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Original Research Article

Flexible and porous geopolymer filter of metakaolin/ mica/talc (MMT) containing nanosilica for CO_2 absorption

Ashraf Heiadaripour[1]*, Parsa Seddiqi[2]

[1] *Department of Chemistry, Khajeh Nasir Toosi University of Technology, Tehran, Iran*
[2] *Research Center Karaj Moallem, Karaj, Iran*

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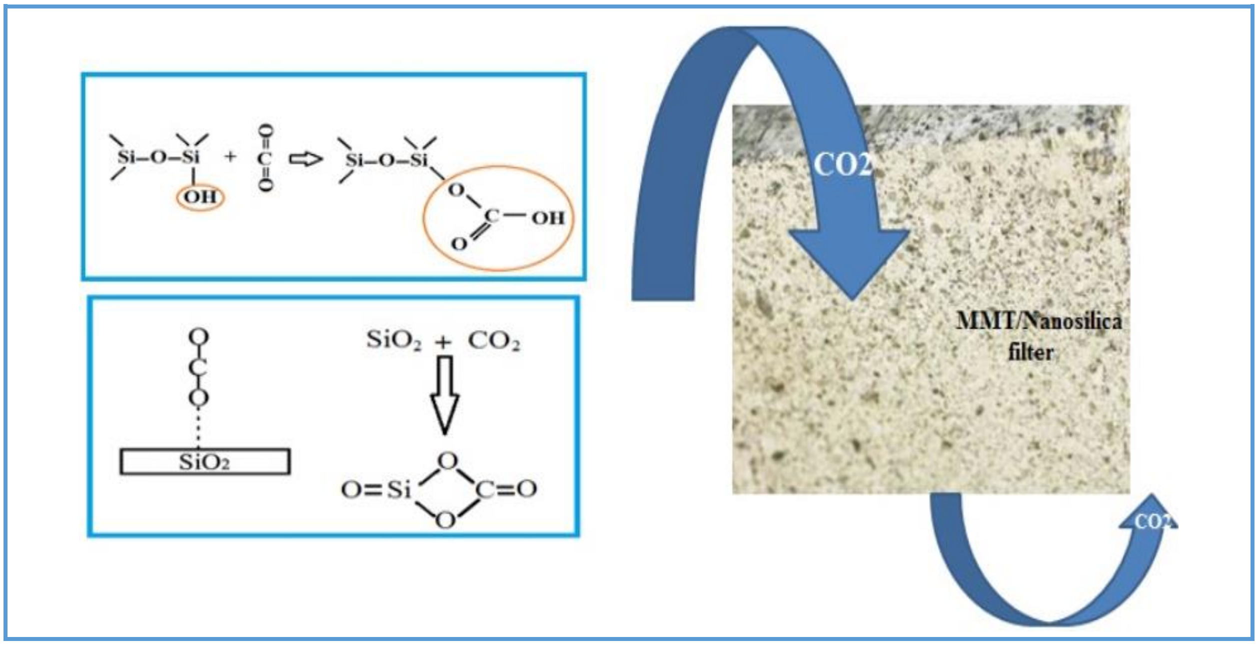
ABSTRACT

In this study, a geopolymer composite has been prepared using metakaolin/mica/talc (MMT) and modified with nanosilica (MMT/Nanosilica) which can be used for the carbone dioxide (CO_2) absorption in filters. The MMT geopolymer were restructured by the alkaline activating agent (NaOH) in the presence of the foaming agent, Heydrogen Peroxide (H_2O_2). The foaming agent of H_2O_2 creates an amorphous and porous geopolymeric composite by producing oxygen. To check the nanosilica effectiveness in the optimal CO_2 absorption in the MMT filter, the different amounts of nanosilica were added to the MMT composite. Since geopolymers do not have sufficient flexibility and porosity, polyurethane foam impregnated with polyvinyl alcohol (PVA) was used as a template for the MMT mixture which has high flexibility, malleability, and porosity. The amount of CO_2 absorption on the MMT/Nanosilica filter was estimated by the pH measurement of alkaline solution into which CO_2 is finally introduced.The results showed the high capability of MMT/Nanosilica filter in CO_2 absorption. The optimal amount of nanosilica was determined in the MMT geopolymer. Fourier transform infrared spectroscopy (FTIR) admited the effective CO_2 absorption. Likewise, the images of the field emission scanning electron microscope (FESEM) showed the cavity structure with micron and nano dimensions.

