



# Piperazine-modified activated carbon as a novel adsorbent for CO<sub>2</sub> capture: modeling and characterization

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## Abstract

In this study, activated carbon and piperazine-modified activated carbon adsorbents were prepared and used for CO<sub>2</sub> adsorption. The effect of various parameters including adsorbent particle size, adsorbent amount, piperazine weight percent, pressure, and temperature were investigated on the CO<sub>2</sub> adsorption capacity. The adsorbents were characterized using nitrogen adsorption/desorption isotherms and FTIR analyses. The results showed that the adsorption capacity decreases with temperature increasing and increases with pressure increasing. In addition, the surface modification of activated carbon improved the CO<sub>2</sub> adsorption capacity more than the unmodified adsorbent, and the highest CO<sub>2</sub> adsorption was obtained 203.842 mg/g at 25 °C and 8 bar. Additionally, to determine the adsorbent behavior, CO<sub>2</sub> adsorption experimental data were fitted by isotherm and kinetic models. CO<sub>2</sub> adsorption isotherm modeling was studied up to 8 bar at 25 °C, and kinetic modeling was investigated up to 85 °C at 6 bar. The results show that Hill isotherm model and Elovich kinetic models have a good agreement with the adsorption data. Finally, thermodynamic modeling was carried out for modified and unmodified adsorbents, and enthalpy, entropy, and Gibbs free energy changes of adsorption for piperazine-modified activated carbon at 25 °C and 6 bar obtained 17.078 kJ/mol, − 0.039 kJ/mol.K, and − 5.318 kJ/mol, respectively.

**Keywords** Activated carbon · CO<sub>2</sub> adsorption · Piperazine · Isotherm · Kinetic · Thermodynamic

## Introduction

The increasing of CO<sub>2</sub> production in the environment necessitated more studies and experiments on the removal of this pollutant. Available technologies for CO<sub>2</sub> capture are cryogenic distillation, membrane separation, physical and chemical absorption, and adsorption by solid adsorbents (Amiri et al. 2017; Estalkhazir et al. 2018; Ghaemi et al. 2009; Penchah et al. 2021c; Rezakazemi et al. 2017). Adsorption in porous solids such as activated carbon is an attractive alternative technology to overcome the technological and economic constraints of the mentioned technologies (Hauchhum and Mahanta 2014; Najafi et al. 2020; Penchah et al. 2020;

Shafeeyan et al. 2015). Generally, adsorption technology is widely considered for gas purification due to its flexibility and efficiency (Penchah et al. 2019, 2021a). Activated carbon is a high microporous material with a large surface area and attractive carbon-based materials to remove gas-phase pollutants (Etemad et al. 2015; Zhua et al. 2014).

In recent years, adsorbent modification has been considered to enhance its essential properties, which include cation or ion exchange within the porous material or the functionalization of pore structure as well as saturation with amines (Najafi et al. 2021; Niknafs et al. 2015; Penchah et al. 2021b; Shafeeyan et al. 2010; Shafeeyan et al. 2015; Sreńscek-Nazzal et al. 2016). To improve the CO<sub>2</sub> adsorption capacity, different modifications can be made in the form of physical or chemical processes. Due to corrosion, low stability, and high cost of amine materials, alkaline bases have been used to improve the performance of porous adsorbents (Amiri et al. 2017; Taheri et al. 2019; Yong et al. 2001). One of the possible cases for adsorbing CO<sub>2</sub> from the air is using of strong bases such as calcium hydroxide, potassium hydroxide, and sodium hydroxide (Mohammad et al. 2019; Naeem et al. 2016; Shafeeyan et al. 2010).

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Tan et al. studied the efficiency of modified activated carbon from coconut shells with NaOH to adsorb carbon dioxide in an adsorption column (Tan et al. 2014). Casco et al. introduced and presented activated carbon from oilfields and modified that with KOH, for adsorbing CO<sub>2</sub> at atmospheric pressure (168 mg/g at 298 K) and high pressure (1500 mg/g at 298 K and 4.5 Mpa) (Casco et al. 2014). Deng et al. reported on activated carbon from peanut shells and sunflower seeds to adsorb carbon dioxide. They optimized the activation of activated carbon with a ratio of about 1 KOH/carbon. The CO<sub>2</sub> adsorption capacity of the activated carbon of peanut shell and sunflower shell obtained 1.54 mg/g and 1.46 mg/g at 298 K and 0.15 bar, respectively (Deng et al. 2015).

Nazzal et al. investigated the correction of active carbon to improve the CO<sub>2</sub> adsorption capacity by activating with KOH, ZnCl<sub>2</sub>, and K<sub>2</sub>CO<sub>3</sub>. The maximum carbon dioxide adsorption was obtained 14.44 mmol/g at 313 K and 40 bar (Sreńscek-Nazzal et al. 2016). In 2001, Ro'denas et al. modified active carbon by activation with NaOH and KOH. The results show that chemical activation with NaOH can be successfully used to produce activated carbon with high surface area and microporous volume; also, pore volume by KOH activation was higher than that with NaOH (Lillo-Rodenas et al. 2001).

Huang et al. worked on CO<sub>2</sub> capture using metal-organic framework NH<sub>2</sub>-MIL-101 that was grafted with amine. NH<sub>2</sub>-MIL-101 is a standard metal-organic framework adsorbent with a chromium basis that is synthesized and modified with tetraethylenepentamine (TEPA) by wet impregnation method. As a result, NH<sub>2</sub>-MIL-101 is modified with 50 %wt. So this amine-grafted adsorbent with a high CO<sub>2</sub> capture capacity is found as an efficient material for CO<sub>2</sub> adsorption (Huang et al. 2016).

