

Fly ash based zeolite analogues: versatile materials for energy and environment conservation

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Fly ash is combustion residue from burning of pulverised coal in electric utility generating stations. The annual production of fly ash in India is around 100 MTPA and is responsible for several environmental hazards, which is quite well documented. There are stringent norms for its land disposal and hence utilisation of fly ash is imperative. Fly ash has more than 85% of SiO_2 and Al_2O_3 content and is therefore a tailor made raw material for production of zeolite. An innovative process has been developed for synthesis of zeolites using fly ash as a substitute for conventional raw materials viz. sodium silicate and aluminate. The process consists of three major steps viz. fusion of caustic soda and fly ash for optimal extraction of silicate and aluminate, aging step which provides time for formation of nuclei and hydrothermal crystallization resulting in activation of nuclei into well defined crystals. Low temperature operation, simplicity of process and optimal recycling of unused reactants and process water are special features of these processes. Zeolites have high internal and external surface areas and also exhibit high exchange capacities, which makes them versatile materials for targeting wide range of pollutants, ranging from cationic to anionic and hydrophilic to hydrophobic molecules. The major uses of zeolites are in adsorption, ion exchange and as catalysts. The use of zeolites in environmental remediation is restricted due to procurement problem and prohibitive cost, which can be overcome by using low cost fly ash based zeolites (FAZs). The synthesis of FAZ-A and FAZ-Y and their modifications either by transition metal incorporation or by surfactant treatment for various environmental applications in air, water and soil remediation are addressed in this review.

KEY WORDS: fly ash; zeolites; catalyst; heavy metals; soil remediation.

1. Introduction

Urgent need to encourage interdisciplinary research on development of environmental materials has been realized, which involves novel approaches to adopt newly developed synthesis protocols for designing novel materials and characterizing the nanostructures. Synthesis of zeolites from fly ash and its functionalisation to impart specific surface characteristics is one such approach. Fly ash has a great potential as an environmental threat. In India, due to the increasing use of high ash containing coal in power generation, it is expected that the generation of fly ash will increase from 100 million tons/year in the year 2000 to 175 million tons/year by the year 2007. The utilization of fly ash for production of zeolites can target a meagre 1–2% of the total fly ash generation. Though the production of fly ash based zeolite (FAZs) is not a complete solution to the fly ash menace, it will definitely provide cost-effective alternative to commercial zeolite in applications where zeolite purity can be compromised. As fly ash contains more than 85% as silica and alumina, they serve as the most suitable and convenient raw material for the synthesis of zeolites. Also, the synthesis of zeolites from fly ash is expected to resolve the problem of disposal of fly ash at least partially and thereby minimize its impact on environment. Holler and Wirshing [1] have success-

fully developed the method for the production of zeolite-A from powder coal ash [1]. Since then, a large number of technical articles have been published in past few years reporting different hydrothermal activation methods for synthesis of different types of zeolites from fly ash (Table 1). Our group at NEERI has been engaged in research pertaining to synthesis of fly ash based zeolites and delineation of their environmental applications for more than a decade. We have successfully developed the processes for synthesis of zeolite – A and Y from fly ash [7,8].

Zeolites exhibit important characteristic properties like cation exchange, adsorption, molecular sieving, etc. and hence are widely used for variety of applications such as detergent builder, catalysts for chemical/petrochemical industries, adsorbents for a wide array of cationic and anionic pollutants, as ion exchanger for nuclear waste treatment etc. Several environmental and energy technologies can emerge with substantial benefits from zeolite based materials, which includes reduction in waste, improved energy efficiency, environmentally benign composite structures, waste remediation and energy conservation. Some important works related to environmental and energy related processes being pursued at NEERI includes:

- Simpler and newer routes for material synthesis
- Development of new, improved materials for enhanced adsorption capacity, selectivity and kinetics

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Table 1
Different type of zeolites synthesized from fly ash

Zeolite type	Reference
Faujasite	[2,3]
Zeolite X	[2, 4, 5]
Zeolite Y	[6, 7]
Zeolite A	[2, 4, 6, 8, 9]
Zeolite P	[3, 4, 9–14]
Zeolite P1	[2, 5, 15–22]
Gobbinisite	[21]
Analcime	[2, 16–18, 23]
Herschelite	[2]
Sodalite	[2, 10, 11, 13, 18, 20, 22–25]
Hydroxyl sodalite	[3, 4, 12, 14, 15, 19, 21, 24, 26]
Sodalite octahydrate	[19]
Cancrinite	[23]
Hydroxy cancrinite	[2, 18, 20]
Gmelinite	[16]
Phillipsite	[19]
Nepheline hydrate	[16,18]

- Development of new improved materials for enhanced catalytic and photocatalytic activity
- Precise and low cost development of materials for detection and monitoring of pollutants.

An interesting possibility being explored for designing of novel materials is to understand the surface chemistry of nanostructured materials and tailor the surface for material-mediated reactions. This would facilitate to address various issues related to environmental and energy applications. In this connection the ongoing activities include the following:

1.1 Air pollution control

1.1.1. Surface modified fly ash zeolites (SMFZ) as versatile materials for VOCs monitoring in indoor environment

SMFZ have been developed through surface modification of FAZs for monitoring of VOCs. VOCs in indoor air are of serious concern because of the health hazards associated with them and their reactivity as the photochemical precursors towards other pollutants as well as their specific toxic potential. Activated carbon and tenex are being widely used for indoor air monitoring in various samplers. These adsorbents are beset with the drawback of lack of selectivity and versatility, which has been overcome by developing a new class of materials viz. surface modified zeolites (SMZs), prepared by properly treating the zeolites surface with surfactant. These SMZs have been developed from FAZ for indoor air monitoring of VOCs vis-à-vis conventional adsorbents. The usage of SMFZ in indoor air monitoring would provide an accurate and correct scenario of VOCs in indoor air, which in turn would facilitate identification of suitable control measure to mitigate the health hazards associated with VOCs.

