



## Molecular electron density and nitrate-phosphate sorption efficiency of zeolite-A: Physico-chemical and DFT analyses

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Design of nitrate and phosphate carrying molecular scaffolds is significant in various sectors of applied interest. Motivated towards this interesting field, herein a combined experimental-DFT study of zeolite-A is reported. The sorption efficiency of this complex framework towards nitrate and phosphate ion has been analyzed. The implications of surface modification, change in pH and temperature upon the property of ion adsorption/absorption have been discussed. An increasing trend in sorption is observed up to pH~7 and up to temperature ~ 40 °C. In addition to experimental measures theoretical calculations have also been added to discuss the optimal frame work of the zeolite using Stuttgart-Dresden basis set and WB97XD as functional. Molecular simulations involving spectroscopic and electrostatic potential determination have been computed after optimization. A combined experimental and theoretical thermodynamic study has also been the active part of the study. From the study it may be established that the experimental results are in good agreement with the DFT based speculations.

**Keywords:** Sorption, Zeolite, DFT, Nitrate, Phosphate

Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ) are crystalline solids and highly soluble in water. They are extremely useful in agriculture as a source of high-nitrogen, phosphorus and potassium<sup>1</sup>. Ammonium nitrate is considered as an important fertilizer having NPK rating 34-0-0 (34% nitrogen)<sup>2</sup>. Also, ammonium nitrate is more stable and does not release nitrogen to the atmosphere quickly. MKP powder of fertilizer-grade contains the equivalent of 52%  $\text{P}_2\text{O}_5$ , 34%  $\text{K}_2\text{O}$  and is called NPK 0-52-34 often used as a nutrient source in the greenhouse trade and in hydroponics. Since  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  and soil particles are negatively charged and hence are not strongly retained in the soil. In addition  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  are very mobile and get easily solvated by water. Consequently, they are susceptible to be leached through the porous soil particles to groundwater and thus are made unavailable to plants for longer time. When high  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  content water reaches a lake or any other water body, the growth of aquatic plants is enhanced causing depleted oxygen levels and as those plants die, they are decomposed by microorganisms. Hence, fishes and other aquatic animals cannot survive under these anoxic conditions and die, resulting in eutrophication<sup>3-5</sup>. Management practices that can be

used in slow release fertilizers (SRFs) are better alternatives to soluble fertilizers as the nutrients are slowly released throughout the season. Also plants can utilize most of the nutrients without wastage by leaching. Hence, aluminosilicate minerals (*viz* zeolites) can be suggested to act as efficient and optimal fertilizer carriages<sup>6,7</sup>.

Density functional theory (DFT) is considered a powerful tool in the current times that is applicable in every field of research<sup>8</sup>. Before synthesizing any desirable material theoretical calculations are made on priority bases to infer the possible applicability of a material. By this way, both time and labour are meticulously consumed for a task. By the multifold applications of DFT even fantasy chemical features can be evaluated. Due to the potentiality of depicting molecular structure, theoretical spectroscopic measurements, reactive properties and other surface or sub-surface descriptors, computational science has evolved to a significant zenith<sup>9</sup>.

In conspicuous fascination towards zeolites for nitrate and phosphate sorption study, here a combined experimental-DFT analysis of zeolite-A is reported. Synthesis and characterization of this aluminosilicate with application as nitrate/phosphate adsorbent under composite experimental-theoretical means has been

made in this work. In addition to various physico-chemical formulation techniques, molecular charge density plots and molecular electrostatic potential of the zeolite has been discussed.

### Materials and methods

Sodium hydroxide (95%), sodium aluminate and sodium metasilicate were supplied by Merck. All the chemicals that were used were of AR grade. It may be noted that all the chemicals were used as received without any further purification.

Zeolite-A along with other materials were characterized by the help of Powder X-Ray diffraction (XRD), fourier transform infrared (FTIR) spectrophotometer (Shimadzu) and UV-visible Systronics 114 spectrophotometer. The diffraction patterns of all the materials were recorded at room temperature on PW 3064 diffractometer. The spectra was scanned using  $\text{CuK}\alpha$  radiation of wavelength ( $\lambda$ ) = 1.54060 Å and the diffractograms were recorded in the range  $2\theta = 5^\circ\text{--}60^\circ$  at the scanning speed of 1 step/ second. Sorption and desorption data have been obtained by using electronic spectral measurements. The ion exchange capacity was calculated by versene method (EDTA titration).

At each level of experimental formulation theoretical calculations using Gaussian09 package were also carried out. The proposed structure of Zeolite-A was made as input file for arriving at the energy minimal structure using SDD basis set and WB97XD as functional<sup>10,11</sup>. The optimized framework was then computed for various spectroscopic evaluations including electron density plots and frontier orbital analysis. To add interest in respect to adsorption, absorption or ion exchange capacity of the aluminium silicate, each ion (nitrate and phosphate) were also separately investigated theoretically to present comparative insights of the respective study. In addition to other structural parameters electron density plots were also evaluated<sup>12</sup>.