Pino et al. modified activated carbon with two amines, polyethyleneimine (PEI) and tetraethylenepentamine (TEPA), using wet impregnate method. The effects of amine amount (from 10 to 70 %wt.), the concentration of CO<sub>2</sub> in the feed, temperature and gas hourly space velocity were investigated on the CO<sub>2</sub> adsorption capacity. The best sorption capacity was 6.90 mmol/g, when the adsorbent was modified with 70 wt.% of supported TEPA at 70 °C and the stream contained 80 vol.% of CO<sub>2</sub> (Pino et al. 2016).

Gholami et al. carried out a series of experiments in order to find the optimum condition for grafting 3-[2-(2-aminoethylamino) ethylamino] propyltrimethoxysilane (TRI) on bi-modal porous structure MCM-41(BPS-MCM-41). The optimum conditions for the modified adsorbent was obtained 85 °C, 0.3 cc/g, and 1.5 cc/g for temperature, water to support ratio, and aminosilane to support ratio, respectively. The BPS-MCM-41 grafted with amine achieves 2.31 mmol/g adsorption capacity under this condition (Gholami et al. 2015).

Bezerra et al. (2014) studied the CO<sub>2</sub> adsorption on Zeolite 13X as solid adsorbent which was functionalized with amine groups. They found that more loading of amine to the

adsorbent caused more decrease in micropore volume and adsorbent was pore-blocking with monoethanol amine (MEA). According to this study, one part of loaded MEA is bonded to the zeolite structure covalently, and excess MEA is adsorbed physically that can be desorbed by raising the temperature more than MEA boiling point (Bezerra et al. 2014).

Chiang et al. investigate the material properties of activated carbon fibers (ACFs) modified with potassium hydroxide (KOH) or tetraethylenepentamine (TEPA) to determine the CO<sub>2</sub> adsorption capacities of adsorbents. The results showed that the KOH-modified ACFs exhibited a great deal of pore volume and a specific surface area of 1565 m<sup>2</sup>/g. Also, the CO<sub>2</sub> uptakes at 1 atm and 25 °C on KOH-activated ACFs reached 2.74 mmol/g (Chiang et al. 2019).

Acevedo et al. prepared activated carbon from lignocellulosic material, African palm shells, by chemical impregnation of the precursor with solutions of cupric nitrate at five different concentrations. The results showed that the BET surface areas varied between 473 and 1361 m<sup>2</sup>/g and micropore volume between 0.18 and 0.51 cm<sup>3</sup>/g and the CO<sub>2</sub> adsorption capacity was obtained between 103 and 217 mg/g (Acevedo et al. 2020).

Giraldo et al. studied on CO<sub>2</sub> adsorption by chemically modified activated carbon with nitric acid and ammonium aqueous. The results show that the activated carbons had a BET surface area between 634 and 865 m<sup>2</sup>/g, with a micropore volume between 0.25 and 0.34 cm<sup>3</sup>/g. CO<sub>2</sub> adsorption capacity at 273 K and 1 bar was achieved between 205 and 333 mg/g (Giraldo et al. 2020).

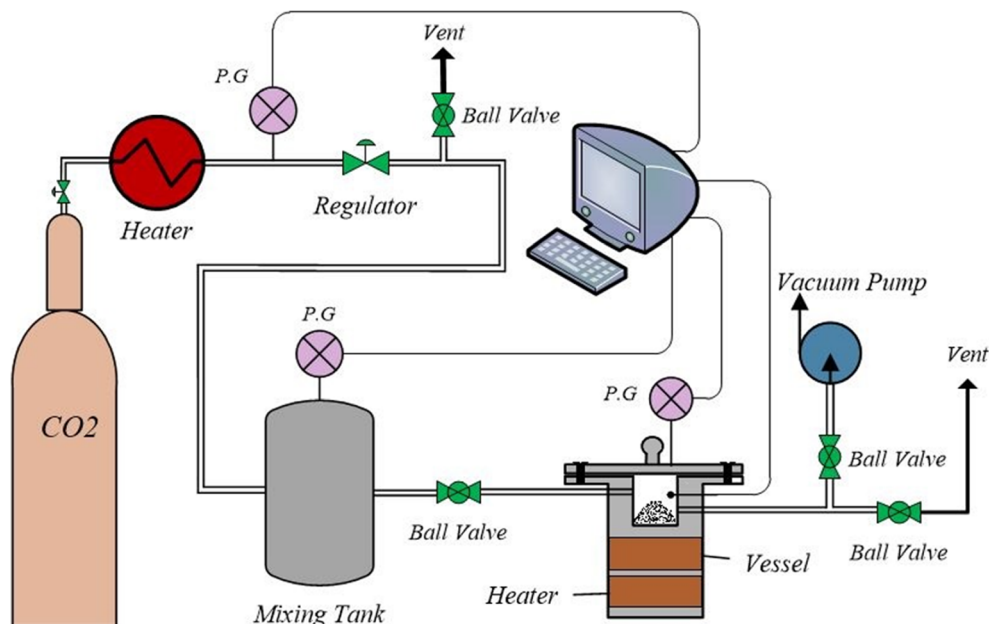
Considering the previous researches, CO<sub>2</sub> adsorption, because of its advantages, was an appropriate method to omit CO<sub>2</sub> as pollutant. In this study, activated carbon because of its high adsorption capacity and low price was chosen as the base adsorbent for modifying. Improvement of the activated carbon for CO<sub>2</sub> adsorption was carried out by piperazine that is an organic compound and consists of a six-membered ring containing two nitrogen atoms. Also, unmodified and modified adsorbent characterizations were carried out by FTIR and BET analyses. The effect of various parameters such as adsorbent particle size, adsorbent amount, piperazine amount, piperazine weight percent, pressure, and temperature were investigated on the CO<sub>2</sub> adsorption capacity. Finally, isotherm, kinetic, and thermodynamic modeling were accomplished using the CO<sub>2</sub> adsorption system.

