



## Template Assisted Method for Enhancing the Zeolite's Ability to Capture Methionine

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### Abstract

To investigate template effect on physicochemical properties of zeolite and enhance the molecular sieving properties, adsorption of methionine amino acid was studied by spectroscopic methods. Four zeolites such as methionine templated analcime, methionine templated zeolite-P, N, N-dibenzyl-N,N,N,N-tetramethylethylenediamine (DBTMED) templated analcime and free template analcime were synthesized as adsorbents and characterized with scanning electron microscopy (SEM), Fourier transformation infrared spectroscopy (FT-IR) and N<sub>2</sub> adsorption-desorption analyses. The influence of methionine concentration and pH on the adsorption ability of zeolites was examined; furthermore, the adsorption isotherms of methionine on zeolites were studied and the experimental data were fitted with Freundlich and Langmuir equations in order to obtain sorption parameters.

The results indicated that the adsorption of amino acid was not only depended on zeolites surface areas but also on their pore size. The existence of template in zeolite synthesis could help enlarging the pore size and enhancing the adsorption ability.

**Keyword:** *Analcime zeolite, Zeolite-P, Methionine adsorption, Template assisted method.*

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## **Introduction**

As amino acids are used in industry such as animal food supplements and food industries, their recovery from absorbent materials is important [1]. There are many sorbent materials in the world, which occur naturally or are produced synthetically such as zeolites [2]. To date, there are relatively few studies on the adsorption process using zeolites, particularly for amino acids, which are small enough to fit easily within the pores of a wide range of mesoporous molecular sieves [3-6]. Several investigations indicated that the interaction between amino acid and silica was electrostatic force type or came from the hydrophobic effect between adsorbent and amino acid [7, 8].

In the synthesis of zeolite, there are several parameters that play important roles in determining the final structure of the zeolite. For instance, the structure-directing agent (SDA) can direct the formation of a specific crystalline structure. Recently, a number of successful examples have been reported on the preparation of mesoporous zeolites by addition of mesoscale templates including nanostructured carbons [9], mesoscale cationic polymers [10] and mesoscale organosilanes [11]. The effect of the SDA on the resulting zeolites depends on the shape and size of the molecules [12]. These mesoporous zeolites compared to conventional zeolites exhibited superior catalytic properties. Amino acid molecules as a template play an important role in the structure of zeolites. To understand the contribution of proteins in biosilification, several amino acids have been directly studied in silica polymerizing agents [13]. Chiral imprinting with amino acids of ordered mesoporous silica exhibits enantioselectivity after calcinations [14].

In our previous research, the effect of d-methionine on the transformation of zeolite Y to analcime and zeolite P was investigated and these two zeolites were synthesized in the presence of d-methionine as a template [15]. In this study, the methionine adsorption ability of synthesized zeolites was studied to evaluate the effect of template on the physicochemical properties of synthesized zeolite and investigate the adsorbate-adsorbent geometric matching content.

## **Experimental**

Different adsorbents were provided according to the reported procedures [14]; the sol-gel mixture was prepared by mixing an aluminate and a silicate solution. Aluminum powder (0.108 g) was dissolved in a caustic solution of 3.3 M at 40 °C to yield the aluminate solution. Sodium hydroxide (25 ml, 2.5 M) was mixed with silicic acid (5.9 g) until the solid was completely dissolved to yield the silicate solution. Afterwards, the aluminate solution was added to the silicate solution with stirring in order to produce the sol-gel. The templates (0.002 mol) was dissolved in H<sub>2</sub>O (4 ml) followed by heating to 50 °C. Subsequently, the hot template solution was added to the aluminosilicate sol-gel. Then, the Teflon bottle was transferred to the stainless-steel autoclave, and