Corresponding author, email: ashrafheidaripour@gmail.com (A. Heidaripour).

Graphical Abstract



Introduction

On polluted days in capital cities and industrial centers, the amount of air pollution is often related to particles whose concentration varies between 40 and 200 μgr/m^3. To deal with pollution, filters should be installed at the source of pollution, which can absorb up to 90% of solid, liquid, and gas pollution. However, a large percentage of pollution is related to toxic gases, which are important and vital to remove, but are often not easily absorbed in filters. For this purpose, it is necessary to design specialized filters for the special absorption of toxic gases. One of these gases that are highly polluting and harmful is CO_2 [1,2].

The natural concentration of CO_2 in the air is currently about 0.040% or 404 ppm, but this concentration is higher in polluted industrial cities. The removal of excess CO_2 is one of the necessities of the industry, because a higher than standard increase in the CO_2 concentration causes respiratory poisoning in addition to greenhouse and warming effects. The main goal of this study is to find a way to effectively remove the CO_2 [3,4].

Zeolites and geopolymers as solid absorbents

Usually, several techniques are used for the CO_2 absorption and its removal, which include membrane separation, absorption by solvents such as amine and ionic liquids, as well as absorption by solid adsorbents. Among the many methods, the absorption method by solid adsorbents like zeolites and geopolymer is more recent than other methods and has received increasing researches [5-8]. Zeolites are porous aluminosilicates whose pore size is less than 5 nm, and their use as adsorbents for polluting water ions is very common on a small scale [7]. However, there are limitations in the use of zeolites as absorbers of toxic gases, including the difficulty in preparation and the high cost of the method. Geopolymers are further porous aluminosilicate compounds that are structurally similar to zeolites, but are more disordered, non-crystalline with micron and nano-sized pores. The advantage of geopolymers over zeolites is that they have many properties of zeolites and at the same time, their preparation is easier and less expensive [6-8]. Geopolymer materials are prepared from raw materials such as kaoline, metakaolin, mica, talc, and many other materials that contain aluminum Al_2O_3 and silicate SiO_2 compounds. Geopolymers are classified as safe materials that are abundant and readily available. For the geopolymer formation, an alkaline activator such as soda ash is used, which breaks down the components of aluminosilicate raw materials and provides the basis for the formation of geopolymer macromolecules [7,8].

CO_2 capture using liquid and solid absorbents

Various methods have been proposed for CO_2 absorption, from liquid to solid absorbers. Each of these absorbers has its own advantages and disadvantages. High absorption capacity and variety are the merits and advantages of liquid absorbent. However, volatility, sensitivity to temperature, difficulty in working with liquids, and their large volume are among the disadvantages of liquid absorbents [9-11]. The advantages of working with solid adsorbents include the simplicity of working with solid materials, the ability to be placed in different formats, the possibility of regenerating the adsorbent and using the adsorbent multiple times. Disadvantages of solid absorbent are the high cost of preparation and the low adhesion to the mold. If solid adsorbents are available at a reasonable price, using them is preferable to using liquid adsorbents [12,13]. To determine the CO_2 absorption in a solid filter, among the different methods, the best is to measure the pH of alkaline solution in which the excess CO_2 is blown after passing through the filter. As the CO_2 concentration entering the solution decreases, the pH changes less in the alkaline solution. For every unit of CO_2 that enters the alkaline solution, the alkalinity of the solution (NaOH) decreases by two units [4].