## Materials and methods

### Materials

Activated carbon was chosen as adsorbent and was prepared from BASF Company of Germany. Piperazine with the IUPAC name of hexahydropiprazine as the amine that

Fig. 1 Adsorption setup



consists of a six-membered ring containing two nitrogen atoms and methanol with the 99.99% purity as solvent was used and prepared from Merck. Furthermore, CO<sub>2</sub> with purity of 99.99% was bought from Sablan Gas Co., Iran.

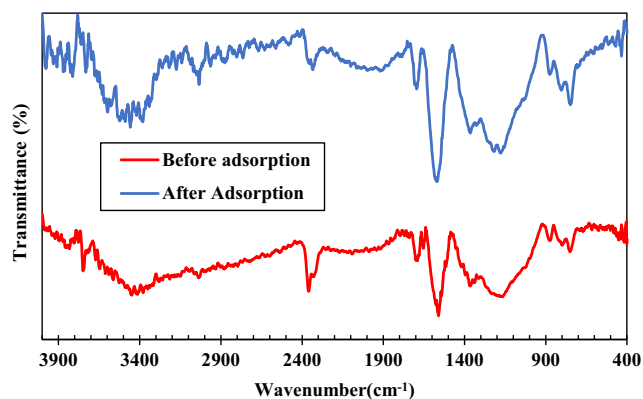
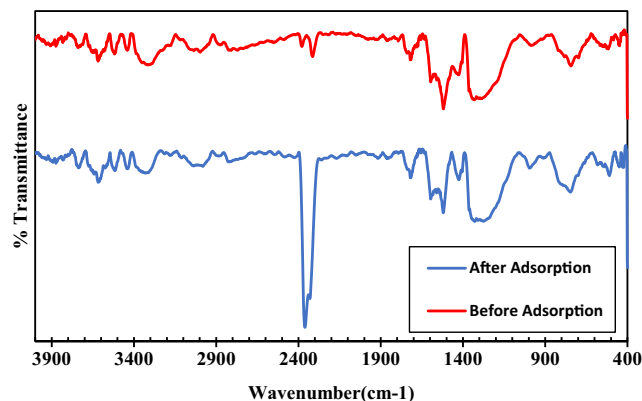
### Adsorbent modification

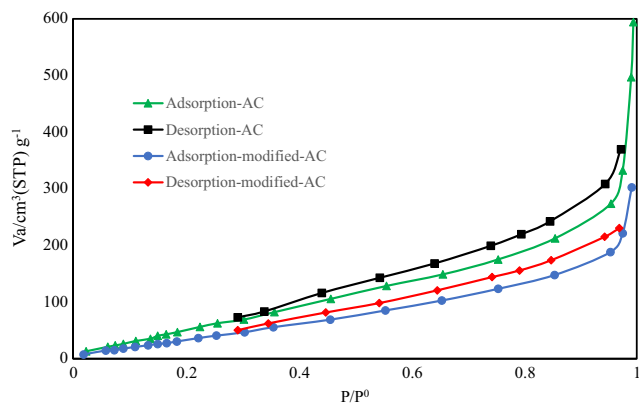
For the modification of the activated carbon with piperazine, at first, the adsorbent was washed by nitric acid to create C-O-O-H group on activated carbon surface to link with piperazine under reflux condition with concentrated nitric acid for 24 h. The adsorbent was washed with ionized distilled water until its pH reached to 5, and then, it was dried under 100°C for 24 h in the oven. 1 %wt piperazine in different amount of methanol (5, 10, 20, and 60 ml) was used for modifying of 1 g of activated carbon. Each sample was stirred for 6 h at temperature of 45 °C. After that, it was dried at temperature of 75 °C for 24 h in oven. The adsorption experiment was done for each sample. Finally, the modified sample with 5 ml of piperazine

solution in methanol had the best result. It was assumed that in other loading of piperazine in methanol, this amount of solution was the optimum amount. So, 5 ml of varied weight percentage of piperazine in methanol solvent was prepared, and the effect of weight percentage of piperazine (1–4%) was investigated. The adsorbent that was modified with 5 ml of solution with 2 %wt of piperazine in methanol had the maximum adsorption capacity. So, investigating the effect of the temperature and the pressure on the adsorption capacity was continued with modified adsorbent with 5 ml of 2 %wt of piperazine in methanol.

### Adsorbent characterization

Surface structure, morphology, and porosity properties of adsorbent were accomplished by nitrogen adsorption and desorption at 77 K at a pressure of 106.65 kPa (Micromeritics, Model ASAP 2020, USA). FTIR spectroscopy analysis was

Fig. 2 FTIR spectra of activated carbon before and after CO<sub>2</sub> adsorptionFig. 3 FTIR spectra of piperazine-modified activated carbon before and after CO<sub>2</sub> adsorption



**Fig. 4** Nitrogen adsorption-desorption diagram at 77 K for activated carbon and modified activated carbon

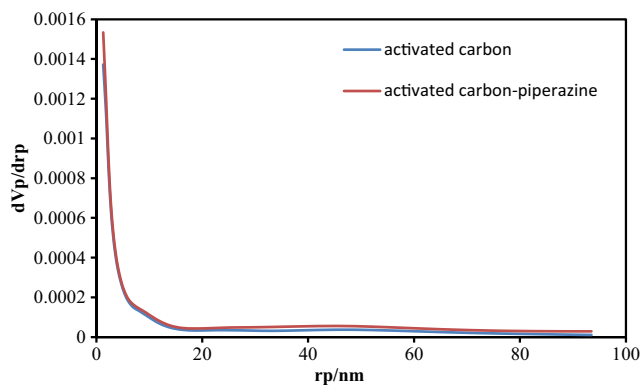
performed using a spectrometer (Perkin Elmer, Model 2000 FTIR, USA) to identify surface functional groups of modified and unmodified activated carbon.

