Jang, J., Han, M., Moon, Y., Kim, J., & Kim, J. (2024). Amino-functionalized nanocellulose aerogels for the superior adsorption of CO_2 and separation of CO_2/CH_4 mixture gas. *Carbohyd. Polymer., 323*, 121393. DOI: 10.1016/j.carbpol.2023.121393

Zhu, W., Yao, Y., Zhang, Y., Jiang, H., Wang, Z., Chen, W., & Xue, Y. (2020). Preparation of an amine-modified cellulose nanocrystal aerogel by chemical vapor deposition and its application in CO_2 capture. *Indust. Eng. Chem. Res., 59*(38), 16660-16668. DOI: 10.1021/acs.iecr.0c02687