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Dynamic adsorption of DMMP over synthetic zeolite-Alpha

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Abstract Zeolite-Alpha was synthesized under hydrothermal and static conditions and was characterized by N2 BET surface area, XRD, SEM–EDAX analysis, NH_3-TPD and FTIR. The dynamic adsorption experiments were carried out on a TPD plus Chemisorption system (Micrometrics ASAP 2920 unit). Adsorption was found to be high initially and it then decreases with an increase in the injected volume. It was found that adsorption increases with an increase in contact time between DMMP and zeolite-Alpha only up to 8 h after which it remains almost constant. Desorption pattern was analyzed which shows two types of peaks, sharp peak with onset temperature of around 30 °C which represents desorption of physisorbed DMMP and a broad peak with the onset temperature of around 110 °C which represents the desorption of strongly chemisorbed DMMP.

1. Introduction

Zeolites are aluminosilicates with small practical size used to remove organic matter, drug residues, trace metal ions and lots of pollutant from the wastewaters due to their adsorption and ion exchange capacity. These mineral-based functional materials show a great variety of applications in catalysis, adsorption, environmental remediation, polymers, etc. Zeolites exhibit good properties of adsorption and have been used for the minimization of toxicological effects of toxic metal ions and other pollutants. The previous studies of us show the sorption of trace metal ions from wastewater on clintonite (Khanday et al., 2012). Wagner and Bartram (1999) examined zeolite adsorbency with potential chemical reactivity in a study of NaY (and AgY) zeolite activity against VX and one of its simulants, O, S-diethyl phenyl phosphonothiolate (DEPPT).

Dimethyl methylphosphonate [DMMP, CH3PO(OCH3)2] due to its organophosphorus composition mimics nerve agents and is commonly considered as a simulant for chemical warfare agents (CWAs) and insecticides, such as the G-series nerve agents tabun (GA), sarin (GB), soman (GD) and paraoxon (Bartelt-Hunt et al., 2008). DMMP has also become a significant environmental and food chain pollutant due to its large consumption as a common additive for anti-foaming agents, plasticizers, stabilizers, textile conditioners and antistatic agents (Rudel and Perovich, 2009). Consequently, DMMP sensors and adsorbents with high sensitivity, rapid response, low energy consumption and good reversibility at room

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temperature are highly desirable, not only for neurotoxin detection for counter-terrorism purposes, but also for environmental protection and medical diagnoses for risk management (Brunol et al., 2006; Ying et al., 2007; Comini et al., 2002). Templeton and Weinberg (1985) described the adsorption and decomposition of DMMP on aluminum oxide surface at temperature ranging from 200 to 673 K. Ekerdt et al. (1988) discussed the decomposition chemistry of organophosphorus compounds interacting with metal and metal oxide surfaces. He has also highlighted on significant research directions for surface chemical sciences, surface reaction chemistry, solid-state synthesis and organometallic cluster chemistry. Work has also been carried out for the infrared study of adsorbed organophosphorus on silica (Kanan and Tripp, 2001). Attempts were also made by Cao et al. (2001) to study the higher temperature thermo catalytic decomposition of dimethyl methylphosphonate on activated carbon to carbon dioxide, methanol and phosphorus pentaoxide. Yang et al. (2006) studied sorption and decomposition of DMMP to methylphosphonate on Sodium X-type faujasite zeolite.

DMMP a low molecular weight and highly volatile toxic chemical needs to be removed from the environment. Zeolite-Alpha synthesized in the present study will perform the physical adsorption of DMMP and also hydrolysis of some amount of physisorbed vapors by the water content present on the surface of zeolite-Alpha.

2. Experimental

2.1. Reagents and chemicals

Anhydrous sodium aluminate (50–56% Al_2O_3, 0.05% Fe_2O_3, 40–45% Na_2O) from Riedel-deHaën, tetramethylammonium hydroxide (TMAOH) 99%, from Aldrich, precipitated silica (Aerosil 200) from Degussa, DMMP from Merck and deionized water.

2.2. Instrumentation

Teflon lined autoclave for zeolite-Alpha synthesis, Shimadzu XRD 6000 equipment for X-ray diffraction (XRD), Shimadzu FT-IR spectrophotometer for Fourier transform-infrared spectroscopy (FT-IR), Autosorb 2120 for surface area measurements by N_2 BET method, Micrometrics ASAP 2920 unit for thermal programed desorption (TPD), JEOL JSM 5800, SEM–EDAX for scanning electron microscopy (SEM), Oxford INCA system for electron dispersion spectroscopy (EDS) and thermal programed desorption plus Chemisorption system (Micrometrics ASAP 2920 unit) for dynamic adsorption and thermal desorption studies.