**Adsorption setup**

An adsorption batch system was designed for CO<sub>2</sub> adsorption capacity measurement (Fig. 1). As it is shown, the setup included a stainless steel batch vessel (with the height of 9 cm, internal radius of 3 cm, and internal volume of 255 cm<sup>3</sup>), CO<sub>2</sub> gas cylinder, pressure adjusting valves, electrical heater, pressure and temperature transmitter, and a computer. The vessel was able to control the main parameters that are effective in CO<sub>2</sub> adsorption like temperature, pressure, and the amount of adsorbent. At the first of each experiment, gas temperature was set, and then, the sample of adsorbent was put in the vessel. After that, related valves and pressure gauge set the initial pressure of CO<sub>2</sub> in the vessel. After setting the pressure and reaching the temperature to the set point amount, the experiment started and in the computer; temperature and pressure were saved versus the time. The amount of adsorption capacity was calculated using the real gas law by measuring the loss of pressure due to CO<sub>2</sub> adsorption (Eqs. 1 and 2).

**Table 1** BET-analysis properties for activated carbon and modified activated carbon with piperazine

Parameter	Activated carbon	Modified activated carbon
S <sub>BET</sub> (m <sup>2</sup> /g)	713.49	620.73
V <sub>t</sub> (cm <sup>3</sup> /g)	0.5732	0.4991
V <sub>p</sub> (cm <sup>3</sup> /g)	0.65	0.51
Mean pore diameter (nm)	2.49	2.42



**Fig. 5** BJH plot for activated carbon and modified activated carbon

$$q = \frac{m_i - m_f}{w} = \left( \frac{VM_w}{Rw} \right) \left( \frac{P_i}{Z_i T_i} - \frac{P_f}{Z_f T_f} \right) \tag{1}$$

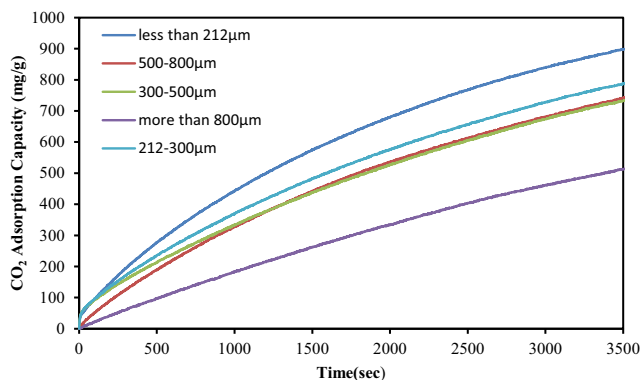
$$Z = 1 + \frac{BP}{RT} \tag{2}$$

where *i* and *f* subscripts refer to initial and final conditions. P, T, V, Z, M<sub>w</sub>, R, w, B, and m are pressure, temperature, reactor volume, compressibility factor, gas molecular weight, universal gas constant, mass of adsorbent, virial second coefficient, and mass of adsorbed gas, respectively.

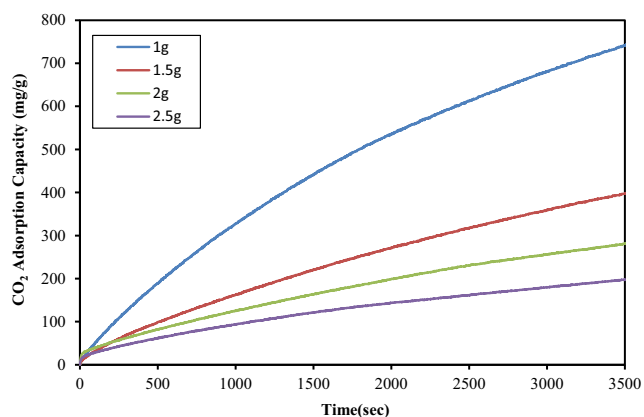
**Result and discussion**

**Characterization**

The FTIR spectra of activated carbon and piperazine-modified activated carbon before and after CO<sub>2</sub> adsorption are presented in Figs. 2 and 3. According to Fig. 2, in the range of 1300–1400 cm<sup>-1</sup>, the vibration of C-O bond and, at the point of 1600 cm<sup>-1</sup>, the vibration of C=O (aromatics) bond were noticeable and observed. In the range of 1700–1800 cm<sup>-1</sup>, the vibration of C=O (carboxylic acid) bond was evident. As it is shown in Fig. 2, the FTIR spectra are developed after adsorption (Li et



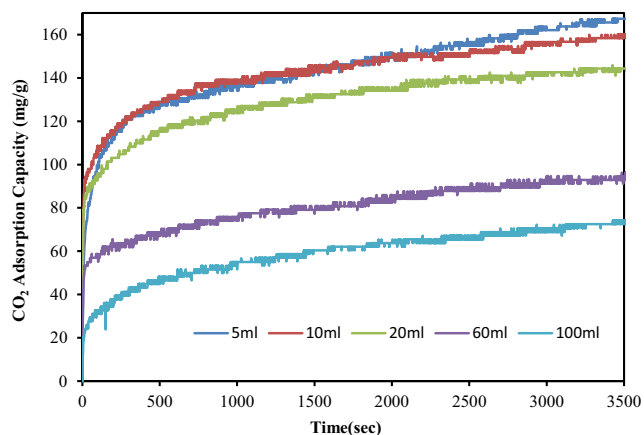
**Fig. 6** Effect of particle size on CO<sub>2</sub> adsorption using activated carbon