### Synthesis of zeolite-A

The synthesis of zeolite-A was carried out following a slightly modified procedure described previously<sup>13,14</sup>. 0.723 g of NaOH were added to 80 mL of water and stirred until completely dissolved. Mark this solution as "A". Solution A was made into two equal parts of 40 ml each in polypropylene bottles namely solution B and C, respectively. 8.258 g of sodium aluminate were added to solution B and stirred gently in a capped bottle until giving clear

solution D. To solution C, 15.48 g sodium metasilicate were added and mixed gently until clear solution E was obtained. Now the solutions D and E were mixed (silicate solution into aluminate solution) thoroughly until homogenized in the tightly capped bottle to give a final mixture. The composition of the above mixture in terms of oxide molar ratio was 3.165  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:1.926 \text{SiO}_2:128.\text{H}_2\text{O}$  called batch composition. The solution was kept for crystallization in a teflon-lined stainless steel autoclave under static condition at 373 K for 5-6 h. After recovering the product, it was cooled to below 303 K, filtered and washed with de-ionized water until pH of filtrate was below 9 and finally dried at 353-383 K overnight to obtain the final product. The yield was about 11 g.

Analytical data: Zeolite A batch composition: 3.165  $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:1.926 \text{SiO}_2:128 \text{H}_2\text{O}$ , Si/Al: 50:50. XRD data  $\text{CuK}\alpha$  ( $\lambda$ ) = 1.54060 Å.  $2\theta$  value: 35. FTIR data ( $\text{cm}^{-1}$ ):  $\nu(\text{Si-Al-O})$  500,  $\nu(\text{OH})$  3500. SEM crystal size: 1-10  $\mu\text{m}$ , non uniform surface. BET surface area: 355-435  $\text{m}^2/\text{g}$ , pore size: 0.2-0.6 nm.  $\text{NH}_3\text{-TPD}$ : 13324 a.u.

### Surface modification of zeolites

The zeolite was synthesized hydrothermally and modified with a quaternary alkyl ammonium cation, Hexadecyl trimethyl ammonium bromide (HDTMABr). A pre weighed quantity of washed zeolite sample was mixed with HDTMA solution prepared in ethanol/water (50/50). The concentrations of various HDTMA solutions used for the synthesis of surface modified zeolites were 300, 600, 900 and 1200  $\text{mgL}^{-1}$ . The suspension was stirred at room temperature for 24 h, centrifuged at same temperature, washed with ethanol/water (50:50) and then with distilled water. The material was made  $\text{Br}^-$  free by filtration and washing until as determined by  $\text{AgNO}_3$  test. These modified zeolites were kept in closed bottles at room temperature until used.

### Results and Discussion

The main area of interest in zeolite synthesis is their crystal morphology. To determine the crystalline nature of synthesized zeolites various studies have been performed on both the materials. In the present work instrumental techniques viz. XRD, FTIR, UV-visible spectroscopy and EDTA titration were used.

### Powder X-ray diffraction (XRD) and DFT based framework optimization

The synthesized zeolites were characterized by XRD after hydrothermal crystallization as shown in

Fig. 1. It was observed that zeolite framework has not undergone any remarkable structural change by the incorporation of metal ion and the crystallinity of zeolite was preserved, though, only slight change in the intensity of the bands was noticed. The changes in intensities of the peaks suggested that the porous structure of zeolite can store these metal ions without any strain. The main framework of the zeolite was undamaged, which indicates that the crystallinity and morphology of zeolite remains preserved during ion exchange process. The XRD patterns reveal that Zeolite-A is semi-crystalline and in highly dispersive state. The diffraction signals at  $2\theta$  corresponding to 35.4 for Zeolite-A is clearly observed.

Zeolite-A as representative parent material was initially optimized to obtain an energy minimal structural frame-work. Geometric optimization is the main step in density functional theory calculation. In the material under discussion no imaginary frequency was found under the theory applied for the calculation. This clearly shows the structural form (Fig. 2) as the energy minimal state. The main optimization parameters *viz* bond lengths and bond angles have shown suitably effected by the alternate substitution of different atoms and their impact on the real values. The significant bond lengths like Al(11)-O(3) comes out to be 1.75Å, O(3)-Si(16) 1.71Å and Si(16)-O(1) 1.71Å. The material shows mainly two types of bonds in an alternate fashion which are O-Si-O and O-Al-O. The calculated values indicate former angle to be  $99^\circ$  and the latter  $126^\circ$ . This affirms the fact that the material shows the desirable properties to act as porous material depending upon the nature of different elemental entities<sup>15</sup>. It is here to mention that the O(1)-Si(16)-O(3) moiety shows some deviation as compared to other corners. Such deformity has also been observed in experimentally as discussed in FTIR section.

