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Adsorption and Kinetic Studies of Volatile Organic Compounds (VOCs) on Seed Assisted Template Free ZSM-5 Zeolite in Air

Abdul Aziz[1], *Minji Kim*[1],*Sungyoun Kim*[2] *and Kwang Soo Kim*[1,2,*]

[1]Department of Construction Environment Engineering, University of Science and Technology (UST), 217 Gajeong-ro, Yuseong-gu, Daejeon, 305-350, Korea.
[2]Environmental and Plant Engineering Research Division, Korea Institute of Civil Engineering and Building Technology (KICT), 283 Goyangdae-ro, Ilsanseo-gu, Goyang-si, Gyeonggi-do, 411-712, Korea.

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Abstract: This work presents a thorough evaluation of the adsorption properties of template free synthesized ZSM-5 for the removal of organic pollutants in air. The ZSM-5 material has been prepared by the hydrothermal synthesis method using ZSM-5 seed assistance, instead of organic template. This material has been compared with the ZSM-5 prepared by using TPAOH as an organic template. The influence of the seed assisted method on the structure, textural properties and adsorption capacity has been investigated. Benzene, toluene, ethylbenzene and xylene (BTEX) have been used as model organic pollutants. The adsorbents made have been characterized by BET surface area, XRD, SEM, TPD and FTIR spectroscopy. The characterization reveals that seed assisted organic template free ZSM-5 synthesis method is a suitable hydrothermal ZSM-5 a synthesis procedure, for obtaining a well MFI structured particles with BET surface area, porosity and crystallinity. The results presented in this work show that nature of organic pollutant and ZSM-5 physicochemical characteristics have an influence on the adsorption ability. The template free ZSM-5 shows good agreement with the adsorption ability of ZSM-5 with template, along with the benefit of no calcinations after synthesis and less environmental pollution.

Keywords: Zeolite, ZSM-5, BTEX, Adsorption, Air pollution.

1 Introduction

Since organic pollutants (volatile organic compounds) are toxic, carcinogenic, therefore removing these BTEX from industrial and indoor air, instead of discharging these into the environment is one of the solutions to control BTEX emissions. Among many other processes that have been used, adsorption has stood up an attractive alternative because of its low cost, ease to perform, stability and environment friendly nature. Hence, in the last few years, a lot of research work in the field of adsorbent materials has done, especially in the field of zeolitic adsorbents. Generally, zeolites are hydrophilic and have a high affinity for polar molecules. These relations take place between the electric field of zeolite and the quadrupole moment of the polar pollutant molecule. In addition, these adsorbents have a regeneration property. Desorption of gas molecule from the zeolite can be done effectively with appropriate operation parameters.

ZSM-5 has hyrophobicity in contrast to zeolites as belonging to high silicious family of zeolites with MFI structure giving high temperature stability and adsorption properties. These materials have acidic and catalytic properties as well towards organic pollutants [1]. Argauer and Landolt synthesized the characteristic MFI structure of zeolite, in 1972 [2, 3]. It was published that ZSM-5 zeolites has two channel systems with ten-membered ring holes running across each other. The diameter and shape of the channels make it very attractive for many industries and environment applications. Recently, these materials are used for several applications all over the world like removal of nitrogen compounds, VOCs, cracking, alkylation, MTG process (gasoline production from methanol) and many more uses as catalysts in the petroleum industry [4-8].

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[*]Corresponding author e-mail: kskim@kict.re.kr

Typically, the ZSM-5 type zeolites were prepared in hydrothermal conditions. The silicate sources (silica sol, sodium silicate TEOS), other framework cation (Al), base (NaOH) and organic structure directing agents (organic compounds) [9] were used for building the crystal structure of ZSM-5 zeolite. Conversely, these structures directing organic compounds are expensive and environment unfriendly and consequently, an alternate is searched for. Recent studies show that the organic compounds having quaternary ammonium ions are not necessary for making the crystal structure of ZSM-5 zeolite [2]. It may be seeked in the presence of other compounds like aliphatic amines, diamines, alkanol amines, glycerol, aliphatic alcohols, ammonia, dodecylbenzenesulfonate, and a without any template substances [10].