Recently, geopolymers have been considered as an abundant and cheap source for preparing ionic adsorbents in water. However, geopolymers have been less used as absorbers of toxic gases, which is due to the low flow of gas through the holes. It is a good idea to place the geopolymer on a mold with enough holes. But it is practically impossible to use flexible foams as molds because geopolymers are fragile. In this study, a mixture of three geopolymers, metakaolin, mica, and talc (MMT) was used to prepare a geopolymer filter with a foam mold for CO_2 absorption. Polyvinyl alcohol has been used to reduce the geopolymer fragility. Selection of these three geopolymers is based on the articles that indicate the good performance of these three compounds together [14-16]. Flexible geopolymer filter for CO_2 absorption is a new and innovative idea.

Experimental

Materials and equipment

Nanosilica with dimensions of 13 nm, metakaolin, mica, and talc with 200-300 μm size were purchased with analytical grade. Furthermore, HCl, NaOH, $NaHCO_3$, and polyvinyl alcohol (PVA) were used with analytical grade. Polyurethane foam was used as a monolith base for the filter mold. The devices include the VGT-1620T ultrasonic bath with 50W power and 40 kHz frequency, the Hanna pen pH meter model HI98113 and a heater -stirrer. The analysis equipment of the MMT/Nanosilica material includes; field emission scanning electron microscope

(FESEM) model TeScan-Mira III, Fourier transfer infrared spectroscopy (FTIR) model Spectrum RXI.

Preparation of MMT/nanosilica filter

A piece of polyurethane foam was used as a mold to place the geopolymer on it. The foam was cut into 12 pieces with dimensions of 2 x 2 x 0.3 cm^2. The foam pieces were soaked in water and then placed in a beaker containing PVA saturated solution to be impregnated with PVA. PVA solution was used as an adhesive to bond geopolymer (inorganic material) to polyurethane foam (organic material) [17], and then MMT mixture containing nanosilica was prepared as follow.

Metakaolin, mica, talc, NaOH and DI water were first carefully mixed with certain amounts that were extracted from [16], as listed in Table 1.

Secondly, 12 bakers were labeled from 1 to 12. The amount of 3 g of prepared MMT mixture was poured into each baker. The value of 10 mL of 1% nanosilica mixture was prepared and dispersed well in an ultrasonic bath. A certain amount of 1% nanosilica mixture (0.1 to 1.1 mL) was added to the MMT mixtures in bakers (2 to 12), as presented in Table 2. The MMT mixture of number 1 was considered as a control sample without nanosilica. After that, 1 mL of H_2O_2 solution (4%) was added to each baker, which acts as a foaming agent. The mixtures were mixed well on a stirrer at room temperature. The contents of each baker were poured on a piece of foam impregnated with PVA and all its parts were coated with MMT mixtures from all six directions to prepare the MMT/Nanosilica filters. Finally, all MMT/Nanosilica filters were completely dried at room temperature for 48 hr.

Setup for evaluation the MMT/Nanosilica filter

According to Figure 1, a simple setup was prepared consisting of a three-hole glass balloon containing 200 mL alkaline solution (NaOH, pH = 11), a source of CO_2 production,

Table 1. Composition of MMT geopolymer mixture

Material	Metakaoline	Mica	Talc	NaOH	H_2O
gr	20	19	2	9	50

Table 2. Composition of the MMT mixture containing nanosilica

Number	MMT Geopolymer /gr	Nanosilica solution/mL	H_2O_2/mL
1	3	-	1
2	3	0.1	1
3	3	0.2	1
4	3	0.3	1
5	3	0.4	1
6	3	0.5	1
7	3	0.6	1
8	3	0.7	1
9	3	0.8	1
10	3	0.9	1
11	3	1	1
12	3	1.1	1

a funnel for placing MMT/Nanosilica filter and the pH meter. The CO_2 was produced from the reaction between $NaHCO_3$ and HCl according to Equation (1) in a plastic bottle.