the sealed autoclave was put into an air oven and heated to 50 °C for 120 h. The template assisted analcimes (N, N-dibenzyl-N,N,N,N-tetramethylethylenediamine (DBTMED) and methionine) were prepared at 160 °C for 96 hours while zeolite-P was obtained at 100 °C for 42 hours. The template-free synthesis pathway for analcime zeolite was similar to preparation method for the above-mentioned zeolite, but the template-adding step was not carried out. The summarized synthesis parameters such as Si/Al ratio, crystallization temperature and synthesis time for four different synthesized types of zeolites were 9.3, 160 °C and 96 h as well as for zeolite-P were 9.3, 100 °C and 42 h, respectively. For adsorption processes, 0.1g pre-weighed zeolite as adsorbents was placed in adsorption cells containing 10 ml of methionine solution with a certain initial concentration for overnight. After equilibration, the residual methionine concentration in the liquid phase was analyzed using fluorescence spectroscopy. The physical properties of synthesized zeolites were confirmed using FT-IR spectrometer (Vector 22-Bruker), N<sub>2</sub> adsorption/desorption (BEL Japan), and scanning electron microscopy (JEOL JXA-840 SEM).

At the end, the quantum-chemical calculations were performed in order to study the effect of template in the pore size and formation of zeolite. Optimized calculations of methionine molecule were completed using Gaussian 03W software. The input files were compiled and the output ones were viewed in Gauss View software. Theory method/basis group of B3LYP/6-31G (d) was used for calculation.