2.3. Synthesis of zeolite-Alpha

The hydrothermal synthesis of layered aluminosilicate alpha zeolite was carried out under static conditions using tetramethylammonium hydroxide (TMAOH) as an organic template for preserving its pore. A total of 15.6 g of anhydrous sodium aluminate (50–56% Al_2O_3, 0.05% Fe_2O_3, 40–45% Na_2O, purchased from Riedel-deHaën) was dissolved in 46.4 g of deionized water. The solution was thoroughly stirred until complete dissolution, and then 111.7 g of tetramethylammonium hydroxide (TMAOH, 99%, from Aldrich) was added drop wise with vigorous stirring. To this, 44.5 g of precipitated silica (Aerosil 200, Degussa) was added in small portions and the resulting slurry continued to be stirred vigorously. After 40 min of stirring, at room temperature, a gel formed was kept for 48 h in polypropylene bottle and then placed in a Teflon lined autoclave at 90 °C for 24–30 h. After immersing the autoclaves in cold water, the resulting material was washed and centrifuged until pH $\leqslant 9$ and subsequently dried at 110 °C. The obtained sample of Na-alpha zeolite was calcined in the absence of air at 540 °C for 7 h in order to remove water and organic precursor.

3. Results and discussion

3.1. Characterization of zeolite-Alpha

The synthesized zeolite-Alpha was characterized by XRD, FTIR, N_2 BET surface area, NH_3-TPD, SEM and EDS techniques.

3.1.1. X-ray diffraction

For X-ray Diffraction, the samples were sieved in an ABNT n° 200 (0.074 mm) sieve and then placed in an aluminum sample holder for X-ray diffraction assays, using a Shimadzu XRD 6000 equipment. The operational details of the technique were set as follows: Copper Kα radiation at 40 kV/30 mA, with a goniometer speed of 2°/min and a step of 0.02° in the 2θ range scanning from 2° to 50°. The only d-spacings of interest in the X-ray patterns were the basal spacings along the *c* axis. X-ray diffraction pattern of calcined zeolite-Alpha is displayed in Fig. 1. The XRD pattern reveals that zeolite-Alpha is crystalline and is in a highly dispersive state. The diffraction signals at 2θ corresponding to two peaks at 14.5° and 25.5° are clearly observed.

3.1.2. Fourier transform-infrared spectroscopy

For FTIR analysis, the alpha zeolite sample was submitted to physical treatment in accordance with the KBr method, which consists of mixing 0.007 g of the sample and 0.1 g of KBr, grinding and pressing the solid mixture to 5 tons for 30 S in order to form a pellet that allows the passage of light. Characterization was performed using an infrared spectrophotometer Shimadzu FT-IR in the wavelength ranging from 4000 to 400 cm^{-1}, with increments of 650 cm^{-1} and a resolution of 4 cm^{-1}. FT-IR spectra of zeolite-Alpha (Fig. 2) shows absorption bands at around 450 cm^{-1} which is attributed to Si, Al–O bond, and those at 1030 and 750 cm^{-1} are, respectively attributed to asymmetric and symmetric stretches of the zeolite framework. A band for the OH group is observed at 3470 cm^{-1}. An absorption band at 1460 cm^{-1} is attributed to the NH_4^+ functional group of the organic template (TMAOH). A band at 1700 cm^{-1} is attributed to the typical deformation band of adsorbed H_2O.

3.1.3. N_2 BET surface area

Surface area measurement was performed on an Autosorb 2120 by nitrogen adsorption at liquid nitrogen temperature using the multipoint N_2 BET method. BET surface area of zeolite-Alpha was found to be around 350 m^2/g zeolite. Fig. 3 re-

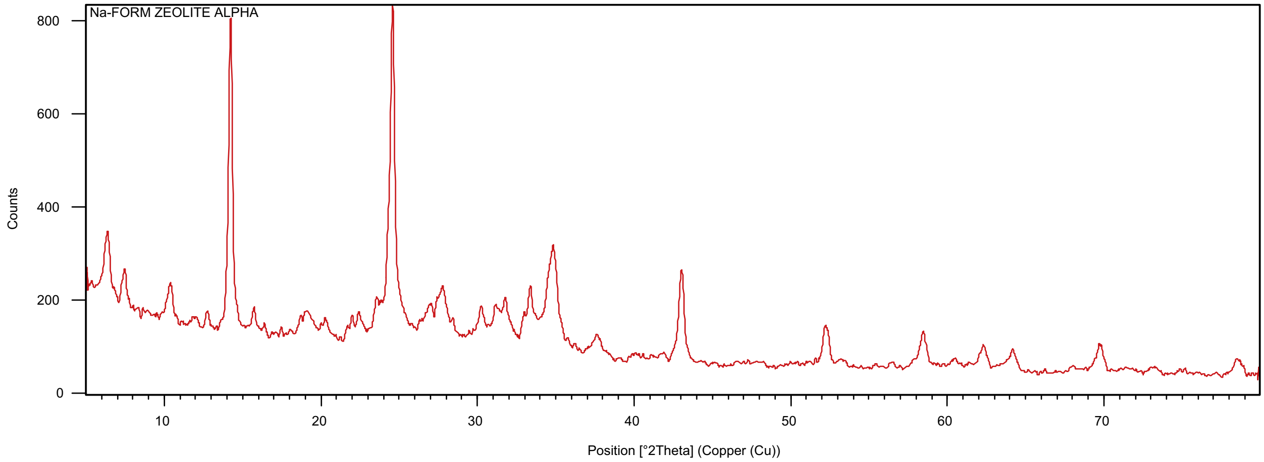


Figure 1 X-ray diffraction pattern of zeolite-Alpha.