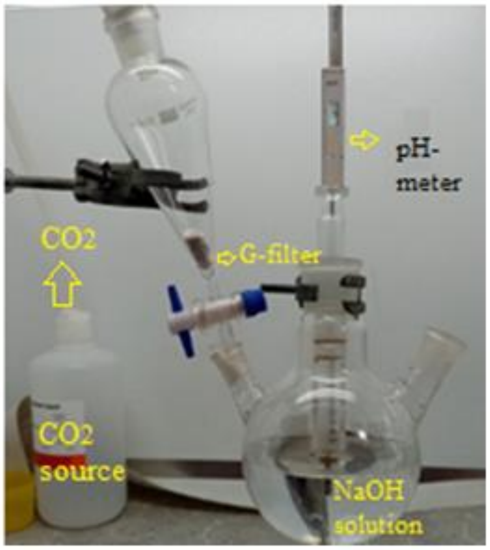


Figure 1. Setup to check the efficiency of the MMT/Nanosilica filter and the amount of CO2 absorption

For each mole of $NaHCO_3$ and HCl (precursor), 1 mole of CO_2 is released. 1 mole of CO_2 has a volume of 22.4 L at standard temperature and pressure. In this experiment, the concentration of precursors was 0.17 M, which leads to the production of 0.4 L of CO_2. As the CO_2 is generated and increased within the source, the CO_2 is transferred through the laboratory silicone tubing to the funnel containing the MMT/Nanosilica filter and pass through the filter and be absorbed as much as possible. The excess CO_2 that was not absorbed finally entered the alkaline solution. When CO_2 enters alkaline solution, according to Equation (2), reacts with H_2O and produces H_2CO_3. H_2CO_3 neutralizes twice its equivalent of alkaline NaOH solution and gradually the alkalinity of the solution decreases and the pH becomes less than 11.

$$NaHCO_3 + HCl \rightarrow NaCl + CO_2 \uparrow + H_2O \quad (1)$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (2)$$

$$H_2CO_3 + 2NaOH \rightarrow 2Na^+ + CO_3^{2-} + 2H_2O \quad (3)$$

In this way, the pH of the alkaline solution changes during the experiment. If the CO_2 absorption is higher in the MMT/Nanosilica filter, the pH change is lower in the alkaline solution. Each experiment was given 10 min to complete the CO_2 absorption in the MMT/Nanosilica filter and the pH of the alkaline solution no longer changed. Initially, the experiment (TN=0) was performed without filter in the setup, which became the basis for comparison with the subsequent experiments. The next experiment (TN=1) was performed in the presence of the MMT filter, and then 11 experiments (TN=2-12) were performed in the presence of MMT/Nanosilica filters, which differed only in the amount of nanosilica. In each experiment, the alkaline solution inside the balloon was replaced with a new solution and the source of CO_2 production was charged with new precursors.

Result and discussion

Results of pH measurement

The pH measurement of the alkaline solution and its changes (11-pH) is provided in Table 3 after passing a certain amount of CO_2. In the case that there is no filter inside the funnel (TN=0), within 10 minutes, the pH of the alkaline solution changes from 11 to 8.7. In the presence of the MMT filter without nanosilica (TN=1), the pH value of the alkaline solution changes from 11 to 9. Likewise, in TN= 2 to 12, with the presence of MMT/Nanosilica filters, the amount of pH decreases significantly, which is a sign of the CO_2 absorption on the filter surface.

Table 3. Changes in pH of alkaline solution with changes in CO_2 absorption in MMT/Nanosilica filter

Test number (TN)	Filter	Nanosilica (mL)	pH	11-pH
0	No filter	-	8.7	2.3
1	MMT filter	-	9.0	2
2	MMT/Nanosilica	0.1	9.2	1.8
3	MMT/Nanosilica	0.2	9.3	1.6
4	MMT/Nanosilica	0.3	9.4	1.4
5	MMT/Nanosilica	0.4	9.7	1.3
6	MMT/Nanosilica	0.5	9.8	1.2
7	MMT/Nanosilica	0.6	9.9	1.1
8	MMT/Nanosilica	0.7	10	1.0
9	MMT/Nanosilica	0.8	10.1	0.9
10	MMT/Nanosilica	0.9	10.1	0.9
11	MMT/Nanosilica	1.0	10	1
12	MMT/Nanosilica	1.1	10	1

The CO_2 absorption in the MMT/Nanosilica filter is related to the presence of micron and nano holes in the filter, where CO_2 is trapped and then physically or chemically absorbed. The CO_2 absorption can be further related to the presence of hydroxide groups in geopolymer, which leads to chemical absorption, as depicted in Figure 2.