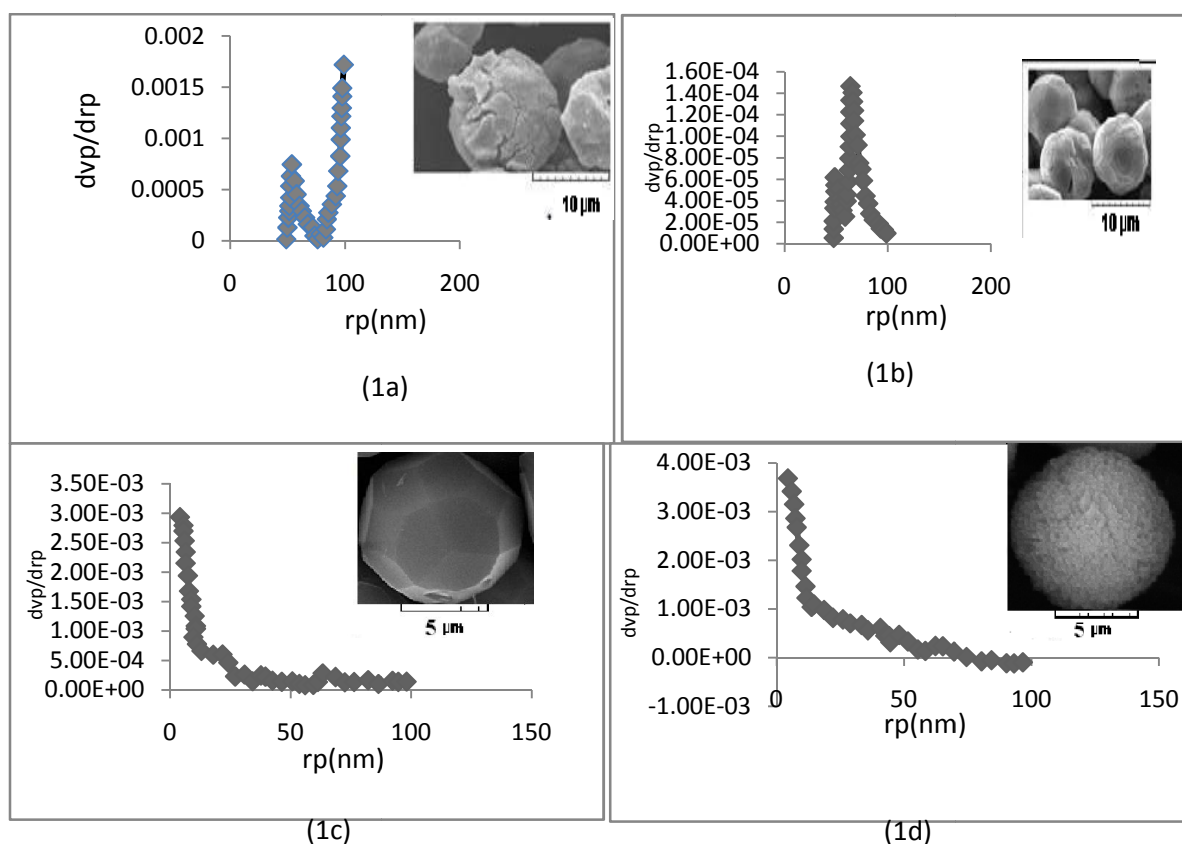
## **Result and discussion**

### *Structural Characteristics of Mesoporous Materials*

As reported in our previous research [15], analcime and P zeolites were synthesized in the presence of methionine as a template. Figure 1 represents the pore size distributions and SEM images of synthesized zeolites. DBTMED templated analcime had crystals with diameter of 4~6 μm and pore diameter of 1.4 nm (Figure 1a); icositetrahedral crystal morphology with rough surface was obtained for methionine templated analcime with crystals size of 8~10 μm and pore diameter of 1 nm (Figure 1b). The free templated analcime had icositetrahedral crystal morphology with 6~8-μm crystal size and 0.6-nm pore diameter (Fig 1c). Furthermore, the homogenous and spherical particles with approximate diameter of 5 μm and pore diameter of 0.7 nm were obtained for zeolite-P (Figure 1d).

It is known that the type of adsorbent and its size are limiting factors for adsorption efficiency [6]. Table 1 illustrates the BET surface area, pore volume and pore size of the synthesized zeolites. This table also shows that the methionine and DBTMED templated analcimes have smaller surface areas

compared to the free template analcime. Under the pretreatment conditions, the framework of analcime may be distorted leading to modification of the pore openings [16].

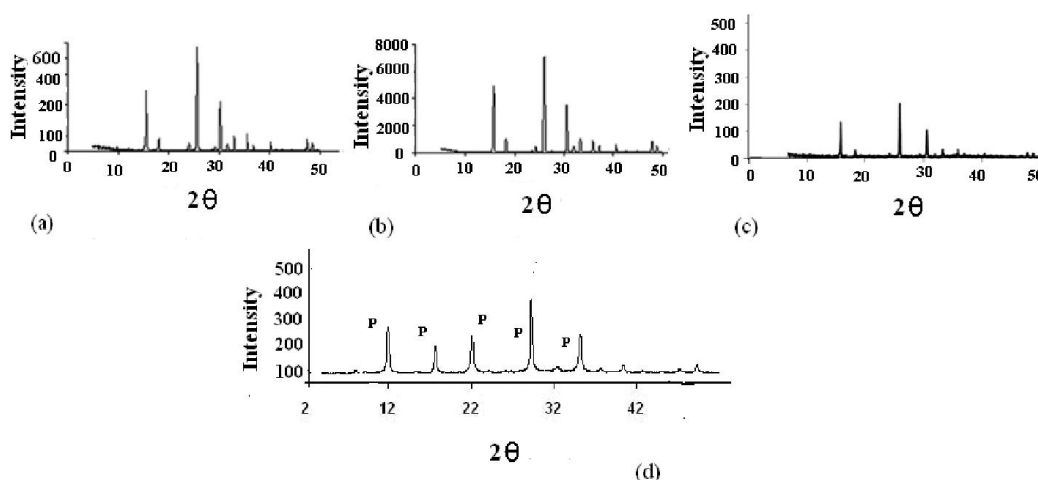


**Figure 1.** SEM micrographs of synthesized zeolites (the inset is the corresponding barrett-Joyner-Halenda (BJH) pore size distribution from N<sub>2</sub> sorption): (a) DBTMED templated analcime, (b) methionine templated analcime, (c) free template analcime, and (d) methionine templated zeolite P.

