ABSTRACT:

Introduction: Large amount of CO₂ emissions from combustion of fossil fuels will lead to environmental crisis. One method for removing CO₂ is adsorption by modified adsorbents. In this study, mesoporous silica, MCM-41, modified by monoethanolamine, was used for CO₂ removal from exhaust gases of methane combustion.

Materials and methods: MCM-41 was synthesized by using tetraethyl orthosilicate (TEOS) as silica source, according to classic method. MCM-41 was modified with different amounts (25, 50 and 75 %) of monoethanolamine (MEA) by impregnation method. Amine modified MCM-41 were used in filters and adsorption experiments were conducted to determine adsorption capacity by passing CO₂ in different concentrations (2000 -5000 ppm), different flow rates (100 – 400 ml/min), and different temperatures (25, 55 and 90 °C) individually. CO₂ was analyzed by ND IR CO₂ analyzer.

Results: Time to reach adsorption equilibrium of carbon dioxide on to examined adsorbents was about 10 h. Maximum carbon dioxide adsorption capacity for MCM-41 was determined 5.0 mg/g. Maximum adsorption rate was due to MCM41- MEA 50 % with adsorption capacity of 50 mg/g for CO₂ concentration of 5000 ppm. By increasing temperature from 25 to 90 °C, adsorption capacity was increased only about 10 %. Maximum CO₂ adsorption capacity was achieved at gas flow rate of 100 mL/min, and by increasing flow rate, capacity was decreased. By increasing amine loaded on MCM, CO₂ adsorption capacity was decreased.

Conclusions: Modification of MCM-41 using monoethanol amine by simple impregnation method will result in the production of adsorbsents with a higher absorption capacity for carbon dioxide removal. By using amine modified MCM-41, it is possible to remove carbon dioxide from exhaust gases of methane combustion.

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INTRODUCTION

Global warming and climate change have arisen due to the massive release of greenhouse gas emissions from industrial activity in the twentieth century. Carbon dioxide is one of the most important greenhouse gases that enters more than others to the earth’s atmosphere. According to official reports, carbon dioxide emissions in 2015 were more than 35 gigaton [1]. The current concentration of carbon dioxide in
the atmosphere is more than 400 ppm, which is considerably higher than before the industrial revolution (280 ppm), and the trend of increasing its concentration with steep gradients continues. About half of the carbon dioxide released into the earth’s atmosphere comes back to the ground from paths such as absorption in the ocean and absorption by the plants, but its remained that amount in the air is so high therefore, it causes an annual increase of about 2 ppm in the earth’s atmosphere [2]. Each ppm of carbon dioxide in the atmosphere is equivalent to 2.1 gigaton of pure carbon and 7.7 gigaton of carbon dioxide [3]. Therefore, to reduce carbon dioxide emissions to the atmosphere, the use of renewable energy sources, the use of alternative fuels and the development of clean technology for use in the current century are planned. But with all these efforts, fossil fuels will still be used in the decades to come. Therefore, efforts are being made to reduce carbon dioxide emissions into the atmosphere and to stabilize atmospheric carbon dioxide concentrations using carbon dioxide adsorption and carbon dioxide storage (CCS) techniques proposed by the researchers [4 – 7]. Different technologies have been proposed for removal of carbon dioxide, including: physical absorption [8, 9] chemical absorption and [10, 11], physical adsorption [12, 13]. But the application of these methods to remove carbon dioxide from combustion gases in industries has its own limitations. Chemical absorption by alkanolamine solutions are in the group of the best carbon dioxide removal technologies has been proposed before 2030 [14], but it has limitations such as high corrosion, high energy consumption for recovery, and the need for a huge amount of absorbent material [15]. The method of adsorption of carbon dioxide by adsorbent at high pressure and then its desorption by reducing pressure is one of the methods. In this method, the rate of adsorption from the gas phase to the adsorbent pore is 3 times greater than the transition to the liquid in the chemical absorption method [16]. However, the influence of the adsorbents of this group (such as activated carbon and zeolite) by other gases, and consequently the reduction of carbon dioxide separation factor, is one of the limitations of this method. Another problem is the reduction of the adsorption capacity at low pressures (0.1 and 0.2 atmospheres) [14, 17, 18], as well as the rapid reduction of adsorption capacity at ambient temperatures [9]. One of the solutions proposed to eliminate problems in the adsorption method is the adsorbent modification with amine-containing compounds [21]. Amine modification of the adsorbent is done by two methods including amine impregnation and amine grafting [21, 22], which has been considerably focused on the method of impregnation due to its ease of conduction and the increase in adsorption capacity [23]. In addition, toxic solvents such as toluene, which are used in the traditional method of making MCM-41 grafted with amine, are not required in this method [24, 25]. In the present study, CO₂ adsorption capacity of MCM-41 before and after modification with monoentanolamine under normal conditions of methane combustion has been compared. Parameters such as temperature, amine loading, inlet CO₂ concentration, feed flow rate, as well as application of nitrogen gas in adsorbent regeneration have been investigated.