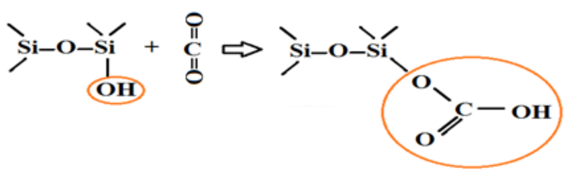


Figure 2. Chemical absorption of CO_2 in MMT geopolymer

In TN=10, compared to 9, there was no change in the alkalinity of the solution. Likewise, in TN= 11 and 12 (Figure 3), the alkalinity of the solution changes more than in TN= 9 and 10 which is due to less CO_2 absorption in the MMT/Nanosilica filter. In fact, the lowest pH change of the alkaline solution is related to TN= 9 and 10, when the amount of 0.8 and 0.9 mL of nanosilica was added to the MMT geopolymer mixture. In this way, increasing nanosilica in MMT does not lead to more CO_2 absorption.

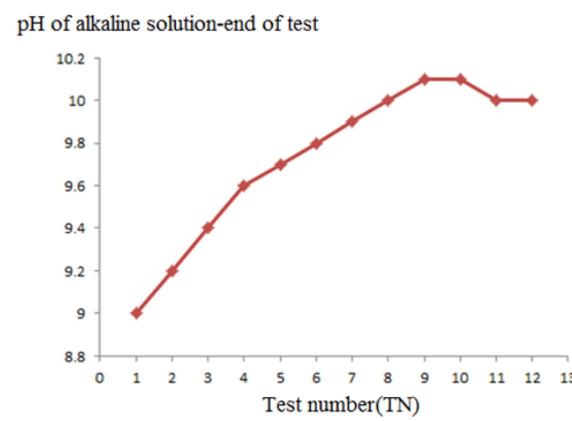


Figure 3. pH of alkaline solution as a measure of CO_2 absorption in the MMT/Nanosilica filter

The best ability of MMT/Nanosilica filter is related to TN= 9 and 10 with 0.8 and 0.9 mL nanosilica, which is equivalent to 8 and 9 mg of nanosilica in 3 g of MMT mixture. In other words, the presence of 0.26 to 0.30 % of nanosilica in MMT mixture shows the best CO_2 absorption capability. The role of nanosilica in the CO_2 absorption is related to the reaction of CO_2 with nanosilica [5]. In this way, first CO_2 is physically absorbed by nanosilica (Figure 4a) and then, a chemical connection is established between nanosilica and CO_2 (Figure 4b).

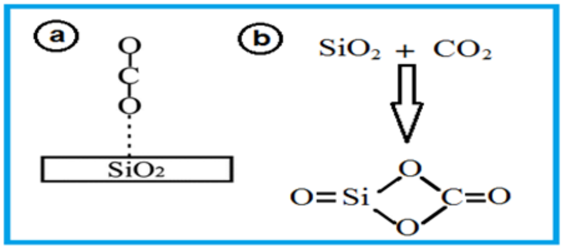


Figure 4. (a) Physically and (b) chemically absorption on nanosilica.

FTIR Spectroscopy of MMT/Nanosilica

The FTIR spectroscoy of CO_2 is demonstrated in Figure 5, which is extracted from an article [4]. This spectrum includes three peaks: a double absorption peak around 3700 cm^{-1}, a sharp absorption peak at 2240 cm^{-1}, and an absorption peak at 700 cm^{-1}. These three absorption peaks are related to stretching and bending vibrations of CO_2. If CO_2 is absorbed on the MMT/Nanosilica surface, it is expected that these three peaks will be observed in the FTIR spectrum with a slight change and displacement [4].