**Table 1.** Physicochemical properties of synthesized zeolites.

Zeolite type	BET surface area(m <sup>2</sup> /g)	Pore volume(cm <sup>3</sup> /g)	Micropore diameter(nm)
Methionine template analcime	0.45	0.039	1
(DBTMED) template analcime	0.26	0.015	1.4
Free template analcime	312	0.015	0.6
Methionine template zeolite p	191	0.014	0.7

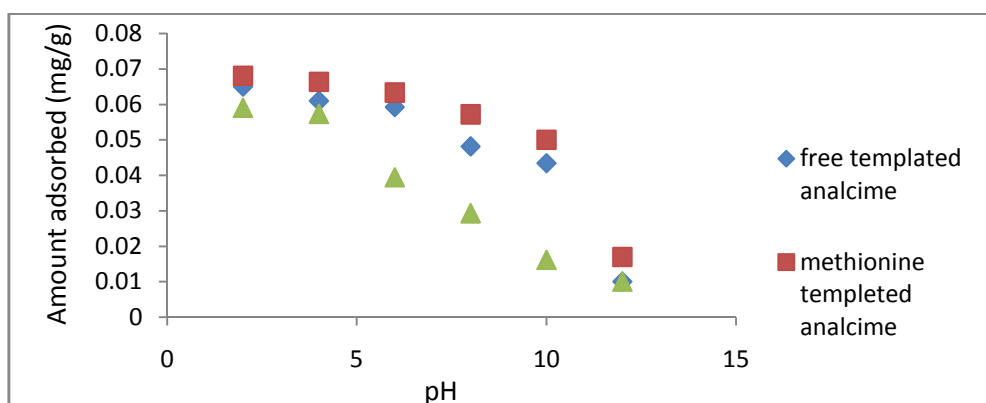
On the basis of quantum-chemical calculations, introducing the template molecules with high dipole moment was so effective in the formation of zeolites with large pore size. High dipole moment of amino acids could be responsible for the formation of water clusters around the molecules; therefore, it could be effective on pore size of zeolites after calcinations [16]. Figure 2 shows the XRD powder patterns of synthesized zeolites.



**Figure 2.** XRD powder patterns of (a) DBTMED templated analcime, (b) methionine templated analcime, (c) free template analcime and (d) methionine templated zeolite P.

### *Influence of pH on the adsorption*

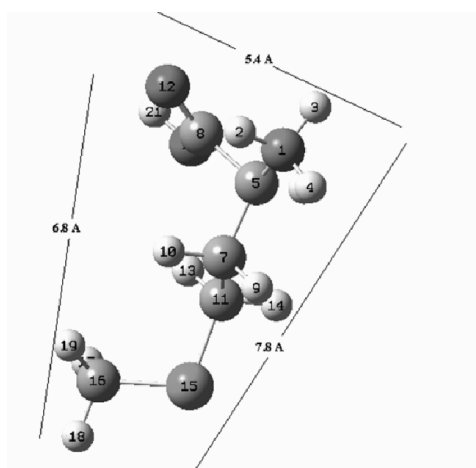
Methionine is a sulfur-containing essential amino acid ( $pI = 5.74$ ). Figure 3 shows the methionine adsorption by synthesized zeolites at different pH values. Methionine was exclusively adsorbed under acidic condition and decreased at higher pH. This behavior could be due to the electrostatic interactions between the positively charged amino group at acidic media and negatively charged lattice of zeolites.



**Figure 3.** Effect of pH on the sorption of methionine.

### *Influence of templates on the adsorption of methionine*

In order to examine the effect of zeolite structure as a function of the template on the adsorption process, the adsorption of methionine on methionine templated analcime, DBTMED templated analcime, free template analcime and methionine templated zeolite P was investigated. The molar volume and dimensions of methionine were calculated using Hartree Fac method (scheme 1).



**Scheme 1.** Theoretically Optimized Geometry of Methionine amino acid distance between H<sub>1</sub>–H<sub>10</sub> is 0.78 nm, H<sub>10</sub>–O<sub>12</sub> is 0.68nm and H<sub>4</sub>–O<sub>12</sub> is 0.54nm.