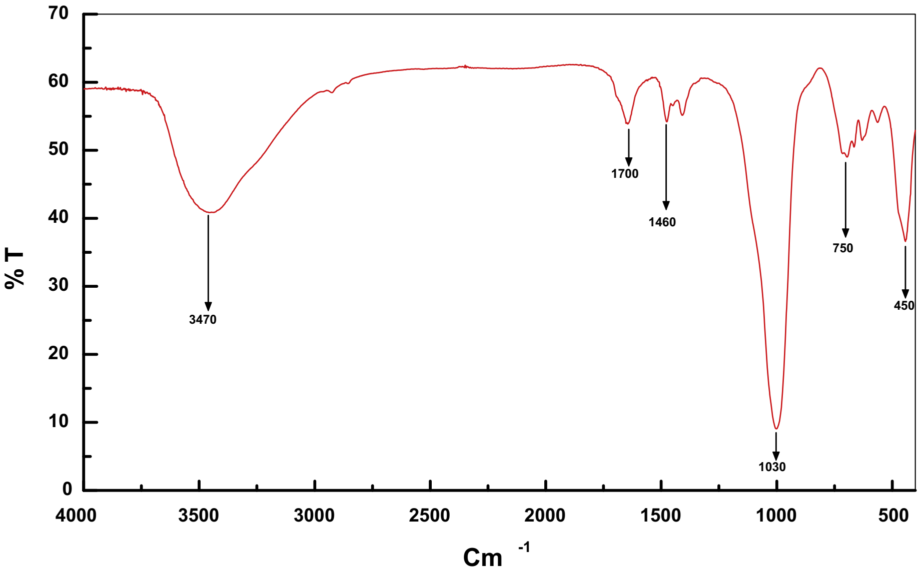


Figure 2 FT-IR pattern of zeolite-Alpha.

veals that zeolite-Alpha exhibits the narrow pore size distribution in the range of 0.2–0.6 nm. According to the definition by IUPAC, the adsorbent pores are classified into three groups: micropore (diameter <2 nm), mesopore (2–50 nm), and macropore (>50 nm) indicating that the zeolite-Alpha prepared in the present study contains only micropores.

3.1.4. Thermal programed desorption

For Temperature programed desorption (TPD) studies sample was pre-treated with N_2 at 450 °C to remove all the impurities. Then ammonia gas was adsorbed on cooling at 30–40 °C and charged into the U-tube reactor for thermal desorption studies. TPD was performed by heating the sample from 30 °C to above 450 °C at a rate of 10 °C/min using helium as carrier. Temperature programed desorption (TPD) of ammonia was performed on Micrometrics ASAP 2920 unit to determine the physisorption and chemisorption sites present on zeolites. TPD pattern of zeolite-Alpha is shown in Fig. 4. The sharp peak with onset temperature of 35 °C and T_{max} around 60 °C is ascribed to the desorption of physisorbed NH_3 confirming the weak adsorption sites. The broad peak with onset temperature of around 150 °C and T_{max} around 250 °C is attributed to the desorption of strongly chemisorbed NH_3 as well as thermal decomposition confirming the strong adsorption sites of the zeolite-Alpha.

3.1.5. Scanning electron microscopy

Surface micrograph of zeolite-Alpha was obtained by JEOL JSM 5800, SEM–EDAX (Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy) instrument. Scanning electron micrograms of zeolite-Alpha were taken at various magnifications (1000×, 5000× and 10,000×) (Fig. 5) for understanding its surface morphology. It appears under the scanning electron microscopy as chunks and sometimes as spheres of 5–10 μm.