In this work, concern was paid to the synthesis of ZSM-5 zeolite in the absence of organic structure directing agent by using ZSM-5 as seed for crystal formation which proved to be one of the practical substitutes of the environment enemy organic compounds. Such alternate could give view of the ultimate understanding of the research findings because seed source belongs among quite easily available zeolites and also cost economic as compared to organic templates in general and TPAOH as particular. The objective of this study has been to search out the practical use of seed assisted synthesis of ZSM-5 without any of the organic template. This template free synthesized ZSM-5 has been compared with ZSM-5 prepared with template TPAOH for the adsorption of BTEX from air as practical application.

2 Materials and Methods

2.1 Synthesis of ZSM-5 zeolite

The precursor gel solution was made using silica sol. (40 wt% SiO_2, Sigma Aldrich, USA), sodium hydroxide (NaOH, SamChun, Korea), sodium aluminate ($NaAlO_2$, Junsei, Japan), distilled water (H_2O), tetrapropylammonium hydroxide (TPAOH 1 molar solution, Sigma Aldrich Switzerland) and ZSM-5 as seed (our laboratory prepared[11]). The molar ratio was 1.0 Al_2O_3: 50.4 SiO_2: 6.2 Na_2O: 1.5 TPAOH: 1248 H_2O. The other sample was synthesized with same molar ratio except TPAOH, instead the ZSM-5 was added to the above mixture at the 5.0 wt% of the gel mixture. After stirring (200 RPM) of 24 hours at 50 ^oC, the aged gel was transferred to steel autoclave lined with Teflon for hydrothermal reaction at 180^{o}C for 48 hours. After that, obtained material was cooled, washed (till the pH of filtrate reached 8.0) and dried at 105 ^{o}C in an air dried oven overnight. The resulting particles were calcined at 550 ^{o}C in furnace for 6 hours and stored for characterization. The reference sample formed with TPAOH was named as R while the sample prepared with seed ZSM-5 was named as S. The synthesis procedure is based on the previous literature[11].

2.2 Characterization of synthesized ZSM-5 zeolite

X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max-2500 with Cu Kα radiation having Ni filter. Scanning electron microscope (SEM) images were acquired on a Hitachi S-4800 microscope. The N_2 adsorption and desorption isotherms were obtained on Micromeritics TriStar 3020 at 77K. The BET surface area was computed by the Brunauer-Emmett-Teller (BET) method. The temperature programmed desorption of ammonia (NH_3-TPD) was performed to know the acidity strengths. The material loss with temperature was monitored by TGA analysis on TG209F3.

2.3 BTEX adsorption test

BTEX removal tests were conducted in batch experiments on the prepared ZSM-5 materials. BTEX was purchased from Airkorea, Korea with fixed 50 mg/L concentration of BTEX (benzene, toluene, ethylbenzene, m-xylene balanced with N_2. The removal performance experiments were conducted in a transparent tedler bag with size ranging from 1L to 10 L (according to requirement). 1.0 mg of ZSM-5/7 mL of BTEX was applied as adosrbent during the whole tests. Gas cylinder (air liquid Australia) with as purchased BTEX was used as VOC feeding. The adsorption material was pre heated at 105 ^{o}C for 24 h in an air circulated oven to throughout any moisture. After that, the VOC mixture was introduced in the tedler reactor followed by adsorbent. The VOC adsorption proceeded, decreasing the concentrations of VOC until the saturation. The VOC concentrations were monitored by using a Ultra Trace GC coupled with Mass spectrometer Thermo-Scientific. The SS coupling tube was maintained at 220^{o}C between GC and MS. 250μL sample with sampling syringe was used for all measurements. The presence of reaction products during the removal reaction was not noted. VOC (Benzene, Toluene, ethylbenzene and m-xylene) removal values were calculated according the following equation, the same as mentioned in our previous studies.

$$\mathrm{Xx} = \frac{\mathrm{Cx\ at\ time\ zero\ t0} - \mathrm{Cx\ at\ time\ t}}{\mathrm{Cx\ at\ time\ zero\ t0}} \times 100\% \qquad (1)$$

Whereas, x is benzene, toluene, ethylbenzene or m-xylene.

2.4 Adsorption isotherms

The isotherm data obtained were analyzed using Langmuir Freundlich and Tekmin adsorption equations. The Langmuir, Freundlich and Tekmin parameters were obtained and correlation coefficients were calculated. The linear form of the Langmuir equation (2) is shown below [12].

$$\frac{Ce}{q} = \frac{1}{QmkL} + \frac{Ce}{Qm} \tag{2}$$

Where qe, Ce are the equilibrium pollutant (BTEX) concentration on adsorbent (mg/g) and in the mixture (mg/L). Qm is the adsorption capacity (mg/g), and k_L is binding constant (L/mg) [13]. An Adsorption isotherm study was done only for the seed sample by varying the catalyst dose from 5mg to 40mg in a 5L tedler bag with a fixed initial concentration of pollutants for 24 h.