MATERIALS AND METHODS

Materials
Cetyltrimethylammonium bromide (CTAB), Tetraethoxysilane (TEOS), Monoethanolamine and Ammonium hydroxide were analytical grade from Merck company.

Synthesis of MCM – 41
2.4 g Cetyltrimethylammonium bromide (CTAB) was added to 120 g of deionized water. For complete mixing, a magnetic stirrer was used. When the solution has become clear, 10 ml of 25% aqueous ammonia was added, stirred for 10 min. Then 10 ml of tetraethoxysilane (TEOS) was added and again stirred overnight. The synthesized white precipitate after filtration and washing with ethanol and distilled water, finally was
calcined at 550 °C for 5 h [26].

**Synthesis of MCM - 41 impregnated with MEA**

Certain volumes of MEA were added to certain amounts of methanol and were stirred for 30 min (volumes of MEA and amounts of methanol were calculated according to amounts of amine (25 %, 50 % and 75 %) which were considered for loading on MCM - 41). After stirring, for each mixture, separately, 3 g MCM - 41 was added and they were sealed and vigorously stirred overnight. Finally obtained products were filtered and the remaining solids were dried at 50 °C for 8 h [23].

**CO₂ adsorption measurements**

First, combustion gases of methane were collected by the collection hopper, then were directed by connection tube to the adsorbent column (adsorbent column was a copper tube by 20 cm height and 1.5 cm diameter). In order to set up the air flow on specified values, adsorbent column was connected by a tube to a rotameter and then to the suction pump. Finally, the concentration of CO₂, which left the adsorbent column, was measured by TES 1370 ND IR CO₂ analyzer. In order to compare the adsorption capacity of MCM - 41, MCM - 41 - MEA- 25 %, MCM- 41- MEA- 50 % and MCM- 41- MEA- 75 %, first, evacuation of the adsorbents from impurities was carried out through nitrogen gas injection, and then 3 g of each adsorbent was placed in copper tube serves as filter. Finally, the CO₂ adsorption capacity of each adsorbent was measured in different temperatures, inlet CO₂ concentrations and feed flow rates. Temperatures were provided by placing the filter in the water bath equipped with a thermostat, feed gas flow rates were set up by rotameter, and the inlet CO₂ concentrations were provided by changing the flame position.

CO₂ adsorption capacity for each adsorbent, is calculated by following Eq. (1):

\[
q = \frac{(C_0 - C_e)(\text{ppm}) \times Q(\text{l/min}) \times t(\text{min}) \times 44000(\text{mg mol}^{-1})}{W(\text{g}) \times 24.45 \times 10^6}
\]

q (mg/g): CO₂ adsorption capacity; C₀ (ppm): inlet CO₂ concentration; Cₑ (ppm): outlet CO₂ concentration at saturation time; Q (l/min): flow rate; W (g): adsorbent weight.

Since low inlet CO₂ concentrations, prolonged the adsorbent saturation process, in order to better show saturation process during long period of adsorption, CO₂ adsorption amount by each adsorbent was calculated at the end of each hour, and simultaneously the CO₂ adsorption capacity of each adsorbent was reported by calculating the

![Fig. 1: The schematic diagram of the system used in the study](http://japh.tums.ac.ir)
cumulative adsorption at the end of the saturation time [6, 27, 28].

**Adsorbent regeneration method**

After the saturation process, regeneration experiments were carried out through injection of nitrogen gas into each saturated adsorbent for 3 h.