3.1.6. Electron dispersion spectroscopy

Sample for EDS (Oxford INCA system) analysis was coated with thin gold foil in order to avoid charge influence. The chemical composition of the material was obtained

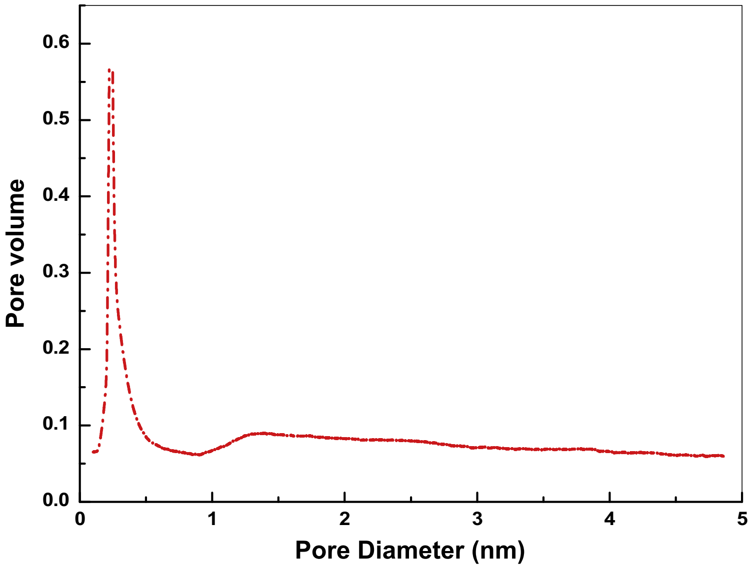


Figure 3 Pore size distribution of zeolite-Alpha.

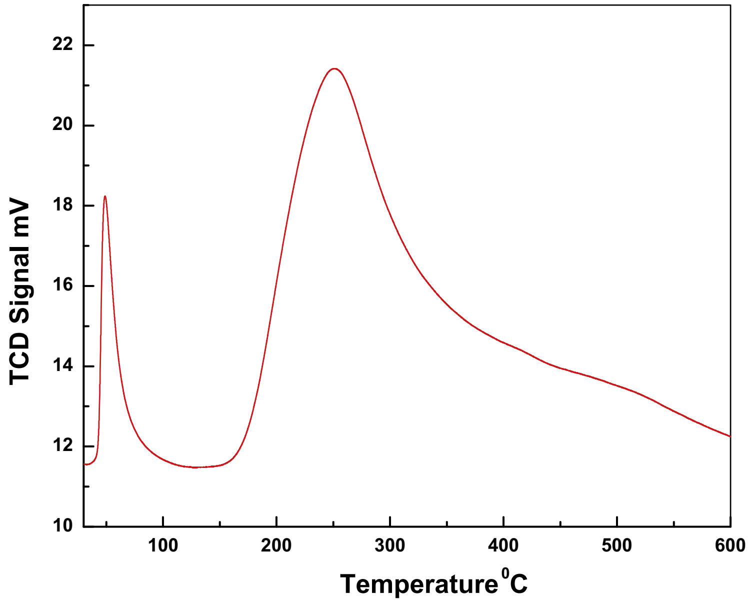


Figure 4 TPD profile of zeolite-Alpha.

quantitatively from energy dispersive analysis (EDS) (Fig. 6). Results obtained for elements like Al, Na, O and Si show that O is present in abundance and is almost half of the overall weight of material. Among Si and Al, Si is found to be in abundance confirming Si/Al ratio greater than 1 and also the elemental ratios are in accordance to the molar composition taken during the synthesis of zeolite-Alpha.

3.2. Dynamic adsorption of DMMP over zeolite-Alpha

The dynamic adsorption and thermal desorption experiments were carried out on the TPD Plus Chemisorption system (Micrometrics ASAP 2920 unit). 100 mg of zeolite-Alpha was taken in a well cleaned over dried Quartz reactor fitted with some amount of quartz wool. This quartz tube was then placed in furnace of the instrument. For dynamic adsorption process, Helium (60 cc/min) was used as a carrier gas and TCD current for helium was kept 108 mA. Detector and Line temperature were kept the same at 100 °C and Gas Sampling Valve and Injector were maintained at 140 °C. 1 μL of DMMP (1 PPMV) was injected through the injector. Since the injector temperature was higher than the boiling point of DMMP, it got converted easily to vapors which were carried by the Helium gas through the reactor containing zeolite-Alpha. Some of the DMMP vapors got adsorbed on the surface of zeolite and the rest passed to detector where the area of the so obtained peak was recorded. Same experiment was repeated by taking the blank reactor without zeolite-Alpha and the obtained peak