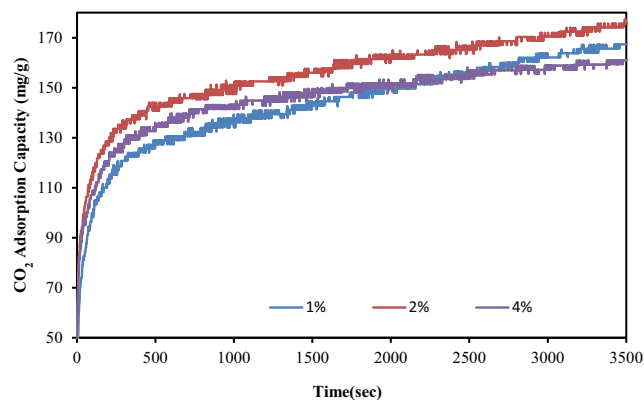
**Fig. 7** Effect of adsorbent amount on CO<sub>2</sub> adsorption using activated carbon

al. 2016). According to Fig. 3, in the range of 1260–1340 cm<sup>-1</sup>, the vibration of C-N bond and, in the range of 1430–1650 cm<sup>-1</sup>, the vibration of C-C bond are shown. Also the vibration of C-H and N-H bonds is visible in the range of 2750–3080 cm<sup>-1</sup> and 3220–3500 cm<sup>-1</sup>, respectively. These vibrations prove the modification of activated carbon surface by piperazine (Li et al. 2016).

BET analysis (Fig. 4) was used to determine the surface area and porosity properties of activated carbon and modified activated carbon by N<sub>2</sub> adsorption-desorption at 77 K. Surface area, total volume, pore volume, and mean pore diameter are reported in Table 1. According to adsorption-desorption curve of activated carbon and adapting it with IUPAC isotherms, this type of curve is isotherm type III, and this type of isotherm shows that the adsorption of the first layer was lower than other layers. Considering the mean pore diameter equal to 10.49 nm, it was found that this adsorbent is mesoporous. BJH curve shows that the highest amount of adsorption is in the range of mesoporous pores (Ruthven and Reyes 2007). Adsorption-desorption curve of modified activated carbon is like of activated carbon. Considering the mean pore diameter equal to 2.49 and 2.42 nm for activated carbon and modified



**Fig. 8** Effect of piperazine modifying solution on CO<sub>2</sub> adsorption capacity



**Fig. 9** Effect of piperazine weight percent in methanol solution on CO<sub>2</sub> adsorption capacity

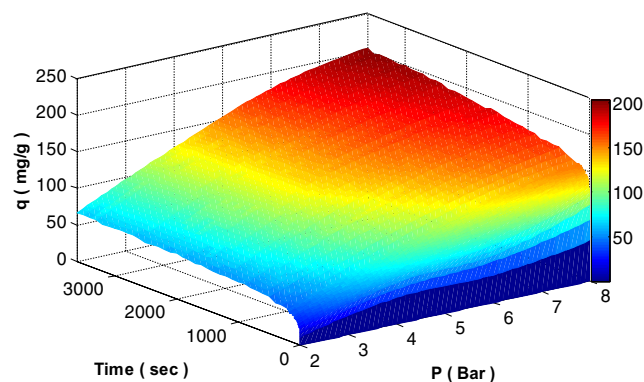
activated carbon with piperazine, respectively, both adsorbents are mesoporous. Figure 5 represents that for both activated carbon and its modified sample, the most adsorption has taken place in mesoporous region and also between particles with 0–20 nm radius.

### Effect of parameters on CO<sub>2</sub> adsorption capacity

In order to investigate the adsorbent particle size in the CO<sub>2</sub> adsorption capacity, different adsorbent sizes are divided by mesh, and adsorption is tested as shown in Fig. 6. According to this figure, it is shown that increasing the particle size decreases the adsorption capacity.

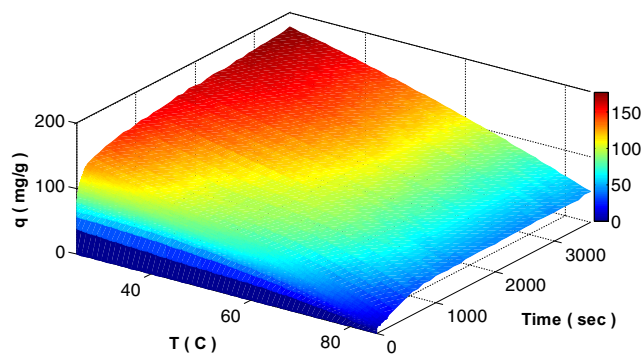
In order to evaluate the effect of adsorbent amount on CO<sub>2</sub> adsorption capacity, different amounts of adsorbent are tested as shown in Fig. 7. In the experiments which were done with different amounts of adsorbent, it was found that by increasing the amount of adsorbent, the adsorption capacity decreases.

In order to modify the activated carbon by piperazine, the effect of the amount of piperazine in methanol (modifying solution) was investigated. Hence, various amounts of piperazine-methanol solution (5–10–20–60–100 ml) were considered for modifying of 1 g of activated carbon adsorbent at 25 °C and 6 bar (Fig. 8). The results show that by increasing



**Fig. 10** Effect of pressure on CO<sub>2</sub> adsorption using piperazine-modified activated carbon





**Fig. 11** Effect of temperature on CO<sub>2</sub> adsorption using piperazine-modified activated carbon

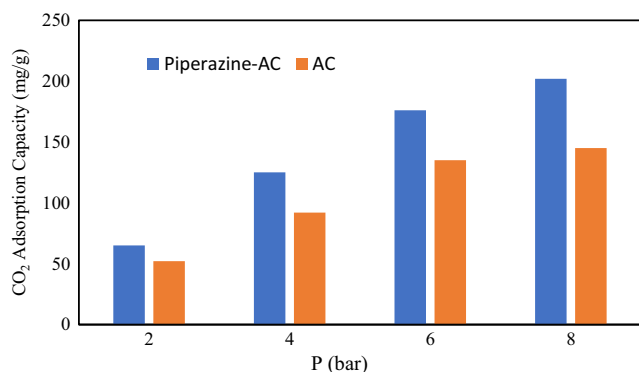
the amount of piperazine in methanol, the adsorption capacity decreases. So in the following experiments, 5 ml of piperazine-methanol solution was used for modifying of 1 g of activated carbon adsorbent (Norouzbahari et al. 2015).