For the analysis of adsorption isotherms, we tried to fit the experimental isotherm (Figures 4 and 5) through Freundlich and Langmuir equations. Freundlich equation isotherm was an empirical model [17]:

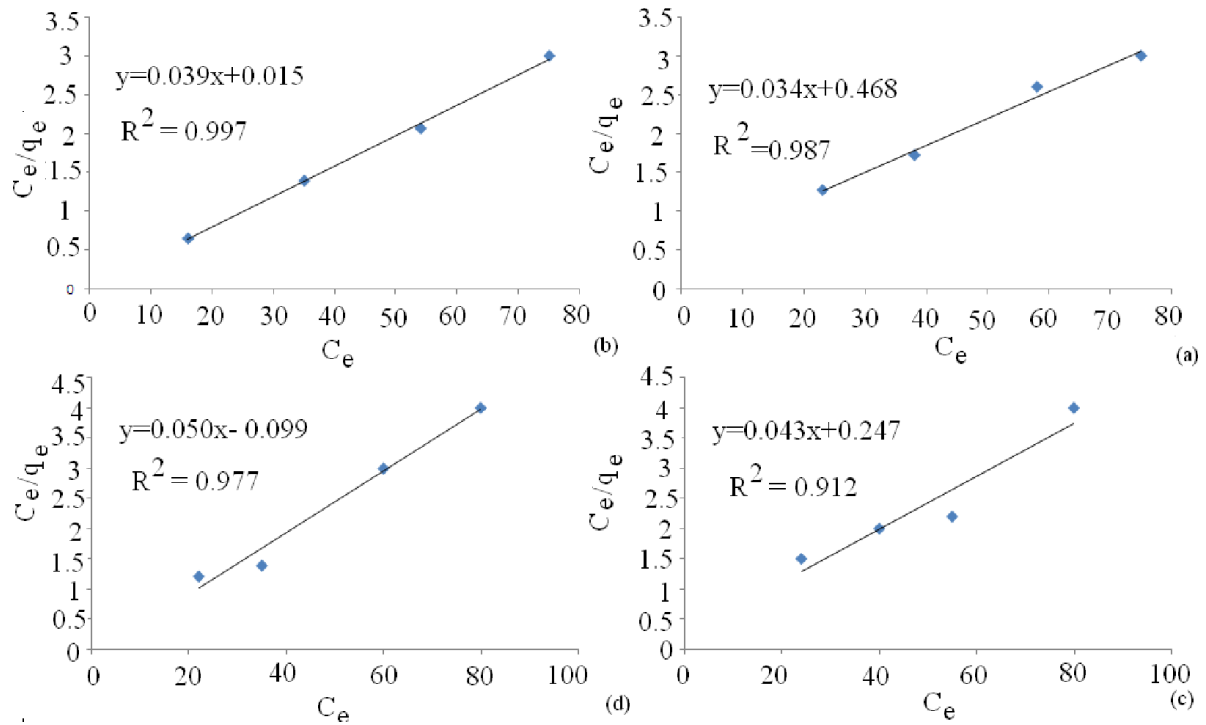
$$\text{Log } q = \text{Log } K_F + (1/n) \text{Log } C_e$$

Where  $q$  is the amount of adsorbed methionine on per gram zeolites and  $C_e$  is the equilibrium concentration of methionine.  $K_F$  is known as Freundlich constant, which is related to the adsorbent capacity and  $1/n$  is an exponent associated to adsorptive strength as well as the favorability [17].