#### Experimental and theoretical infrared spectroscopy

Zeolites are found to exhibit a typical infrared spectroscopic pattern. The spectra can be grouped in two classes of vibrational modes. The first is due to internal vibration of  $TO_{4/2}$  tetrahedron which is primary unit of structure and is not sensitive to other structural vibrations. From Fig. 3(a) It is clear from the peaks between  $950-1250\text{ cm}^{-1}$  and the peak obtained between  $420-500\text{ cm}^{-1}$  is assigned to bending modes of Si-Al frame work. The second type of vibration depends on the overall structure and arrangement of the individual tetrahedral units as well

as on their large pore openings. The presence of hydroxyl group can be confirmed by a peak obtained at  $3550\text{ cm}^{-1}$ . The band at  $3346.50\text{ cm}^{-1}$  is due to the loosely bounded water molecules attached to zeolite framework. On observing the change in the positions of these vibrational bands; sorption and desorption of water (hydration and dehydration) may be easily monitored by IR.

The band at  $550-580\text{ cm}^{-1}$  can be correlated with the structural deformation; especially stretching vibrations of six coordinated aluminium. Deformation of the four membered ring is observed around  $730\text{ cm}^{-1}$  along with the other modes. The bands below  $550\text{ cm}^{-1}$  are usually due to (O-T-O) bending

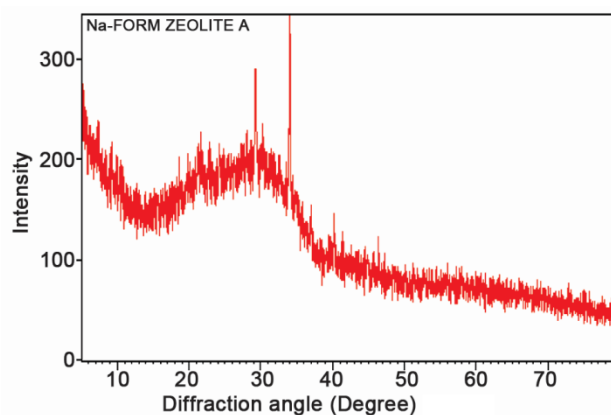


Fig. 1 —XRD pattern of zeolite-A.

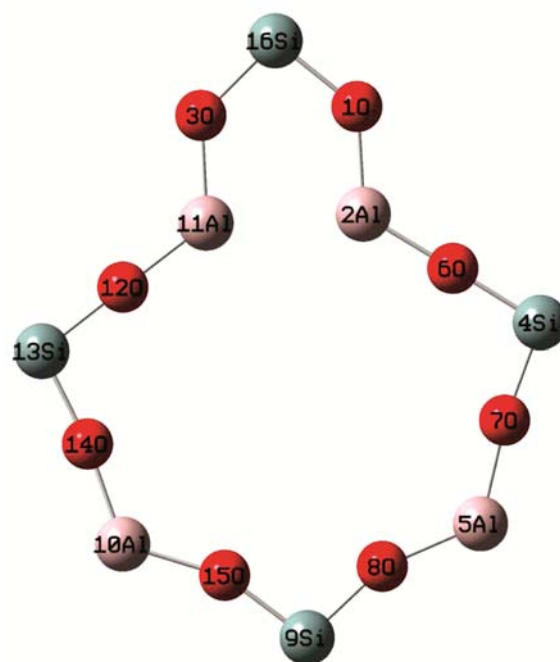


Fig. 2 — Optimized structure of zeolite-A.

and rotation mode. The peaks between  $700\text{--}850\text{ cm}^{-1}$  and  $1000\text{--}1150\text{ cm}^{-1}$  can be attributed to symmetric and asymmetric T-O-T stretching vibration. FTIR spectra of zeolite-A show absorption bands at around  $500\text{ cm}^{-1}$  which is due to Si-Al-O bond, and those at around  $1000$  and  $750\text{ cm}^{-1}$  can be attributed to asymmetric and symmetric stretches of the zeolite framework, respectively. A band for OH group is observed at around  $3500\text{ cm}^{-1}$ . The experimentally discussed bands can be found in close agreement with the theoretical results when compared. Fig. 3(b) is the theoretically generated FTIR spectrum of zeolite-A. The significant calculated vibrational modes include