In order to evaluate the weight percent of piperazine in the modifying solution on adsorption capacity, 1 g of activated carbon was modified with 5 ml of 1, 2, and 4 wt.% of piperazine. CO<sub>2</sub> adsorption capacity is plotted in Fig. 9, and as a result, it is shown that optimum CO<sub>2</sub> adsorption capacity was obtained using the adsorbent sample which was modified with 2 %wt of piperazine in methanol.

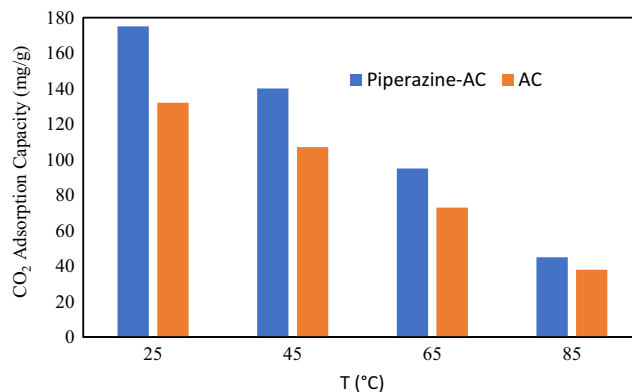
For investigating the effect of pressure on CO<sub>2</sub> adsorption capacity, the adsorption experiments were done with 1 g of piperazine-modified activated carbon in various pressure (2–8 bar) at temperature of 25 °C. As it is shown in Fig. 10, by increasing the pressure, the CO<sub>2</sub> adsorption capacity increases.

For investigating the effect of temperature on adsorption capacity, the adsorption experiments were done at pressure of 6 bar and temperature range of 25 up to 85 °C. According to, Fig. 11, CO<sub>2</sub> adsorption capacity decreases by increasing the temperature.

Figures 12 and 13 show the comparison of CO<sub>2</sub> adsorption capacity between activated carbon and piperazine-modified activated carbon at various pressure and temperature. According to these figures, piperazine-modified activated



**Fig. 12** Effect of pressure on CO<sub>2</sub> adsorption for activated carbon and piperazine-modified activated carbon



**Fig. 13** Effect of temperature on CO<sub>2</sub> adsorption for activated carbon and piperazine-modified activated carbon

carbon has a higher adsorption capacity than unmodified activated carbon.

### Adsorption isotherm

In order to study the amount of adsorbed material on the adsorbent surface and its relation to the gas pressure or the dissolved concentration at a constant temperature, conventional equations for the adsorption isotherms are applied. The isotherm shows the CO<sub>2</sub> adsorption in the adsorbent samples as a pressure function. In physical adsorption, molecules adsorbed to all parts of the adsorbent surface are limited to the number which are compressed in each molecular layer. Langmuir and Freundlich isotherm models are related to adsorption in low temperature and are appropriate for physical adsorption (Langmuir 1916). The Langmuir isotherm model is the best description for physical adsorption because it is

**Table 2** Isotherm model parameters of CO<sub>2</sub> adsorption at 25 °C

Models	Parameter	Activate carbon	Modified activated carbon
Langmuir $q_e = (q_L k_L P_e) / (1 + k_L P_e)$	$q_L$	414.74	609.92
	$k_L$	0.076	0.070
	$R^2$	0.991	0.996
	$R^2$	0.987	0.995
Freundlich <sub>1</sub> $q_e = k_F P_e^{1/n_F}$	$k_F$	33.257	45.03
	$n_F$	1.327	1.293
	$R^2$	0.987	0.995
	$R^2$	0.989	0.969
Dubinin-Radushkevich $q_e = q_m e^{-\beta \epsilon^2}$	$q_m$	158.66	214.22
	$\beta$	1.219	1.119
	$\epsilon$	0.640	0.668
	$R^2$	0.989	0.969
Hill $q_e = q_H P_e^{n_H} / (K_H + P_e^{n_H})$	$q_H$	234.32	399.87
	$K_H$	9.403	10.283
	$n_H$	1.384	1.202
	$R^2$	0.994	0.998

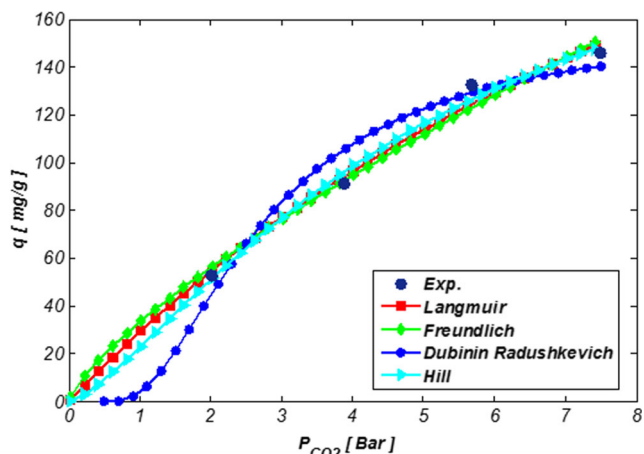


Fig. 14 Experimental data and isotherm models for CO<sub>2</sub> adsorption using activated carbon at 25 °C

limited to one layer on the surface of adsorbent, while Freundlich model indicates a physisorption process. The value of  $n_F < 1$  in Freundlich model indicates that CO<sub>2</sub> adsorption is a chemical process, while the value of  $n_F > 1$  is the indicator of a physical process (Ko and Schmidt 1974).