The Langmuir model assumes, adsorption as monolayer and it depends on the assumption that the surface has active sites with uniform energy and hence, the adsorption energy remains constant.

The linear form of the Freundlich equation (3) is shown below [14].

$$lgqe = lgKf + \frac{1}{n} lgCe \tag{3}$$

k_f, (mg/g $(L/mg)^{1/n}$) is the adsorption capacity of the adsorbent and 1/n constant for Freundlich ranges between zero to one, is the adsorption intensity or may be called surface heterogeneity.

The Freundlich model assumes adsorption as multilayer (heterogeneous) and it depends on the assumption that the surface, strong, active sites are bonded first leading to decrease in binding energy with the increasing degree of active site interaction.

The linear form of Temkin equation (4) is shown below [15].

$$qe = BlnAt + BlnCe \tag{4}$$

Where, A_t is Temkin isotherm equilibrium binding constant (L/g), B (=RT/b_T) is constant related to heat of sorption (J/mol), R (8.314 J/mol) is the universal gas constant and T (K) in the absolute temperature of reaction mixture.

The Temkin model accounts for the adsorbent-adsorbate interactions. It depends on the assumption that due to adsorbent-adsorbate interactions the heat of adsorption for all the molecules in the layer decrease linearly. The uniform distribution of binding energies, up to some maximum extent is characterized by the adsorption.

2.5 Adsorption kinetics

In order to make a useful adsorption process, it is very necessary to predict the kinetics of the proceeding adsorption process. A number of kinetic models have been studied in the past for this purpose. It is well known that the batch operation is more accurate, effective and easy. Keeping in view, in this work, pseudo-first, pseudo-second and intra-particle diffusion kinetic models have been analyzed by doing batch experiments.

Pseudo-first order kinetic model assumes that initially there is no pollutant (adsorbate) ions present at the surface of adsorbent, while with the passage of time the pollutant ions are occupying over the surface of adsorbent. The linear form of pseudo-first order kinetic model (5) is given below [16].

$$\log(qe - qt) = logqe - \frac{K1}{2.303} * t \tag{5}$$

Whereas, q_e (mg/g, also called equilibrium capacity) and q_t (mg/g) are the pollutant adsorbed at equilibrium and at any time t, K_1 is the first order rate constant.

Pseudo-second order kinetic model based on adsorption equilibrium capacity of the adsorption system. It assumes that the adsorption capacity of the adsorbent is related to the number of sites unavailable on the surface. The linear form of the second-order kinetic model (6) is given below [17].

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{t}{qe} \tag{6}$$

Whereas, K_2 (g/mg min) is the pseudo-second order kinetic model rate constant. The values of adsorption capacity and rate constants are calculated from the slope and intercepts of linear plots.

Intra-particle diffusion kinetic model predicts the rate-limiting step for the adsorption process. It is assumed that (a) mass transfer of the adsorbate molecules across the external boundary layer, (b) intra-particle diffusion within the pores of the adsorbent, (c) adsorption is on the surface site. If intra-particle diffusion occurred, then there will be a linear plot between q_t and $t^{0.5}$ and linear line must pass through the origin (means the rate-limiting step is due to intra-particle diffusion). The linear form of intra-particle diffusion kinetic model (7) is given below [18].

$$qt = (Ki)t^{0.5} \tag{7}$$

Whereas, K_i (g/mg h) is the intra-particle diffusion kinetic model rate constant. From the slope of qt versus $t^{0.5}$ K_i is calculated.

3 Results and discussion

3.1 Characterization

Figure 1 presents the XRD patterns of reference and seed samples. Both XRD patterns were obtained after calcinations. A well crystallization of MFI zeolites took place for the R and S samples. As both samples showed the ZSM-5 crystallization pattern. It is reported that the ZSM-5 zeolites show diffraction peaks for 2(Θ) angle at 4°, 6°, 23° and 27°[19]. All these diffraction peaks are present in figure 1.