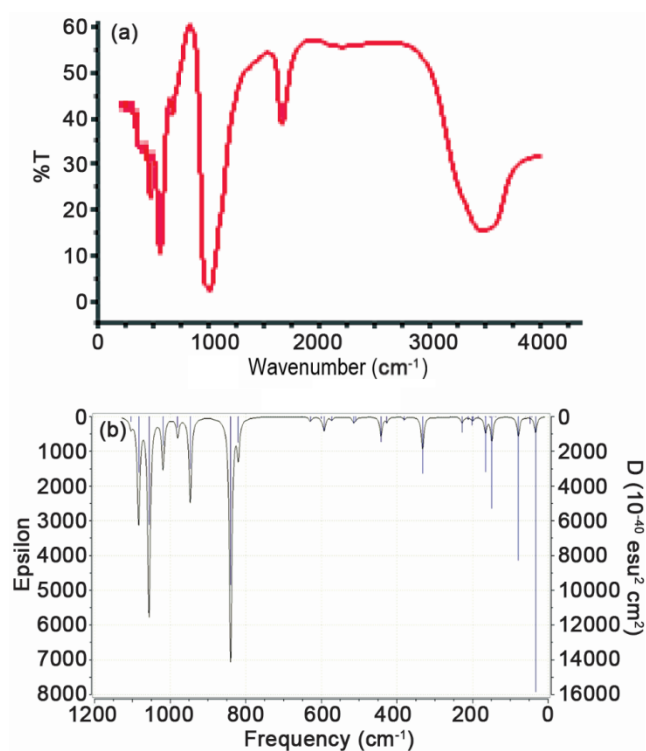


Fig. 3 — FTIR spectra of zeolite-A (a) experimental and (b) theoretical.

O-Si-O vibrating symmetrically at  $514\text{ cm}^{-1}$ . While as  $572\text{ cm}^{-1}$  is visualized as bending zone of O-Al-O moiety. Similarly other assignments can be seen resembling with what was found experimentally.

#### Microstructural studies

Scanning electron microscopy (SEM) was utilized to determine the morphology of zeolites. The SEM images of various ion exchanged forms of zeolites are similar to those observed for Na form of zeolite, which indicate that they possessed the similar morphology, i.e., the framework around the guest molecule (Fig. 4). No significant changes were seen in SEM images of the catalyst as the particle boundaries on the external surface of zeolite are clearly distinguishable. The SEM images of synthesized zeolite-A suggest the crystal size of the material to be in the range of  $1\text{--}10\text{ }\mu\text{m}$ . SEM of zeolite-A were taken at  $10,000\times$  magnifications to analyze their surface morphology. The Zeolite-A appear to have relatively non uniform surface and also slightly uneven pore morphology.

The small size of synthesized ion exchanged material can be determined more easily by using transmission electron microscopy (TEM) rather than SEM. Another reason to perform TEM study is its ability to reveal the aggregation of individual particles clearly. TEM analysis was performed by JEOL-JSM-1230 microscope with a tungsten filament source and accelerating voltage of  $120\text{ KV}$  (Fig. 4b). The chemical composition of the final modified material was analyzed for the presence of metal ions Na, K, Ca, Al and Si using energy dispersive spectrometry. There was found proximity between the composition of prepared material to that of the composition reported in literature. The most important step in synthesis of zeolites is to produce a desired composition which is critical in improvement of the material for many environmental applications. The chemical composition of zeolite A is given in Fig. 4c.

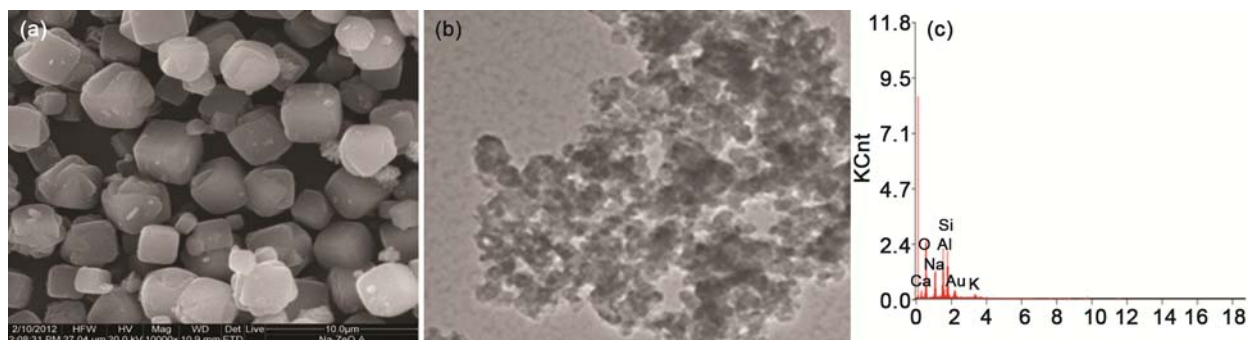


Fig. 4 — (a) SEM image, (b) TEM image and (c) EDS image of zeolite-A.

Results obtained for elements like Al, Ca, Mg, Na, O & Si show that O was found in abundance and was almost half of the overall weight of material. Among Si and Al, Si was found to be present in abundance confirming Si/Al ratio greater than 1 in zeolite-A. The BET surface area of the zeolite-A (Table 1) attains a value of 355 m<sup>2</sup>/g. The zeolite pore size structure reveals that the zeolite exhibits a narrow pore in the range of 0.2–0.6 nm. Temperature programmed desorption (TPD) as shown in the table is indicative of strong adsorption towards ammonia. TPD of ammonia is a widely used method for characterization of site densities in solid acids due to the simplicity of the technique. Ammonia often overestimates the quantity of acid sites. The strongly polar adsorbed ammonia is also capable of adsorbing additional ammonia from the gas phase.