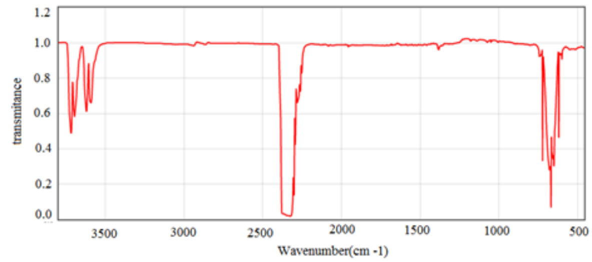


Figure 5. RTIR of CO_2 with three absorption peaks [4].

MMT/Nanosilica filter (number 10), which was one of the best CO_2 absorbent filters, was evaluated by FTIR spectroscopy and its results are demonstrated in Figure 6. FTIR spectroscopy of the MMT/Nanosilica filter before CO_2 absorption (Figure 6a) shows that in the spectral region where CO_2 has infrared absorption, the MMT/Nanosilica filter has no significant absorption. On the other hand, FTIR spectroscopy of the MMT/Nanosilica filter after CO_2 absorption shows an absorption peak comparable to the FTIR spectroscopy of CO_2 (Figure 6b). These absorption peaks includes a double absorption peak at about 3500 cm^{-1}, a series of weak absorption peaks at about 2400 cm^{-1} and a series of absorption peaks in the lower region above 1100 cm^{-1}.

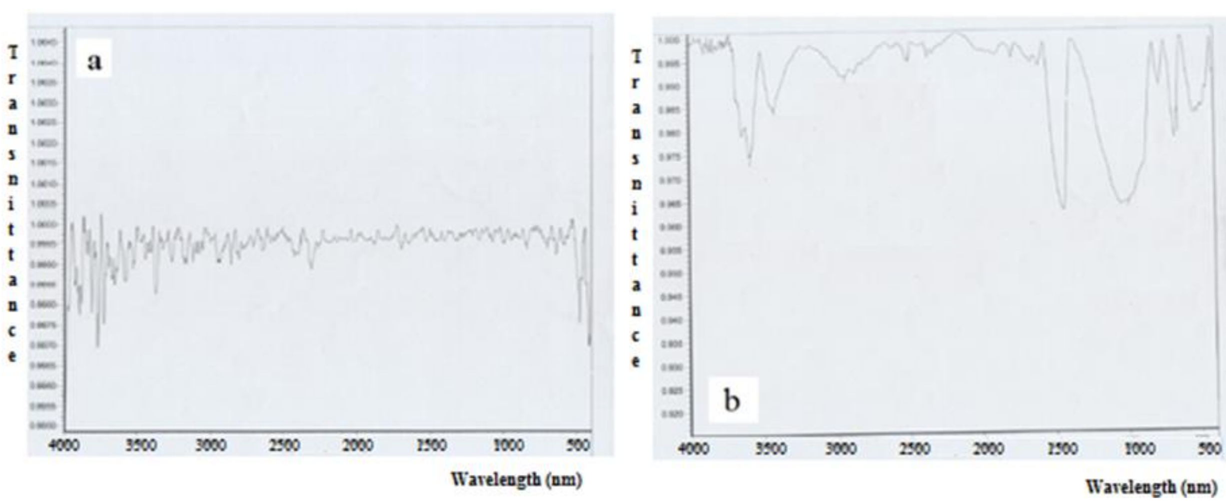


Figure 6. FTIR of MMT/Nanosilica filter number 10, (a) before and (b) after CO_2 absorption.