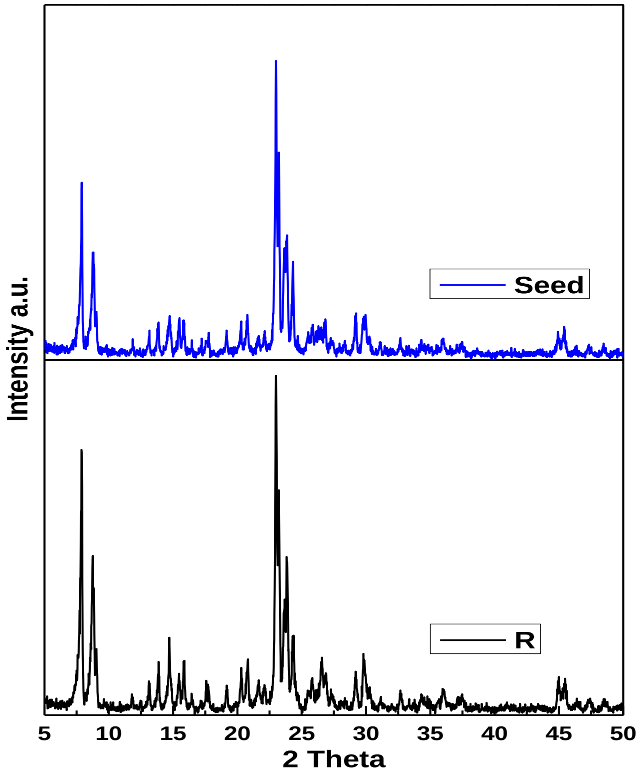

Figure. 1. XRD peaks for samples (R) prepared with TPAOH as reference and (S) prepared with seed ZSM-5.

SEM images of seed sample (S) and TPAOH based reference sample (R) are depicted in Fig. 2. The crystal size of S was varied from about 80-300 nm, which is smaller than the size of reference sample. In addition, the sample S shows less intergrowth of the crystal which is common for the sample prepared with TPAOH [11]. The morphology of R sample is similar to the already published ZSM-5 prepared with TPAOH. While a slight smaller and elongated rectangular morphology is observed, which means, that the S sample has larger surface area.

Figure 3 represents the FTIR spectra of the ZSM-5 crystals prepared with TPAOH (R) and seed assisted (S). The typical absorption peaks for ZSM-5 were seen at 450, 550, 790, 1100 and 1220 cm^{-1}in the literature [20, 21]. All the absorption bands are present in both the samples R and S indicated the presence of double five-rings of ZSM-5. These observations are in agreement with the XRD and SEM results discussed above.

The textural properties, gravimetric loss and acidity of the synthesized materials are shown Table 1. It was clear that with the replacement of structure directing agent TPAOH with ZSM-5 seeds, BET surface area was changed to increase. This effect was due to less intergrowth of the crystals for sample S, which was the case of reference sample R. Moreover, both samples had a BET surface area within the literature-cited range. These findings supported by the SEM images morphologies [22, 23].