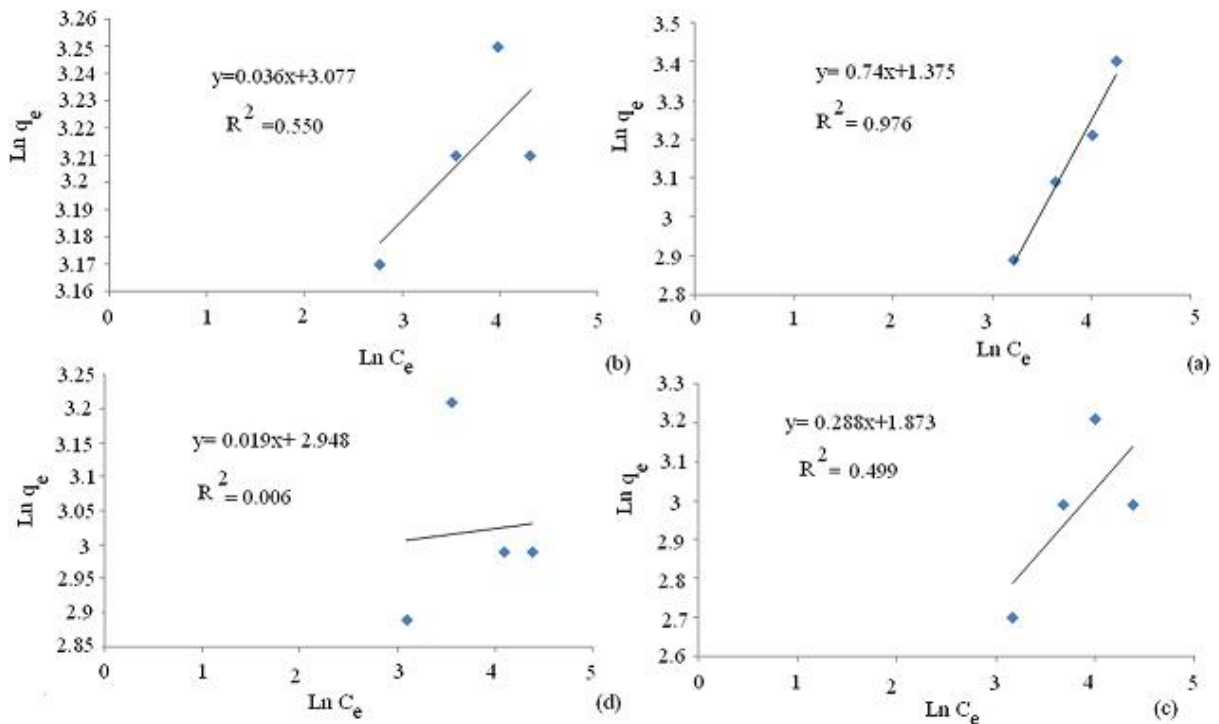
Langmuir equation was originally developed to represent the chemisorptions on distinct localized adsorption sites. The linear form of Langmuir equation was expressed as the followed:

$$C_e/q_e = C_e/q_m + 1/(K_L \cdot q_m)$$

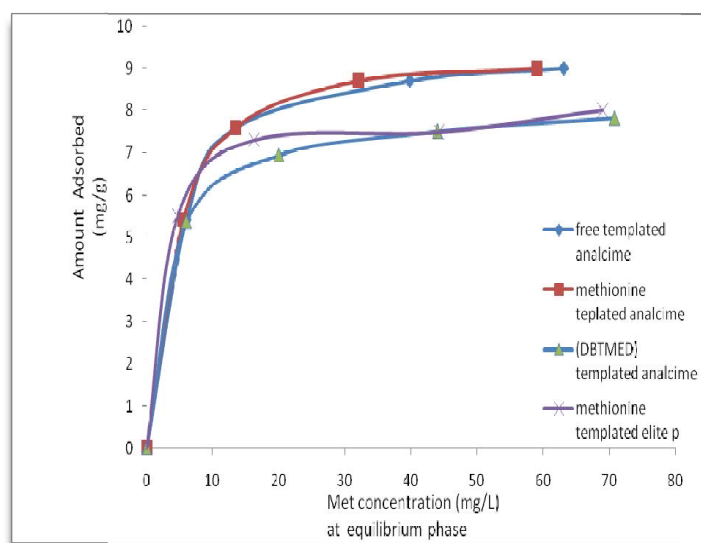
Where  $q_e$  is equilibrium concentration on adsorbent (mg/g),  $C_e$  equilibrium concentration in solution (mg/L) and  $K_L$  is the Langmuir adsorption constant (L/mg). The constant  $K_L$  and saturation capability  $q_m$  can be evaluated by the regression analysis of the linear form of the foregoing equation [18]. Linear fitting of the Langmuir and Freundlich isotherms models are shown in figure 4 and 5 respectively.



**Figure 4.** Linear fitting of the Langmuir isotherms models of (a) methionine templated analcime, (b) free template analcime, (c) methionine templated zeolite P and (d) DBTMED templated analcime.



**Figure 5.** Linear fitting of the Freundlich isotherms models of (a) methionine templated analcime, (b) free template analcime, (c) methionine templated zeolite P and (d) DBTMED templated analcime.