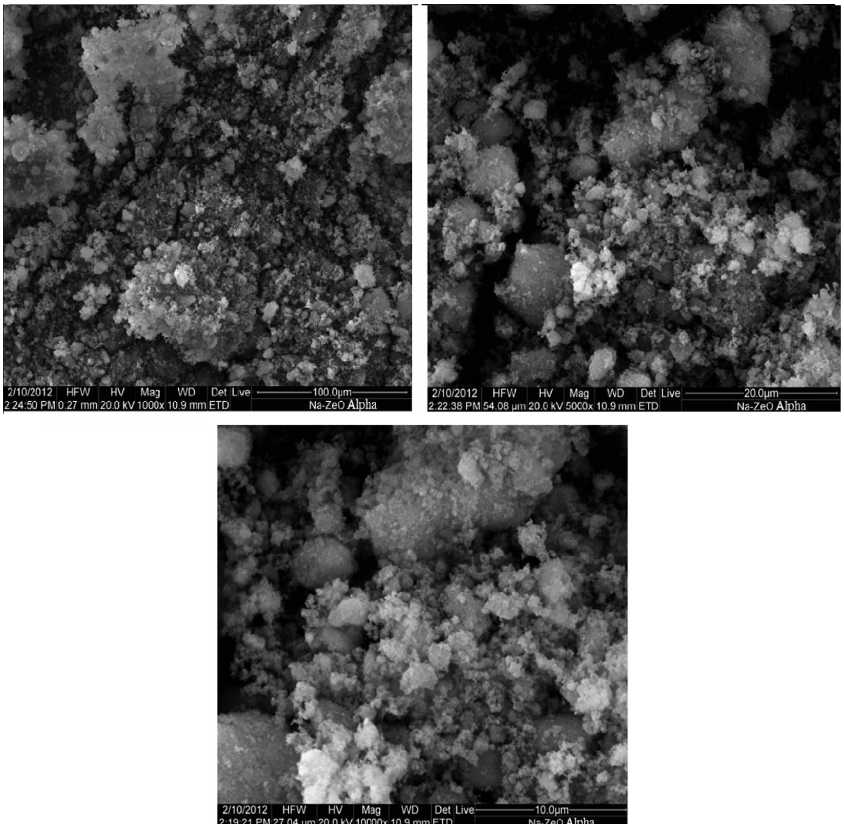
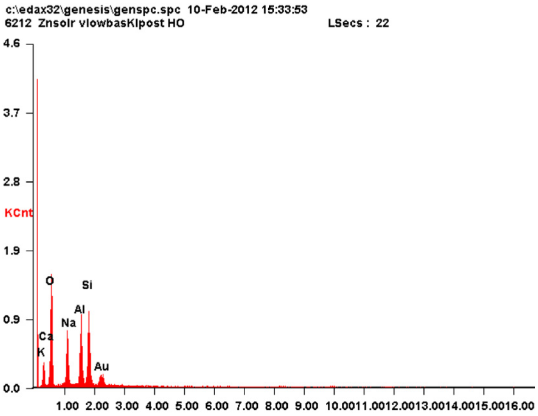


Figure 5 SEM images of zeolite-Alpha at various magnifications.



Element	Wt %	At %
O K	45.66	61.30
NaK	15.37	14.36
AlK	13.55	10.78
SiK	16.45	12.58
AuM	08.97	00.98

Figure 6 EDS analysis of zeolite-Alpha.

was recorded. The exact amount of DMMP adsorbed was calculated by calibrating the area of obtained adsorption peak with the peak obtained for blank experiment.

$$\begin{aligned}\text{DMMPadsorbed(PPMV)} = {} & (\text{Area of blank experiment} \\ & - \text{Area after adsorption})/ \\ & (\text{area of blank Experiment})\end{aligned}$$

Then thermal desorption was carried out to check reversibility of the process. Zeolite-Alpha after desorption process was used further and the same experiment was repeated for each sample twice to check the efficiency each time. Fig. 7 illustrates the adsorption pattern with respect to the injected volume of DMMP over zeolite-Alpha. It is observed that adsorption is more initially for both the runs and then it decreases with subsequent injections, the reason being the saturation of adsorption sites of zeolite-Alpha with increased volume of DMMP. With the increase in volume of DMMP the surface sites present on zeolite-Alpha which are responsible for adsorption get occupied with the adsorbed DMMP, thus reducing further adsorption.

Adsorption of DMMP over zeolite-Alpha for two consecutive runs illustrates the varying adsorption capacities (Fig. 8). The 1st run has a higher adsorption capacity than the 2nd

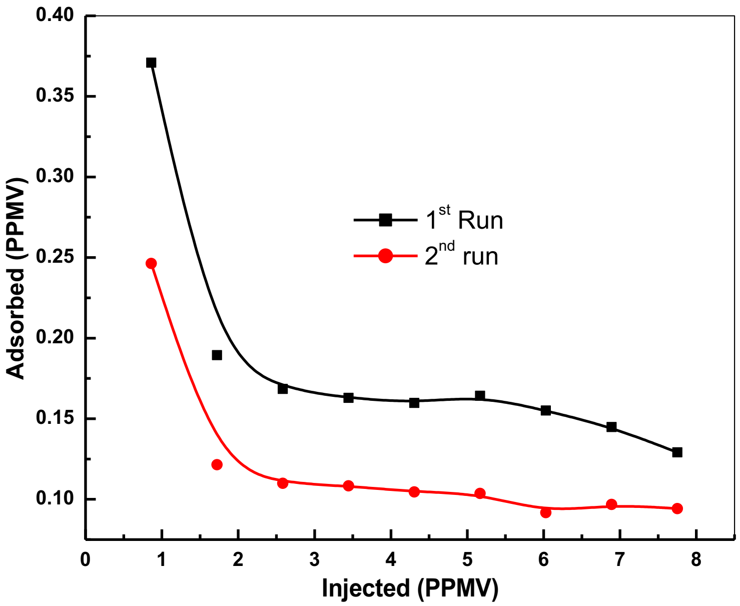


Figure 7 Adsorption pattern of DMMP over zeolite-Alpha.

run; the reason is that loss of some adsorption sites may have occurred during the first run. Further it confirms the recyclability of zeolites but the efficiency is less than 100%.