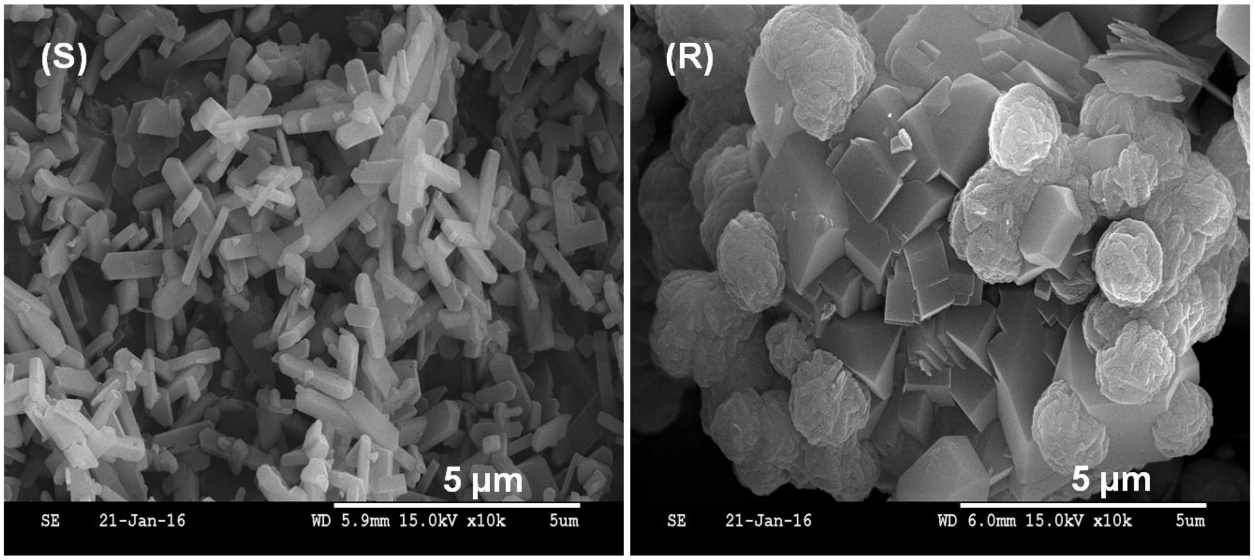

Figure. 2. SEM images for samples (S) prepared with seed and (R) prepared with TPAOH as reference.

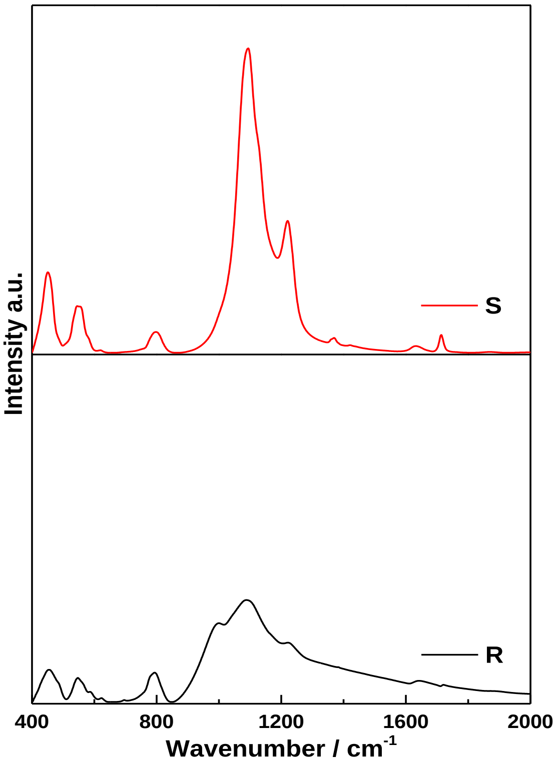

Figure. 3. FTIR spectra for samples (S) prepared with seed ZSM-5 and (R) prepared with TPAOH as reference.

The thermal programmed desorption of ammonia profiles gathered for the R and S materials are shown in Fig. 4. Usually two peaks spanned between 30 to 600 °C temperatures [24] characterize the ZSM-5. From Fig. 4 it is revealed that the first strong peak for sample R appeared at 150 °C (corresponding to Lewis acid sites) while, second weak peak at 270 °C (corresponding to BrØnsted acid sites). However, the first peak for sample S visualized at 165 °C, is more intense than the corresponding peak of reference sample R, whereas the second peak at 270 °C is also more sharp and intense than the corresponding peak of S material. Therefore, it is cleared that the material prepared by seed ZSM-5 has intensified both the peak and shifted the weak acid site towards strong acid sites, showing the more strong acidic character. Besides, the TPD-NH_3 profile for both materials are in coincidence with literature work [24].

Table. 1. Textural and physicochemical prperties

Samples	Symbol	S_{BET} (m^2g^{-1})	$V_{p\text{-total}}$ (cm^3g^{-1})^1	V_{micro} (cm^3g^{-1})	Mass Loss (%)
ZSM-5 (Template)	R	395	0.088	0.086	3.73
ZSM-5 (Seed)	S	365	0.079	0.082	4.25

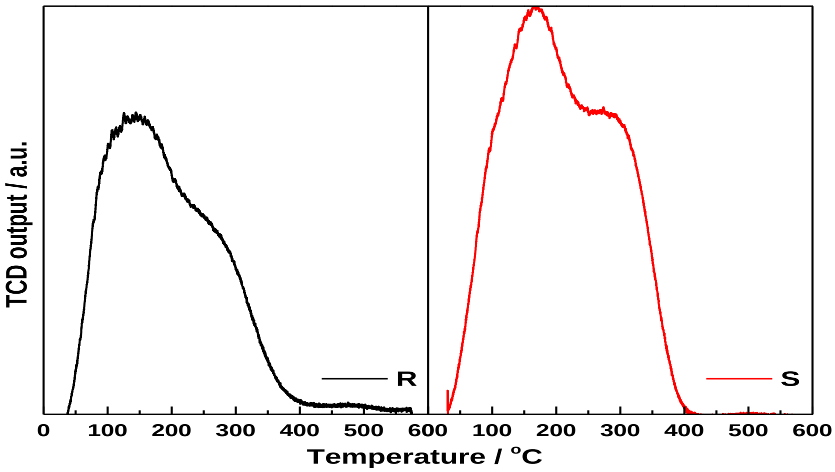

Figure. 4. TPD of ammonia profiles of ZSM-5 (R) synthesized with TPAOH and (S) synthesized with seed