#### Sorption and isotherm experiments

All the estimations of concentrations of nitrate and phosphate were determined spectrophotometrically using Synstronics 114 UV-visible double beam spectrophotometer. The adsorption of nitrate (NH<sub>4</sub>NO<sub>3</sub>) and phosphate (KH<sub>2</sub>PO<sub>4</sub>) on to pure and surface modified forms of zeolite-A in liquid-solid system was studied using a standard and strictly adhered to batch technique. The sorption isotherms were studied at neutral medium at three different temperatures (30, 40 and 50±1°C). The sorption model Freundlich was used to assess different isotherms and their ability to correlate experimental data.

#### DFT-experimental thermodynamics and sorption process

Thermodynamics plays important role in establishing a link between the direction of flow of energy in a physical or a chemical process. Zeolite-A was separately run for the respective calculation of thermodynamic parameters. At the temperature of 298.150 K and pressure 1.0 atm zeolite-A has shown to possess zero point energy (Kcal/Mol) 23.72, translational 0.889, rotational 0.889 and vibrational 33.56. Other parameters in Hartree/Particle including Thermal energy to be -0.555, thermal enthalpy -0.554

and thermal free energy of the order of -0.623.

Experimentally various thermodynamic parameters were evaluated to assess the spontaneity of sorption process. The effect of variation of temperature was examined on the sorption of oxoanions of fixed concentration (NH<sub>4</sub>NO<sub>3</sub> = 100 mg/100 ml and KH<sub>2</sub>PO<sub>4</sub> = 100 mg/100 ml) onto unmodified and surface modified zeolites using 24 hours of equilibration time and 1 ml per 3.5 mg of aqueous/solid phase ratio for 303 K to 323 K. The thermodynamic parameters viz., Gibbs free energy change ( $\Delta G^\circ$ ), heat of sorption ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) for sorption on zeolite materials was calculated for the system as shown in Table 2. The negative values of Gibbs free energy indicates the feasibility and spontaneity of sorption process, the positive ( $\Delta H^\circ$ ) specifies the endothermic natures of sorption and the positive value of ( $\Delta S^\circ$ ) indicates an increase in the randomness or disorder of the solid-solution interface during sorption.

#### FMO, electrostatic potential surface and TD-DFT aspects

Molecular orbital analysis is one of the prime components of theoretical analysis to depict important chemical and physical characters of a target molecule. Fig. 5 shows the resultant molecular orbitals of zeolite-A which are also called as frontier orbitals. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) have shown a band gap of 0.091 a.u. From the color schemes generated for the respective orbital assignment it can be seen that both the ionization and electron affinity sites are showing locus at the same position. This indicates the behaviour of zeolite equal for both cation as well as anion exchange capability.

This can further be understood by taking the molecular electrostatic potential (MESP) of the material under consideration that has been shown in

Table 1 — The BET surface area of the zeolite-A

Zeolite type	BET SA (m <sup>2</sup> g <sup>-1</sup> )	NH <sub>3</sub> -TPD Area (a.u.)
Zeolite-A	355	14437

Table 2 — Thermodynamic parameters of phosphate adsorption on unmodified and HDTMA<sub>4</sub><sup>-</sup> modified zeolites

Sorbent	$\Delta G^\circ$ (kJmol <sup>-1</sup> ) <sup>1</sup>			$\Delta H^\circ$ (kJmol <sup>-1</sup> ) <sup>1</sup>		$\Delta S^\circ$ (Jmol <sup>-1</sup> K <sup>-1</sup> ) <sup>1</sup>	
	303K	313K	323K	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	NH <sub>4</sub> NO <sub>3</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	NH <sub>4</sub> NO <sub>3</sub>
Zeolite-A	-7.274	-8.592	-8.304	8.334	11.361	51.511	60.07
SMZA <sub>HDTMA4</sub>	-11.391	-12.984	-12.654	7.743	8.456	63.150	63.72

Weight of sorbent: 350 mg, pH: Neutral, Initial conc. of KH<sub>2</sub>PO<sub>4</sub>: 100 mg/100ml Equilibration time: 24 h



Fig. 6. MESP is a derivative of total charge density developed by visualizing through color scheme using color codes of different sets of magnitude of electron density. In other words it is a map or graphic plot of halfway potential between electron donating, electron accepting and neutral zones. The green color is meant for neutral character, red for electron rich zone and blue for electron deficient zone. The results in the present case have shown

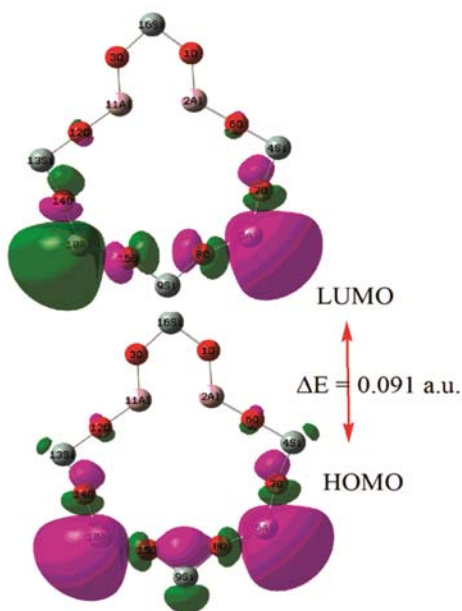


Fig. 5 — FMO diagram of zeolite-A.