**RESULTS AND DISCUSSION**

**Effect of Amine loading on adsorption capacity**

By using unmodified MCM-41, carbon dioxide adsorption capacity was a little amount, as shown in Fig. 2. It was stated by Le et al. (2014) that, in physical adsorbents such as activated carbon and zeolite, water molecules and other gases, are adsorbed on adsorbent pores in competition with carbon dioxide, so carbon dioxide separation factor of these type of adsorbents are very low [29, 30], also It was claimed by Goyal et al. (2005) that, in activated carbon, adsorption is physical and adsorbate molecules are accumulated in several layers on the adsorbent surface by van der Waals forces. At high relative humidity conditions, pores on the surface of activated carbon are filled with water through capillary effect [31]. But in chemical adsorption, according to Nikpey et al. (2012), due to the electron sharing between adsorbate molecules and adsorbent surfaces, which led to the formation of a stronger bond in comparison with van der Waals forces, adsorption, is only limited to specific groups of...
molecules which are able to share electrons [32]. Effect of amine loading on adsorption capacity of modified MCM- 41 have also been shown in Fig. 3. In a study conducted by Song et al., it has reported that when PEI loading on MCM- 41 is higher than 30 wt. %, pore filling with PEI will begin. At PEI loading of 50 wt. %, MCM- 41-PEI with an adsorption capacity of 246 mg/g, showed the highest adsorption capacity, which was 30 times more than MCM- 41 and 2.3 times more than pure PEI [33, 19]. Also it has been noted that the pore volume of MCM- 41 is 1 ml/g and the PEI density is about 1 g/ml, so the maximum PEI that can be loaded into the MCM- 41 pores is 50 %. When the PEI loading was less than 50 wt. %, impregnation with PEI doesn’t occur for all MCM- 41 pores, so the adsorption capacity decreases. And when the PEI loading exceeds 50 wt. %, PEI is coated on the outer surface of the MCM- 41, so the MCM- 41 pore volume and subsequently the adsorption capacity of adsorbent, decreases [32, 33].

**Effect of temperature on adsorption capacity**

As shown in Fig. 4, increase in temperature, increases the adsorption capacity, but on the contrary, the adsorbent saturation process is shortened. Direct relationship between temperature and adsorption capacity of modified MCM- 41 is also illustrated in Fig. 5.

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**Fig. 4. CO₂ adsorption process by MCM- 41- MEA- 25 % in 25, 55 and 90 °C**

**Fig. 5. Effect of temperature on CO₂ adsorption capacity in MCM- 41- MEA- 25%, MCM- 41- MEA- 50 % and MCM- 41- MEA- 75 %**
It was reported by Klepel et al. (2005), that CO$_2$ adsorption by 13X zeolite modified with 50% monoethanolamine, at 75 °C is higher than 50 °C. because at 50 °C, a slight physical adsorption with chemical adsorption occur on active sites, but at 75 °C, due to the full predominance of chemical adsorption, more adsorption sites are activated [34, 35]. It was also claimed by Jadhav et al. (2007), that when the adsorption temperature increases, chemical adsorption will predominant, and amine-modified zeolite, adsorbs more carbon dioxide in comparison with unmodified zeolite [36]. Siriwardane et al. (2001) reported similar results and also noted that increasing temperature, will shortened adsorption process [37].

**Effect of inlet CO$_2$ concentration on adsorption capacity**

Direct relationship between inlet CO$_2$ concentration and adsorption capacity of MCM-41-MEA-50% in 25 °C is illustrated in Fig. 6.

In some studies, it was reported that, for unmodified and modified bone ash, increasing concentration of formaldehyde, reduces the saturation time, but the adsorption capacity increases. They claimed that, by increasing inlet concentration of formaldehyde, more formaldehyde molecules would be available for the adsorbent so the rate of emission and adsorption of adsorbates on the adsorbent pores, increases, accordingly adsorption process is shortened [38, 39]. In other studies it was stated that, by increasing concentration of toluene from 100 to 200 g/l, the length of mass transfer in activated carbon, increases by 10% [40]. Similar results have been reported by other researchers on acetone vapor [41]. Also, as shown in Fig. 6, increasing inlet CO$_2$ concentration produced from combustion of methane, increases moisture content. Many researchers referred to the positive effect of moisture on carbon dioxide capture by MCM-41-PEI and noted that the CO$_2$ adsorption capacity in wet conditions is more than dry conditions, although in the presence of moisture, water is also adsorbed. Xu’s team pointed out that the interaction between carbon dioxide and PEI may change in the presence of water. In dry conditions, the main reaction between amine and carbon dioxide leads to the formation of carbamate which limits the CO$_2$ adsorption capacity to 1 mol of carbon dioxide per 2 moles of amine group.