3.2 VOC removal studies

3.2.1 Effect of time on VOC removal

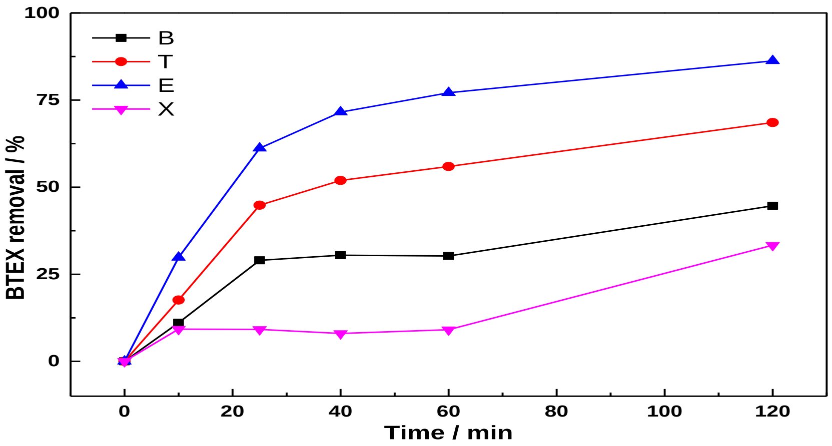

Figure. 5. BTEX % removal with time on seed assisted ZSM-5 0.40 mg/2.7 L at room temperature.

Up until now it is proved that the seed assisted ZSM-5 is as good as synthesized by using costly templating reagent TPAOH. Therefore, onward the whole study focus on the seed assisted ZSM-5 material (S). The time of adsorption process is one of the important variables, affecting VOC adsorption on ZSM-5 zeolite. Fig. 5 shows the effect of time interval on VOC removal on ZSM-5 zeolite (S). As presented in Fig. 5, removal efficiencies of VOC are increasing with the passage of time. However, this effect is different for different component of VOC based on the different interactions of each component with the solid adsorbent. For all the components of VOC, there is no much increase in the removal percentage after 60 minutes. Therefore, all experiments were done up to 60 minutes of adsorption time.

3.2.2 Effect of adsorbent dosage on VOC removal

The adsorbent dosage is also an important parameter for the removal of VOC. Fig. 6 indicates the effect of adsorbent dosage on VOC removal by ZSM-5 zeolite. The results reveal that the removal efficiency of VOC increases with the increase of adsorbent dosage along with the increase of removal capacity. Which is in contrast to removal of organics from water, where adsorption capacity is decreases with the increase of adsorbent dosage [25]. A 0.040 g of adsorbent was selected as appropriate dosage for all next experiments in this study due to higher removal efficiency and capacity.

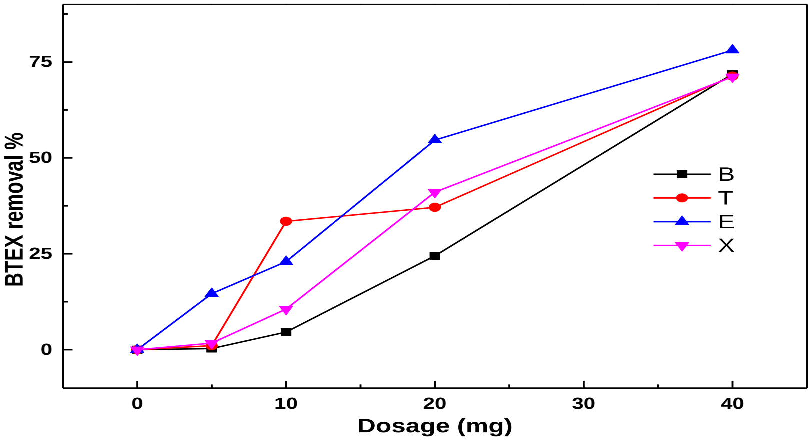

Figure.6. Effect of dosage on the BTEX % removal for the seed assisted synthesized sample