Dubinin-Radushkevich isotherm model give useful information about energy parameters. In these models,  $\epsilon$  and  $\beta$  are adsorption energy and the heat of adsorption, respectively. If  $9 < \epsilon < 16$  kJ/mol, the adsorption is Schmidtchemisorption; otherwise if  $\epsilon < 8$  kJ/mol, the adsorption is physisorption (Ko and Schmidt 1974).

According to the results which are obtained from CO<sub>2</sub> adsorption isotherm on activated carbon (Fig. 14) and piperazine-modified activated carbon (Fig. 15), it is obvious that Hill model has the best correlation coefficient, so this model has the best conformity with experimental data (Table 2). As a result, CO<sub>2</sub> adsorption using activated carbon and modified activated carbon is physical and limited to one layer. Also the maximum amount of CO<sub>2</sub> adsorption using activated carbon and modified activated carbon according to Langmuir model

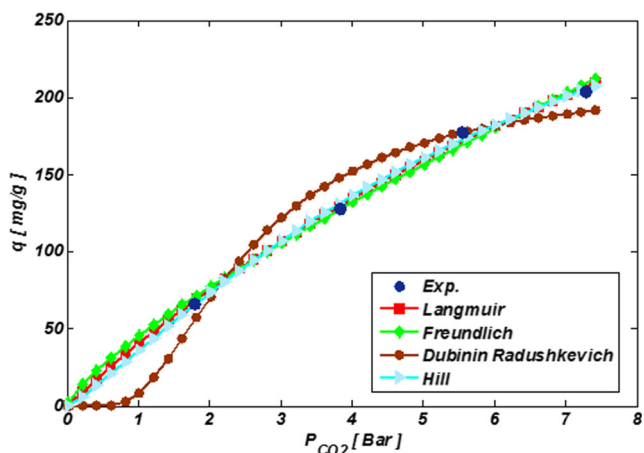


Fig. 15 Experimental data and isotherm models for CO<sub>2</sub> adsorption using piperazine-modified activated carbon at 25 °C

Table 3 Adsorption kinetic model parameters for CO<sub>2</sub> adsorption

Kinetic model	Model parameter	Activated carbon			Modified activated carbon				
		25 °C	45 °C	65 °C	85 °C	25 °C	45 °C	65 °C	85 °C
First order	$q_e$	125.48	98.04	74.98	39.74	159.688	128.73	92.64	44.21
	$k_f$	0.026	0.009	0.010	0.0021	0.01074	0.0056	0.0067	0.0023
	$R^2$	0.932	0.867	0.932	0.9915	0.89663	0.815	0.92605	0.993
Second order	$q_e$	128.46	103.482	77.356	45.97	167.43	138.73	97.25	50.08
	$k_s$	3e-4	1e-4	3e-4	6e-5	1e-4	6e-5	0.00013	6e-5
	$R^2$	0.965	0.947	0.968	0.972	0.96046	0.912	0.976	0.988
Elovich	$\alpha$	1.06194	1.8546	2.6745	4.0178	775.9545	856.568	986.325	1123.12
	$\beta$	15.668	9.6587	6.9947	3.1258	7.8072	6.0258	5.1269	4.1985
	$R^2$	0.989	0.991	0.996	0.994	0.991	0.981	0.985	0.995
Rate controlling	$K_{rc}$	3.5758	2.3258	1.6987	1.0014	2.7985	2.0158	1.7598	1.3658
	$R^2$	0.759	0.724	0.657	0.614	0.698	0.652	0.694	0.635

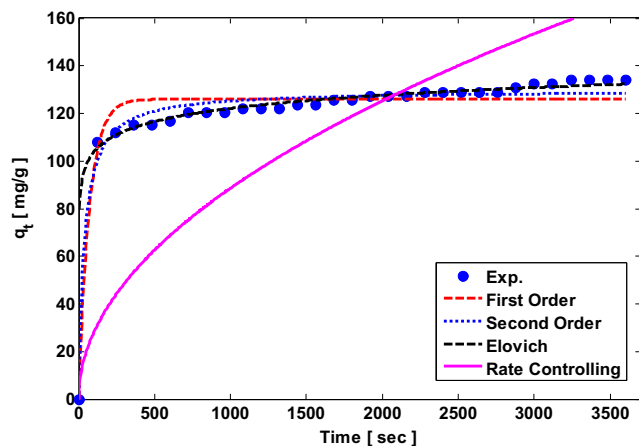


Fig. 16 Experimental data and kinetic models for CO<sub>2</sub> adsorption using activated carbon at 25 °C

can be 414.74 mg/g and 609.92 mg/g, respectively. Considering the high Dubinin-Radushkevich correlation coefficient, it is possible to confirm that CO<sub>2</sub> adsorption by activated carbon and modified activated carbon is a physical process according to its high average energy equal to 0.640 kJ and 0.668 kJ, respectively.