Effect of time on the adsorption of DMMP over zeolite-Alpha was carried out under static conditions using a batch reactor. 20 mL of 10 PPMV DMMP in acetone was taken in a double necked flask and 100 mg of adsorbent was added. Acetone was used only in order to increase the volume of solution and to allow a better adsorbent–adsorbate interaction. Amount of DMMP adsorbed after various time intervals was determined by injecting 1 μL of this solution at that time in GC (gas chromatogram) for quantification. The effect of time on adsorption of DMMP over synthetic zeolite-Alpha at room temperature (25 °C) and adsorbent amount of 100 mg is shown in Fig. 8. It can be seen that adsorption increases with increase in time and the adsorption rate is higher up to a certain time limit (8 h) and then it slows down. An increase in the adsorption with increase in time can be attributed to greater contact time between adsorbent and adsorbate. The driving force for adsorption, which is the concentration difference between the bulk solution and the solid–liquid interface, is initially very high and this results in a higher adsorption rate. However, after the initial period, slower adsorption rate may be due to slower diffusion of DMMP into the interior channels of zeolite-Alpha because the adsorbent surface sites become saturated with adsorbed DMMP. Also there occurs a decrease

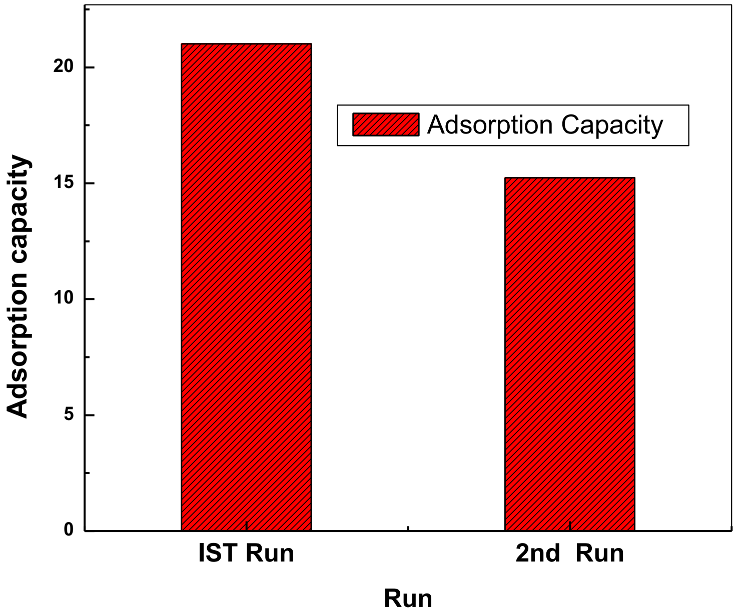


Figure 8 DMMP adsorption capacity of zeolite-Alpha.

in the concentration gradient with time since the initial concentration of DMMP is fixed which also results in a slower adsorption rate after the initial period. (See Fig. 9).

Thermal desorption was carried out by heating the sample to around 500 °C. For this process initial temperature of the furnace was kept at 40 °C, the rate of rise in temperature was set as 10 °C/min and the run time was fixed at 50 min. Area of the so obtained desorption pattern was recorded. Desorption pattern was carried out in the temperature range of 25–550 °C which shows two types of peaks (Fig. 10). A sharp peak with onset temperature of around 30 °C which represents desorption of the physisorbed DMMP (DMMP held by weak adsorption sites) and a broad peak with the onset temperature of around 110 °C which represents desorption of strongly chemisorbed DMMP (DMMP held by strong adsorption sites). From these peaks we can easily distinguish between the physisorbed and chemisorbed DMMP as physisorbed DMMP which is loosely bound to the zeolite surface gets desorbed easily and requires lesser temperature (around 30 °C) than the chemisorbed DMMP which gets desorbed at a higher temperature (around 110 °C). The desorption pattern of the second run shows comparatively smaller peaks than that of first run, this is because of loss of active sites due to thermal decomposition during the first run. FT-IR analysis of