Fig. 6 — MESP of zeolite-A.

the location of half-way potential or neutral property of the frame-work under discussion. Hence it is again affirmed that the zeolite-A can accept both anionic as well as cationic forms of ions. Moreover, the surface diagram clearly shows a cavity at the centre which can be useful consideration for the molecular mesh to act as a desirable carriage for ions discussed in the study and can modified further to enhance this property.

The electron delocalization, acceptance and donation are mainly studied under UV-visible spectral analysis. Herein, the molecular orbital diagram can be co-related with TD-DFT data useful to depict the electronic excitation potentiality of the material. Fig. 7 shows the theoretical UV-visible spectrum of Zeolite-A. The computed data have shown non-zero oscillator strengths for the possible excitations and favoured most possible one in HOMO to LUMO at the cost of visible form of energy. This is again in confirmation of the fact of high reactive nature of the silicate.

#### Estimation of inorganic oxyanions

This parameter was analyzed by estimating the concentration of nitrate and phosphate in aqueous phase. Sorption of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  on zeolites modified with HDTMABr and that on unmodified zeolites has been studied. Sorption experiments were carried out by adding 350 mg of adsorbent in 100 ml liquid phase containing  $1 \text{ gL}^{-1}$  of both  $\text{NH}_4\text{NO}_3$  and  $\text{KH}_2\text{PO}_4$  in 250 ml borosil flasks. The flasks were placed in thermostatic water bath shaker at 303 K for an equilibration period of 24 h. After the stipulated contact time, the conical flasks were taken from the shaker and the content was centrifuged and the concentration of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  in the suspension was determined spectrophotometrically. Batch equilibration experiments were conducted and the amount of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  sorbed onto the

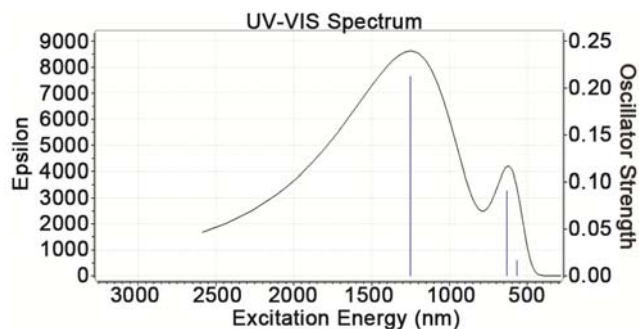


Fig. 7 — TD-DFT UV-visible spectrum of zeolite-A.

adsorbent at equilibrium was calculated in terms of distribution coefficient ( $K_d$ )<sup>16</sup>. The percentage of adsorbed  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  were determined as follows:

$$\text{Sorption percentage} = \frac{C_i - C_e}{C_i} \times 100$$

where,  $C_i$  = initial concentration and  $C_e$  = final concentration after equilibrium.

Experimental data for sorption of  $\text{NO}_3^-$  and  $\text{H}_2\text{PO}_4^-$  on zeolite-A and its modified forms with HDTMA has been obtained to determine the optimum sorption conditions w.r.t. the following parameters:

1. pH of the solution
2. Contact time
3. Differential surfactant loadings
4. Effect of temperature
5. Thermodynamic parameters

#### Sorption studies of $\text{KH}_2\text{PO}_4$ and $\text{NH}_4\text{NO}_3$

The sorption experiments were performed by the batch equilibrium method to find out the effect of different parameters on sorption of  $\text{KH}_2\text{PO}_4$  and  $\text{NH}_4\text{NO}_3$ . The chosen conditions were pH 7, temperature 30 °C, equilibration time of 24 h, aqueous to solid phase ratio 1:3.5 (ml: mg) and initial concentration of  $\text{KH}_2\text{PO}_4$  and  $\text{NH}_4\text{NO}_3$  100 mg:1000 ml. The data obtained by varying one parameter and keeping the others same suggests the following results.

#### Effect of pH on Sorption

0.1 M NaOH and 0.1 M HCl was used to vary pH values from 3 to 11. Fig. 8) represents the influence of pH on the percentage of phosphate sorption on unmodified and modified zeolites. It is evident from the figure that percentage of phosphate immobilized increased with the increase of pH from 3 to 7 and then decreases with the further increase in pH. The high percentage of phosphate sorption occurs between pH 5 to 7. At pH above 3, the binding sites at aluminum are protonated, consequently increasing the coulomb attraction between them and  $\text{H}_2\text{PO}_4^-$  thereby increasing the phosphate ion uptake up to pH 7. At higher pH values >7.5, the tendency of phosphate to precipitate out increases due to repulsion of hydroxylated binding sites with that of phosphate thereby decreasing the uptake of phosphate at higher pH.