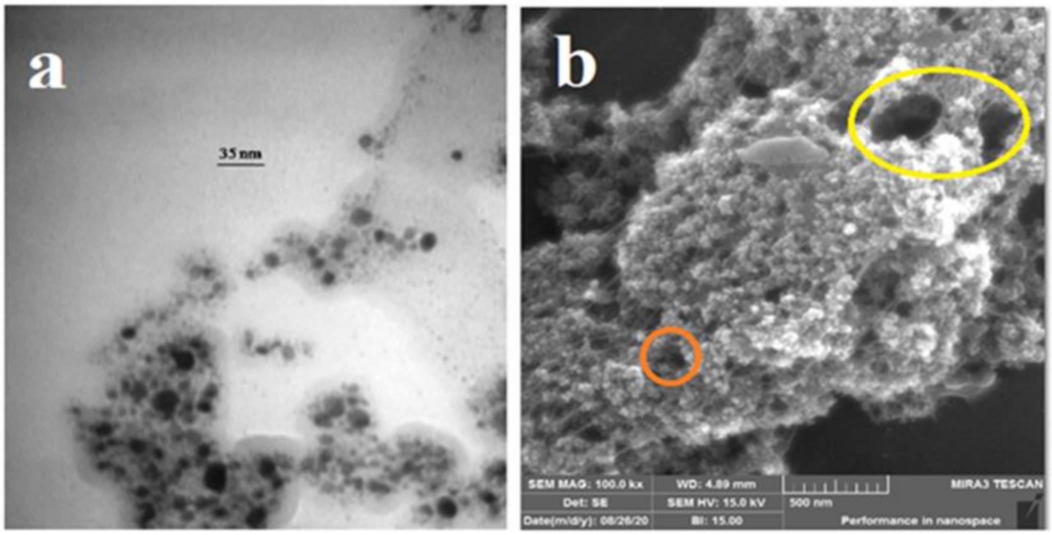


Figure 7. FESEM image of (a) nanosilica and (b) MMT/Nanosilica filter.

These absorption peaks are related to the vibrations of the CO_2 trapped in the MMT structure, but the intensity and position of these peaks are slightly different from what is seen in Figure 5 for the free CO_2. The reason for this difference can be related to the limitation of CO_2 vibrations in the MMT/Nanosilica filter. As previously shown in Figure 2, the CO_2 absorption on the geopolymeric structure is chemical and is accompanied by a change in the CO_2 structure. Therefore, a change is observed in the intensity of molecular vibrations of CO_2. Furthermore, according to Figure 4, the CO_2 absorption on nanosilica is chemical, and with CO_2 binding on the surface, the stretching vibrations of CO_2 are limited and its bending vibrations are practically impossible. For this reason, in the spectral region of 2400 cm^{-1}, which is related to the bending vibrations of CO_2, no noticeable peak is observed in the FTIR spectrum of the MMT/Nanosilica filter that has absorbed CO_2 [4].

FESEM of MMT geopolymer

According to Figure 7a, the nanosilica with dimensions of about 13 nm can be seen, which was used in the construction of MMT filter. Figure 7b is related to MMT/Nanosilica filter (No. 10), in which many micron holes are observed and some of them are marked with a yellow circle. Also, in the MMT geopolymer structure, there are nanometer holes, which are shown with an orange circle.

Conclusion

Metakaolin, mica, and talc materials can be used to prepare geopolymer filter for CO_2 absorption with minimum cost and equipment. Polyurethane foam as a porous and flexible material is a suitable mold for geopolymer. PVA can be used to properly connect geopolymer to polyurethane foam. The MMT/nanosilica filter shows more CO_2 absorption than the MMT filter without nanosilica. By increasing the nanosilica percentage in the MMT filter to some extent, an increase is observed in CO_2 absorption in the filter and then a decreases occurs in the amount of CO_2 absorption. The pH measurement of alkaline solution showed that the presence of nanosilica in the MMT filter increases CO_2 absorption by 12.1% compared to the MMT filter without nanosilica. The FTIR spectroscopy of the MMT/nanosilica filter before and after CO_2 absorption proves the absorption peaks related to the presence of CO_2 in the MMT/Nanosilica filter. The FESEM images obtained from the MMT/Nanosilica filter showed the porous structure with micron and nanometer holes which is a suitable structure for CO_2 absorption.

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Orcid

Ashraf Heiadaripour: 0000-0003-0223-5383
Parsa Seddigi: 0009-0005-3060-5822

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