**Figure 6.** Influence of different synthesized zeolites on methionine adsorption.

According to table 1 and figure 6, the pore diameter and pore volume for this zeolite are very large; thus, the driving force for adsorption is mainly originated from the host-guest interaction. The results indicated that the regression coefficients obtained from the Langmuir isotherm were higher than those gained from Freundlich isotherm, indicating the homogeneous adsorption of methionine on synthesized zeolites. In addition, adsorption amounts were the highest for the methionine template analcime. Langmuir isotherm constants for adsorption of methionine are shown in table 2.

**Table 2.** Langmuir Isotherm Constants for Adsorption of Methionine.

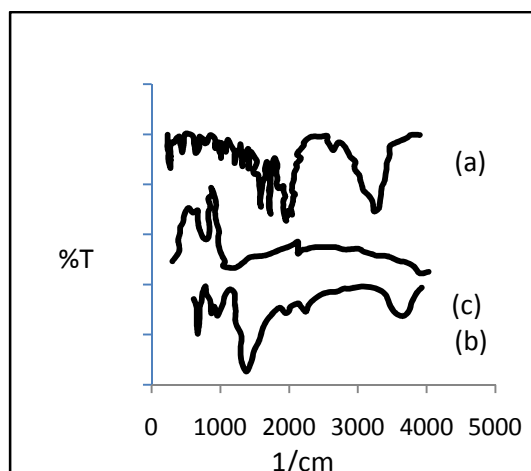
Adsorbate	$q_{\max}(\text{mg g}^{-1})$	$b (\text{dm}^3 \text{mg}^{-1})$	$R^2$
methionine templated analcime	29.41	0.072	0.987
free template analcime	25.64	2.600	0.997
methionine templated zeolite P	23.25	0.174	0.912
DBTMED templated analcime	20	0.505	0.997

### *Infrared spectroscopy*

The FT-IR spectra of the methionine amino acid, analcime zeolite and modified analcime zeolite are demonstrated in figure 7. With comparing the spectra of amino acid and host material, it was concluded that the guest species (methionine) were absorbed by the analcime modified zeolite.



As a result of the interaction between methionine and methionine, the appearing peak in the area of  $3529.90\text{ cm}^{-1}$  was due to N-H stretching vibrations. The wide O-H band ( $\sim 3500\text{ cm}^{-1}$ ) associated with the carboxyl group in the amino acid structure is not visible, probably because of its overlap with the O-H stretching bands of the adsorbed amino acid and water molecules in zeolite [19]. All amino acids containing the  $\text{NH}_3^+$  group exhibit two characteristic bands. One of them is observed at  $1640\text{--}1610\text{ cm}^{-1}$  and the other characteristic is observed at  $1540\text{--}1420\text{ cm}^{-1}$  [19]. For the amino acid under study,  $\text{NH}_3^+$  bending vibrations appeared at  $1656.04\text{ cm}^{-1}$ ,  $\text{NH}_3^+$  was also present in the spectrum of the modified zeolite sample at  $1638.33\text{ cm}^{-1}$ . The other band ( $\text{NH}_3^+$ ) was observed at  $1478.29\text{ cm}^{-1}$ . The absorption band in the frequency range of  $960\text{--}900\text{ cm}^{-1}$  was assigned to OH group bending vibrations. In the spectrum of the modified zeolite sample, this band (OH group bending vibrations) was narrowed and located at  $940\text{--}900\text{ cm}^{-1}$ .



**Figure 7.** FT-IR spectra of: (a) Methionine amino acid, (b) Analcime zeolite, and (c) Analcime templated zeolite.

## Conclusion

The results indicated that two major factors such as the geometric matching content and electrostatic interaction between the methionine and zeolites could be effective during the adsorption process. A large pore size zeolite could be achieved with introducing the large template. Methionine templated zeolite indicated the highest adsorption capacity, which might be due to the fact that the methionine molecules with diameter smaller than zeolite pore size could enter the pore of the adsorbent and then diffuse inside the channels but could not return easily. If there is amine templated zeolite with larger pore size, the adsorption of methionine was reversible.

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