To determine the optimum pH for sorption for  $\text{NO}_3^-$  on modified and unmodified zeolite, the studies

were carried out at pH 3,5,7,9 and 11. For unmodified zeolites and for  $\text{HDTMA}_4^-$  modified zeolites suggesting that the sorption of  $\text{NO}_3^-$  increases with increasing pH values up to pH 7 and then it decreases which may be due to the competition between  $\text{NO}_3^-$  and  $\text{OH}^-$  ions for the positive charged sorbent sites. The solubility which also changes with the change in pH can also influence the sorption.

#### Effect of Equilibration Time on Sorption

The phosphate sorption results show that sorption equilibrium is attained in about 12 h. Results obtained from unmodified and surface modified zeolites with surfactant loading HDTMA are shown in Fig. 9. There was found no further change in equilibrium concentration up to 24 h. The studies for  $\text{NH}_4\text{NO}_3$  were performed at 3, 5, 7, 9 and 24 h. The results obtained suggest that a maximum equilibration time of around 12 h is required to attain the equilibrium. The experiments were performed by taking the maximum surfactant loading of  $\text{HDTMA}_4^-$  (1200  $\text{mgL}^{-1}$ ) in case surface modified zeolites. The sorption first increases rapidly with time but after a particular time it attains a steady state and remains constant. This can be explained by the fact that initially there is large number of active sites present on the zeolite and sorption increases with time. As the active sites get utilized the sorption attains a steady state and remains constant.

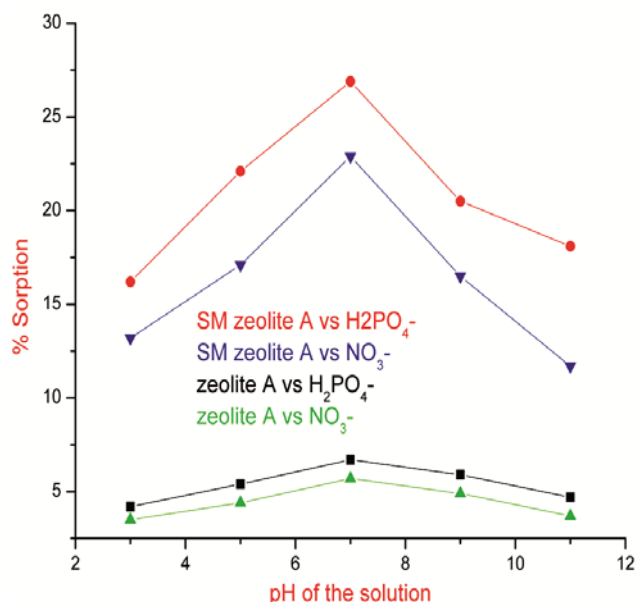


Fig. 8 — Effect of pH of the solution on sorption of  $\text{H}_2\text{PO}_4^-$  and  $\text{NH}_4\text{NO}_3$  on unmodified and HDTMA surface modified (SM) zeolite A.

### Effect of Surfactant loading on Sorption

The adsorption of  $\text{H}_2\text{PO}_4^-$  on surface modified zeolites with different HDTMA surfactant concentrations of 300 mg/l (HDTMA1), 600 mg/l (HDTMA2), 900 mg/l (HDTMA3) and 1200 mg/l (HDTMA4) is shown in Fig. 10 (black curve) for loading of HDTMA. It can be concluded from the data that modification of surfaces greatly increases anion adsorption on zeolite. Furthermore, it can be concluded that the amount of phosphate sorption enhances with the enhancement in surfactant loading on zeolite until a limit is achieved. The surface modification of zeolite results in the change of zeta

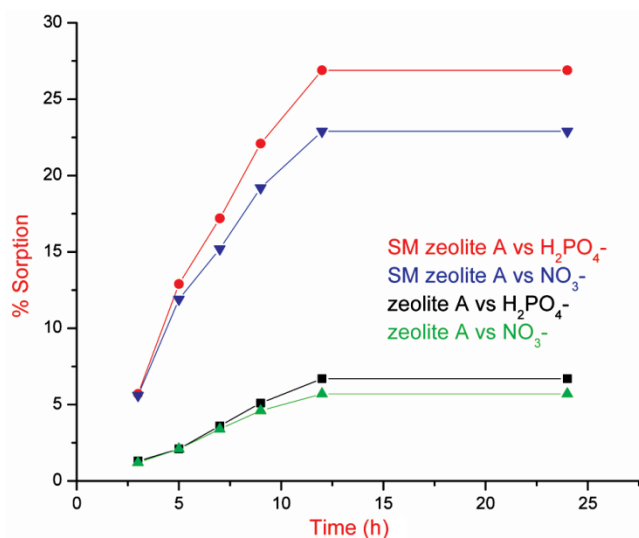


Fig. 9 — Effect of equilibration time on sorption of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  on unmodified and modified zeolite A.