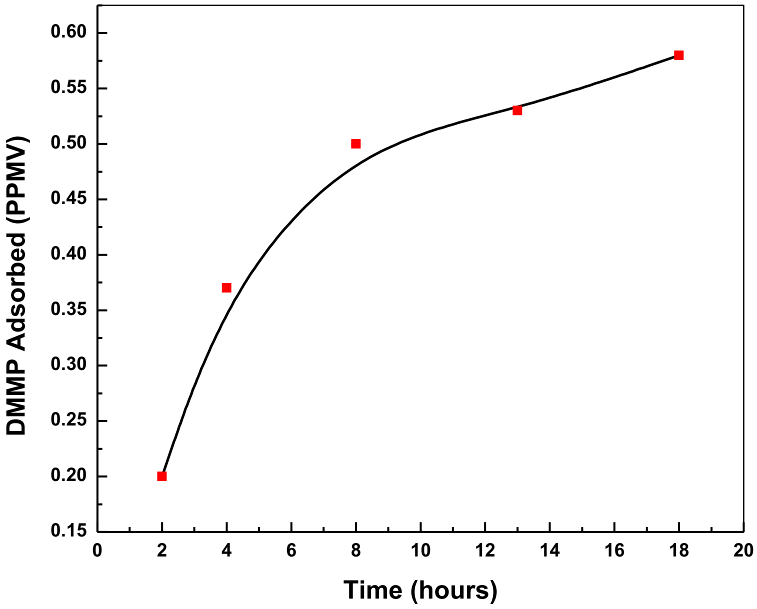


Figure 9 Effect of time on DMMP adsorption over zeolite-Alpha.

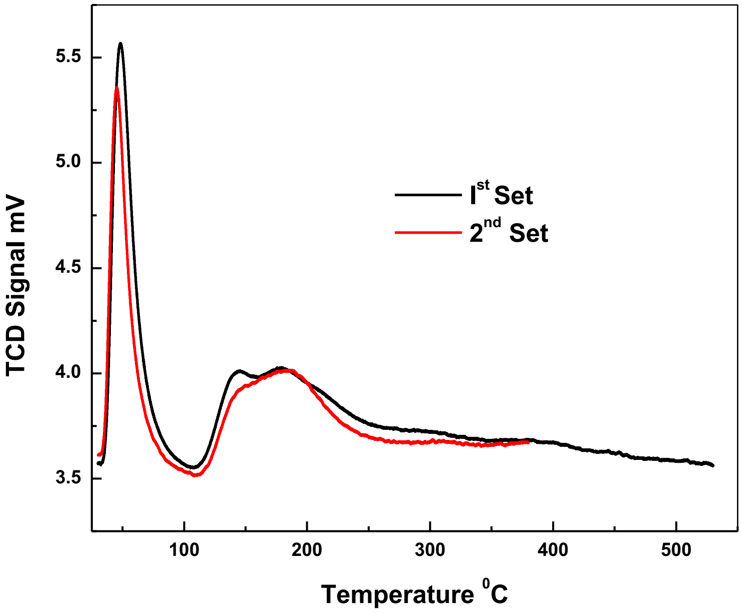


Figure 10 Thermal desorption pattern of DMMP over zeolite-Alpha.

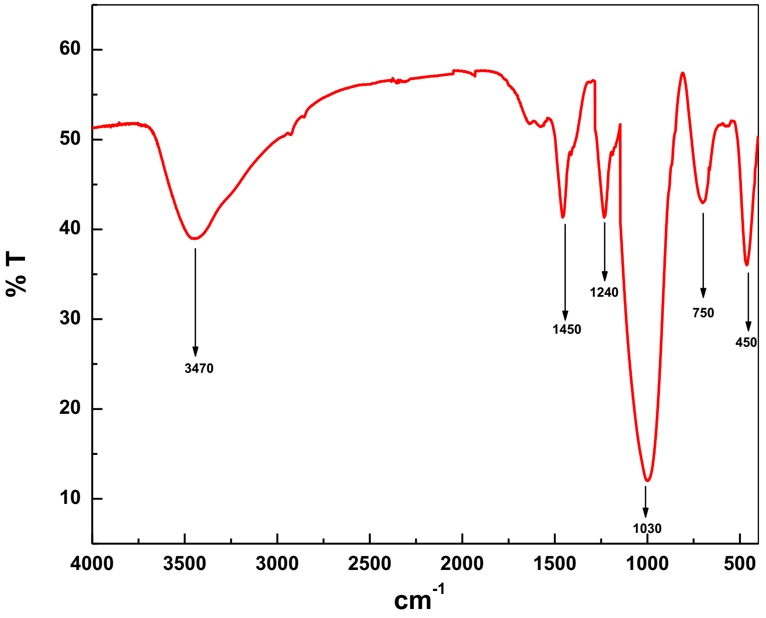
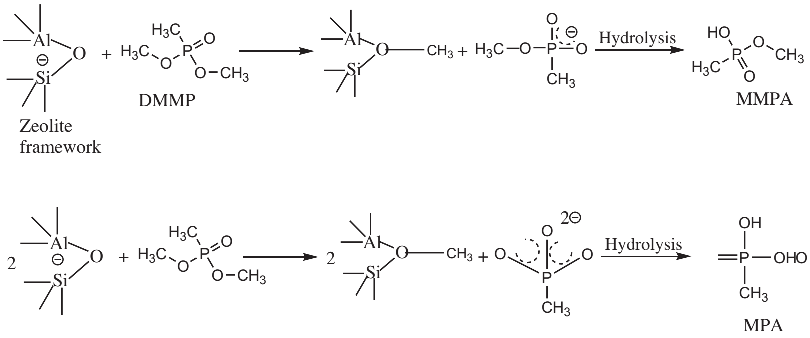