\[
\text{CO}_2 + 2 \text{RNH}_2 \leftrightarrow \text{NH}_4^+ + \text{R}_2\text{NCOO}^- \\
\text{CO}_2 + 2 \text{R}_2\text{NH} \leftrightarrow \text{R}_2\text{NH}_2^+ + \text{R}_2\text{NCOO}^- \\
\text{CO}_2 + 2 \text{R}_3\text{N} \leftrightarrow \text{R}_4\text{N}^+ + \text{R}_2\text{NCOO}^-
\]

But in the presence of moisture, carbamate, after reaction with carbon dioxide and water, forms bi-
carbonate and amine group. Amine group, independently, after reaction with carbon dioxide and water, forms bicarbonate. So in the presence of water, 1 mole of amine groups can adsorb 1 mol of carbon dioxide.

\[
\begin{align*}
\text{R}_2\text{NCOO}^- + 2 \text{H}_2\text{O} + \text{CO}_2 & \iff \text{R}_2\text{NH}_2^+ + 2 \text{HCO}_3^- \\
\text{CO}_2 + \text{RNH}_2 + \text{H}_2\text{O} & \iff \text{RNH}_3^- + \text{HCO}_3^- \\
\text{CO}_2 + \text{R}_2\text{NH} + \text{H}_2\text{O} & \iff \text{R}_2\text{NH}_2^+ + \text{HCO}_3^- \\
\text{CO}_2 + \text{R}_3\text{N} + \text{H}_2\text{O} & \iff \text{R}^+\text{NH}_3^- + \text{HCO}_3^- \ [42]
\end{align*}
\]

So under normal conditions of methane combustion, increasing the adsorption capacity due to increased \(\text{CO}_2\) concentration, can be attributed to the simultaneous effect of both high inlet \(\text{CO}_2\) concentration and moisture content parameters.

**Effect of feed flow rate on adsorption capacity**

As illustrated in Fig. 7, by increasing flow rate, \(\text{CO}_2\) adsorption capacity decreases. Many researchers noted that, in low flow, enough time for the chemical interaction between carbon dioxide and the modified adsorbent bed, is provided. On the contrary, by increasing in flow rate, more \(\text{CO}_2\) molecules will leave adsorbent column without interacting with the adsorbent molecules in column [43]. Other researchers reported a similar results on activated carbon modified with (AMP 2-) amino- 2- methyl- 1- propanol [44].

**Regeneration results**

In this study, 3 h nitrogen injection for the regeneration process didn’t show satisfactory results. Many researchers reported that, for unmodified activated carbon, 4 h nitrogen injection at 60 ml/min at room temperature, leads to adsorbent regeneration. But this method is not suitable for activated carbon modified with AMP and MEA, and significant reduction in adsorption capacity occurs. Because in unmodified activated carbon, carbon dioxide molecules only are adsorbed on the adsorbent pores through the weak van der Waals forces, but in modified activated carbon, strong chemical interaction occurs between the carbon dioxide and modified adsorbent bed, so high energy is needed for bond breaking [45]. Similarly, it was claimed by other researchers that, in unmodified adsorbents, after regeneration process, a slight reduction in adsorption capacity is observed but on the contrary, in modified adsorbent, a significant reduction in adsorption capacity occurs [44].

But some researchers used a different method and achieved satisfactory results. They placed the saturated MCM- 41- MEA in a vacuum drying oven at 120 °C for 8 h and then repeated \(\text{CO}_2\) adsorption experiments. Until the fifth cycle, they didn’t observe any changes on adsorption process.

![Fig. 7. Effect of feed flow rate on \(\text{CO}_2\) adsorption capacity of MCM- 41- MEA- 50 % in 25°C](http://japh.tums.ac.ir)
but from the sixth cycle, the changes were clearly seen. Eventually, the research team introduced MCM-41 modified with monoethanolamine, as a sustained adsorbent during various adsorption-desorption operations.

CONCLUSIONS

Results showed that impregnation of MCM-41 by monoethanolamine increased CO$_2$ adsorption capacity significantly. Temperature did not play an important role in the adsorption of carbon dioxide on examined sorbents. Optimum amine required for modification of MCM-41 was fifty percent by weight. Modified MCM-41 by monoethanolamine can be used as an adsorbent in removing carbon dioxide from exhaust gases of methane combustion.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

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ETHICAL CONSIDERATIONS

This study does not have ethical considerations.

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