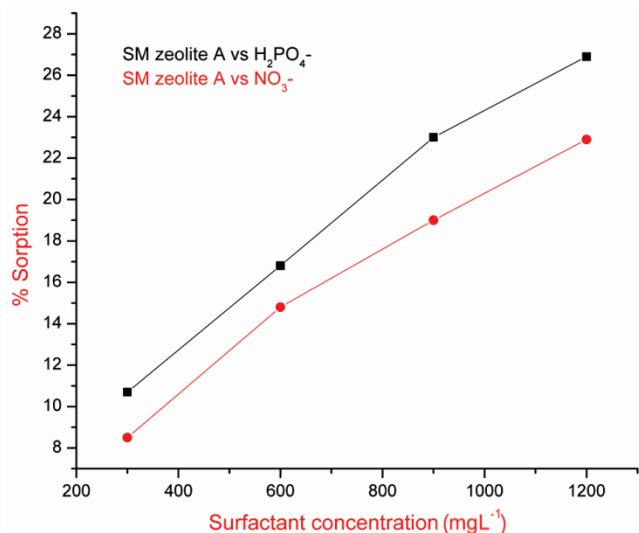


Fig. 10 — Effect of surfactant (HDTMA) loading on sorption of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  on zeolite A.

potential of particles from negative to positive and increase in phosphate sorption capacity. Formation of surfactant bilayer due to increase in the surfactant loading on zeolite surface contributes to the increased sorption of phosphate<sup>17</sup>.

The formation of bilayer results in reversal of charge on external surface of the zeolites from negative to positive. The positively charged surfactant head groups are balanced by counter bromide ions and thus the surfactant modified zeolites can absorb the negatively charged phosphate or nitrate ions from aqueous solution through the processes of anion exchange and electrostatic attraction<sup>18-22</sup>.

Fig. 10 (red curve) shows the effect of HDTMA loading concentrations from 200 to 1200 mg/L on nitrate sorption. The percent of nitrate sorption increases initially with HDTMA loading and shows a maximum value at 1200  $\text{mgL}^{-1}$  HDTMA concentration. This initial concentration exceeds the critical micelle concentration of the surfactant. It is therefore predicted that these micelles attach as such to the external surface and then rearrange themselves in the form of a bilayer that tends to impart anionic characteristics.

### Effect of Temperature on Sorption

The effect of temperature on phosphate sorption was studied in the temperature range of 30° to 50 °C. It was observed that the percentage of phosphate sorption increases when the temperature is increased to 40 °C. However, when the temperature further increased the sorption decreased as shown in Fig. 11. With increasing temperature above 40 °C the

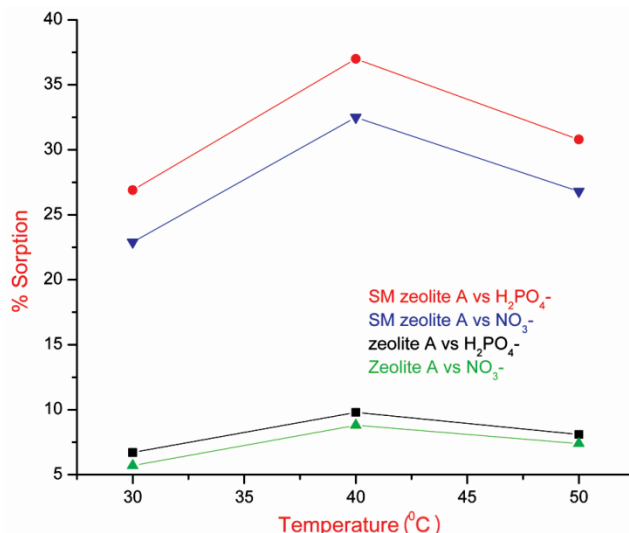


Fig. 11 — Effect of temperature on sorption of  $\text{H}_2\text{PO}_4^-$  and  $\text{NO}_3^-$  on surfactant modified (HDTMA<sub>4</sub>) and unmodified zeolite A.



attracting forces between adsorbent surface and ions get weakened resulting in decreased adsorption<sup>23</sup>.

### Conclusions

Sorption experiments of  $\text{KH}_2\text{PO}_4$  and  $\text{NH}_4\text{NO}_3$  on pure and surface modified forms of zeolite-A were performed by batch equilibrium method. Studies were carried out at pH 3, 5, 7, 9 and 11. Results obtained suggest that the sorption increases with increasing pH values up to pH 7. The sorption equilibrium was attained in about 12 h. The surface modification of zeolite resulted in the change of zeta potential of particles from negative to positive and enhancement of sorption capacity. It was found that the percentage of sorption increases when the temperature is increased to 40 °C. All thermodynamic parameters i.e., standard free energy change, enthalpy and entropy vary with the change in temperature. DFT analysis has also proven the efficiency of zeolite-A at the molecular charge density and spectral analysis<sup>24-26</sup>.

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