Figure 11 FT-IR pattern of zeolite-Alpha after 1st run.



Scheme 1 Mechanism for the hydrolytic conversion of DMMP into MMPA and MPA on zeolite Alpha framework.

zeolite-Alpha was carried out after 1st run and the spectrum (Fig. 11) clearly shows a sharp peak around 1240 cm^{-1} characteristic of the P═O bond of strongly adsorbed DMMP.

Further it was observed that the amount of DMMP desorbed was less than that of adsorbed which means that the process is not 100% reversible. The reason for this loss is that some amount of DMMP would have been hydrolyzed by water present in the zeolite-Alpha framework into methyl methyl phosphonic acid (MMPA) and methyl phosphonic acid (MPA). The proposed mechanism for this hydrolytic conversion is shown in Scheme 1 (Ying et al., 2007).

4. Conclusion

Synthesized zeolite-Alpha was characterized with various techniques and dynamic adsorption of DMMP over it was carried out successfully. Adsorption of DMMP was found to be high initially and it then decreases with an increase in the injected volume. It was found that adsorption increases with increase in the contact time between DMMP and zeolite-Alpha only up to 8 h after which it remains almost constant. Further desorption experiments were also carried out successfully and desorption pattern revealed that desorption has occurred from both weak as well as strong adsorption sites.

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References

Bartelt-Hunt, S.L., Knappe, D.R.U., Barlaz, M.A., 2008. A review of chemical warfare agent stimulants for the study of environmental behavior. Crit. Rev. Environ. Sci. Technol. 38, 112–136.

Brunol, E., Berger, F., Fromm, M., Planade, R., 2006. Detection of dimethyl methylphosphonate (DMMP) by tin dioxide-based gas sensor: response curve and understanding of the reactional mechanism. Sens. Actuators, B 120, 35–41.

Cao, L.X., Suib, S.L., Tang, X., Satyapal, S., 2001. Thermocatalytic decomposition of dimethyl methylphosphonate on activated carbon. J. Catal. 197 (2), 236–243.

Comini, E., Faglia, G., Sberveglieri, G., Pan, Z.W., Wang, Z.L., 2002. Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts. Appl. Phys. Lett. 81, 1869–1871.

Ekerdt, J.G., Klabunde, K.J., Shapley, J.R., White, J.M., Yates, J.T., 1988. Surface chemistry of organophosphorus compounds. J. Phys. Chem. 92, 6182–6188.

Kanan, S.M., Tripp, C.P., 2001. An infrared study of adsorbed organophosphonates on silica: a prefiltering strategy for the detection of nerve agents on metal oxide sensors. Langmuir 17, 2213–2218.

Khanday, W.A., Singh, S.K., Bhaudoriya, J., Majid, S.A., Tomar, S.S., Tomar, R., 2012. Study of Sorption of Pb^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} from wastewater on synthetic analogues of clintonite. Colloid J. 74 (5), 573–581.

Rudel, R.A., Perovich, L.J., 2009. Endocrine disrupting chemicals in indoor and outdoor air. Atmos. Environ. 43, 170–181.

Templeton, M.K., Weinberg, W.H., 1985. Adsorption and decomposition of dimethyl methylphosphonate on an aluminium oxide surface. J. Am. Chem. Soc. 107, 97–108.

Wagner, G.W., Bartram, P.W., 1999. Reactions of VX, HD, and their simulants with NaY and AgY zeolites. Desulfurization of VX on AgY. Langmuir 15 (23), 8113–8118.

Yang, S.W., Doetschman, D.C., Schulte, J.T., Sambur, J.B., Kanyi, C.W., Fox, J.D., Kowenje, C.O., Jones, B.R., Sherma, N.D., 2006. Sodium X-type faujasite zeolite decomposition of dimethyl methylphosphonate (DMMP) to methylphosphonate: nucleophilic zeolite reactions I. Microporous Mesoporous Mater. 92, 56–60.

Ying, Z., Jiang, Y., Du, X., Xie, G., Yu, J., Wang, H., 2007. PVDF coated quartz crystal microbalance sensor for DMMP vapor detection. Sens. Actuators, B 125, 167–172.