3.3 Adsorption Isotherms and Kinetics

The aim of the adsorption isotherms is to disclose the specific relation between the equilibrium concentration of pollutants (BTEX) in the bulk and the amount was adsorbed at the surface or pores of the ZSM-5 material. The isotherm studies of VOC on ZSM-5 at a constant room temperature (25 ^{o}C) were evaluated using three important isotherm models, which includes the Langmuir, Freundlich, and Temkin isotherms. The constants and correlation coefficients for isotherm models are shown in table 2. From the table 2, it can be observed that the adsorption equilibrium data for toluene and ethylbenzene fitted very well to Langmuir isotherm model than the Freundlich and Temkin models, while, benzene adsorption equilibrium data fitted to Temkin model better than other models. The last component of BTEX, xylene however, fitted almost equally to all the three models used for adsorption isotherms. These adsorption isotherms results are not much different from the already published work [26, 27].

Table. 2. Constants and correlation coefficients of isotherm models

VOC's	Langmuir			Freundlich			Temkin		
	K_1(L/mg)	Q_m(mg/g)	R^2	K_f(mg/g (L/mg)$^{1/n}$)	1/n	R^2	A_t(L/mg)	B	R^2
Benzene	49.98	0.160	0.34	0.413	-1.78	0.48	3.15	-6.06	0.79
Toluene	43.58	0.0651	0.66	0.526	-2.36	0.36	1.96	-4.59	0.11
Ethylbenzene	215.71	6.622	0.91	0.320	0.21	0.51	44.13	2.54	0.48
Xylene	57.56	0.761	0.62	0.045	-0.99	0.49	2.54	-5.13	0.52

The kinetics of adsorption illustrate the uptake rate of adsorbate (BTEX) on adsorbent (ZSM-5) and so it effects the equilibrium time. The kinetics parameters are useful for the estimation of adsorption rate. In the current study, the kinetics of adsorption data was studied using three different kinetics models: the pseudo-first-order, pseudo-second-order and Intra-particle models, which are mostly used in kinetic predictions. The fitting kinetic parameters of adsorption of BTEX on seed assisted ZSM-5 zeolite according to the pseudo-first-order; pseudo-second-order and Intra-particle models are tabulated in table 3. High R^2 values for pseudo-first-order model reveal clearly, the best fitting of the pseudo-first-order model. Hence, the adsorption of BTEX in general on seed assisted ZSM-5 zeolite is a first-order reaction. Table 3 shows that, pseudo-second-order model fits the data quite well for the first three components of BTEX, which indicates the usability of second-order model to estimate the adsorption process except for xylene. Moreover, from the table 3, it is clear that Intra-particle diffusion model is not the rate determining step for the adsorption of VOC's on the ZSM-5 zeolites.

Table. 3. Constants and correlation coefficients for kinetics models

VOC's	First-order			Second-order			Intra-particle		
	K_1 (min^{-1})	q_e(mg/g)	R^2	K_2 (g/mg min)	q_e (mg/g)	R^2	K_i(mg/g $min^{1/2}$)	q_e (mg/g)	R^2
Benzene	0.030	0.164	0.94	0.413	1.716	0.90	0.144	0.042	0.94
Toluene	0.0002	0.220	0.99	0.526	0.039	0.94	0.003	0.002	0.94
Ethylbenzene	0.0004	0.192	0.99	0.320	0.047	0.97	0.004	0.004	0.91
Xylene	0.014	0.191	0.90	0.045	7.087	0.01	0.247	0.574	0.63

4 Conclusion

The ZSM-5 zeolite particles were prepared with the help of seed (ZSM-5 particles) without any organic template and compared with routinely synthesized ZSM-5 used template TPAOH by static hydrothermal condition at 180 °C/2 days. Excellent degree of crystallization was obtained. An average pore (textural meso porosity) size increased with the seed assisted sample. Inter-growth of the seed particles led to sharp coffin-shaped ZSM-5 particles. The characteristic five membered double rings of ZSM were assured by XRD and FTIR. The presented method for synthesis of ZSM-5 is a low cost and environmentally friendly, based on decomposition products during calcinations as compared to TPAOH with all equal properties as SDA. The new material showed good adsorptive removal of BTEX from air by following the Langmuir model and first order kinetics for most of the components of VOC under study.

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