### Adsorption kinetic

Kinetic modeling can be used to determine the equilibrium and kinetic constants. Predicting the adsorption rate is the most important factor in the design of process systems and control the time required for the adsorption process. Due to the complexity of predicting kinetic parameters, a conventional approach involves matching the experimental data to a set of fixed models and choosing the best model (Foo and Hameed 2010; Ho 2004). Experimental data and kinetic models of CO<sub>2</sub> adsorption using activated carbon and piperazine-modified activated carbon are presented in Figs. 16 and 17, respectively, and kinetic model parameters are listed in

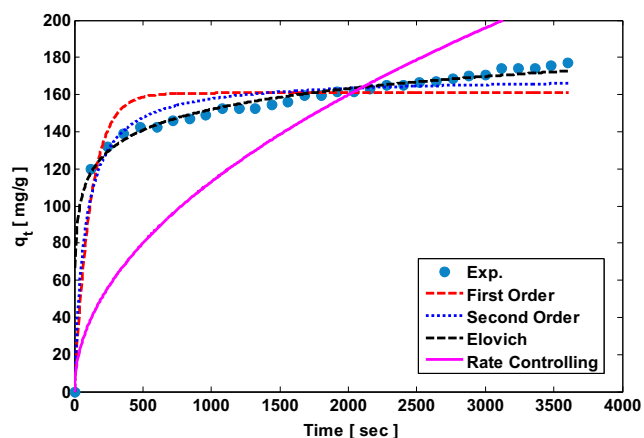


Fig. 17 Experimental data and kinetics models for CO<sub>2</sub> adsorption using modified activated carbon at 25 °C

Table 4 Thermodynamic parameters for CO<sub>2</sub> adsorption on activated carbon and modified activated carbon

Adsorbent	P <sub>CO2</sub> (bar)	ΔH (kJ/mol)	ΔS (kJ/mol.-K)	ΔG (kJ/mol)	25 °C	45 °C	65 °C	85 °C
Activated carbon	6	15.655	-0.037	-4.486	-3.737	-2.987	-2.23812	
Modified activated carbon	6	17.078	-0.039	-5.318	-4.529	-3.740	-2.9511	

Table 3. According to the results, the Elovich kinetic model has the best agreement with the experimental data.

### Absorbent thermodynamic

It is necessary to consider both energy and entropy factors to evaluate the feasibility and spontaneity of a process. Each of the thermodynamic parameters has its significance, and their values and symbols can be help to understand how the adsorption process is performed (Ghaemi et al. 2009; Niknafs et al. 2015). According to Fig. 18, the values of ΔH° and ΔS° are obtained from the slope (ΔH°/R) and the intercept (ΔS°/R) of the line from the plot of ln(k<sub>d</sub>) versus 1/T. This figure shows that modified activated carbon has better CO<sub>2</sub> adsorption capacity than activated carbon. Figure 18 expresses that by increasing the temperature, CO<sub>2</sub> adsorption capacity decreases. So, activated carbon has better CO<sub>2</sub> adsorption capacity in low temperature (Zhang et al. 2014). ΔH, ΔS, and ΔG of activated carbon and modified activated carbon are listed in Table 4. It is considered that the positive value of ΔS and negative value of ΔG show that the adsorption process is spontaneous.

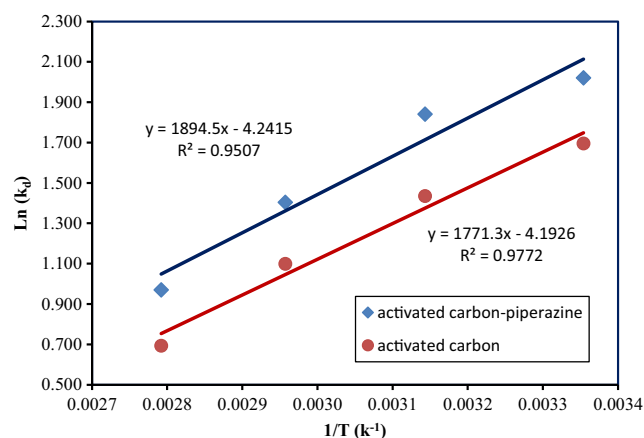


Fig. 18 Plot of Ln K<sub>d</sub> vs 1/T for adsorption of CO<sub>2</sub> on activated carbon and piperazine-modified activated carbon



## Conclusion

In this study, CO<sub>2</sub> adsorption was investigated, and the effect of several effective parameters such as the amount and particle size of adsorbent, temperature, and pressure for adsorption with activated carbon in addition to the amount of modifier solution and the weight percentage of piperazine in methanol for adsorption with modified activated carbon was done. The results show that increasing the amount of adsorbent decreases the CO<sub>2</sub> adsorption capacity; also increasing particle size leads to decrease CO<sub>2</sub> adsorption capacity. By increasing temperature and pressure, CO<sub>2</sub> adsorption capacity decreases and increases respectively. Modification of activated carbon surface shows an enhancement in CO<sub>2</sub> adsorption capacity for both parameters of temperature and pressure more than unmodified activated carbon. Experimental data show that the optimum amount of piperazine in methanol for modification of 1 g of activated carbon is 5 ml, and increasing the amount of solution for this amount of activated carbon decreases the CO<sub>2</sub> adsorption capacity. By investigating different weight percentage of piperazine in methanol, it is found that the optimum weight percentage is 2 %wt.

For investigating adsorption isotherm, Langmuir, Freundlich, Dubinin-Radushkevich, and Hill models and, for investigating adsorption kinetic, first-order, second-order, Elovich, and rate controlling models were used. The results show that the experimental adsorption data by activated carbon and modified activated carbon meets Hill isotherm model. Kinetic modeling shows that Elovich model has a good agreement with the experimental data for activated carbon and piperazine-modified activated carbon and the controlling step is diffusion in boundary layer. Thermodynamic studies of CO<sub>2</sub> adsorption with modified activated carbon show that,  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  are 17.078 kJ/mol,  $-0.039$  kJ/mol.K, and  $-5.318$  kJ/mol at 25 °C, respectively. In addition, for both CO<sub>2</sub> adsorption processes, by increasing the temperature, CO<sub>2</sub> adsorption capacity decreases, and both adsorbents have maximum adsorption capacity in low temperature.

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**Data availability** All data generated or analyzed during this study are included in the manuscript.

## Declarations

**Ethical approval and consent to participate** Not applicable.

**Consent to publish** Not applicable.

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