1.1.2. Low cost molecular sieves for capture of CO₂

Serious environmental implications of carbon dioxide as one of the major contributors towards green house gases have prompted the researchers world wide to control the level of carbon dioxide in atmosphere. Carbon sequestration is the third option being pursued along with improved efficiency and low carbon fuels for green house gas mitigation. It entails the capture and storage of CO₂ that would otherwise be emitted to the atmosphere. This requires separation and capture of CO₂ having concentrations of 12–15% admixed with nitrogen, other impurities and particulates in flue gases. Improvement of CO₂ adsorption/desorption and selectivity performances of the new adsorbents is now in progress. Following approaches are being followed to develop new adsorbents from FAZ for CO₂ capture:

- Hydrophobic surface modified zeolite to avoid desiccation
- Hydrophobic and chemically active zeolites to avoid desiccation with enhanced selectivity and efficiency for CO₂ adsorption.

1.1.3. Artificial photosynthesis for fixation of carbon dioxide through photo catalytically active nano-structured zeolitic materials

An inevitable outcome of combustion of fossil fuels is CO₂, which needs to be addressed to avoid global warming and other related hazards. This problem can be resolved partially by converting CO₂ into value added products, possibly using the non-carbon based energy. In this connection, photocatalytic transformation of CO₂, which involves converting carbon dioxide into some value-added products namely methanol, by using sunlight as the energy source, carbon dioxide, and water as raw materials, in the presence of photocatalyst, is being investigated at NEERI using FAZ-Y as support. It is envisaged that this research of converting carbon dioxide in flue gases from thermal power plants, steel plants, refineries etc. into value added products may lead to significant reduction in anthropogenic carbon dioxide emissions, and provide an inexpensive alternative to renewable energy bases. Thus, “Artificial photosynthesis”, implies production of important chemicals and energy from carbon dioxide in the presence of sunlight through use of systems or materials which, biomimic photosynthetic process of plants.

1.2 Water and wastewater treatment

1.2.1. SMFZ for dearsenification

In the backdrop of the widespread public concern due to consumption of ground water containing high concentration of arsenic; the urgency for delineating appropriate treatment strategy comprising process innovations for

arsenic removal is realized to overcome the grave threat of chronic arsenic poisoning. The new materials being developed include synthesis of novel hybrid materials based on zeolite supports wherein the materials are being systematically functionalised using metal chelating agents and surfactants to modify the surface chemistry and tailor molecular recognition process for arsenate. It was intended to develop materials with tailored properties to sequester anionic pollutants in addition to cationic pollutants. The formation of zeolitic materials with anionic characteristics requires for the zeolitic materials to be treated with surfactant initial concentration greater than its critical micelle concentration (CMC). The sorption of micelle on surface of the zeolite results in rearrangement of the surfactant molecules to form bilayers [27]. The first layer is formed through exchange of the surfactant molecule with the cations on the surface. The second layer is formed by tail-to-tail hydrophobic interactions of surfactant molecule and is stabilized by counter ions. The sorption of oxyanions on surfactant-modified zeolite (SMZ) may be attributed to surface complexation and surface precipitation. Zeolite analogues having anionic characteristics have been developed and have been applied for removal of arsenic in specific. Also iron treated zeolites have been developed and used for dearsenification.

1.2.2. SMFZ for removal of phenolics

SMZs, have been developed from FAZs by treating it with surfactant concentration less than CMC, wherein the molecules exists as monomers and anchor to the surface of SMZ through cation-exchange. The surface treatment with hexadecyltrimethyl ammonium bromide (HDTMA-Br) renders hydrophobicity to SMZs, which shows significant increase in its sorption efficiency to remove organic compounds. The enhanced removal efficiency of SMZs in comparison with faujasitic zeolites as such may be attributed to adsorption and partitioning mechanism. The substantial increase in removal efficiency of SMZ for 2-chlorophenol as compared to monohydric phenol substantiates the hypothesis of hydrophobicity playing a significant role.

1.2.3. FAZ for heavy metal removal

The removal and recovery of toxic metals from industrial effluents has become the field of intensive research. Scientists are now trying to develop new methods and materials for the removal of toxic elements in highly efficient, cost effective and eco-friendly manner. In spite of a number of traditionally available methods, zeolites are gaining popularity in recent years. Zeolites besides having low cost are relatively harmless. In addition, the non-toxic zeolite loaded with heavy metals can be regenerated very easily. The fly ash based zeolites offer a cost effective solution for removal/recovery of heavy metals. We have studied the removal efficiencies of FAZ-A for various heavy metals like lead, cadmium, copper etc. The efficiencies have also been compared with their commercial

counterparts. The FAZ exhibited excellent sorption efficiencies for most of the metal ions and are comparable to commercially available synthetic zeolites [28,29].

1.2.4. FAZ for removal of ammonia

Ammonium nitrogen is an aqueous pollutant, which needs to be appropriately treated prior to its discharge into the water bodies because of the eutrophication problem associated with it. The sorption of ammonium ion on zeolites is emerging as a promising methodology. The FAZ-Y has been evaluated for sorption of ammonium ions [30].

1.3 Soil remediation

1.3.1. FAZ/SMFZ for heavy metal/anion immobilisation

Unique properties and selectivity of zeolites are being exploited for environmental remediation of soils contaminated with heavy metals and oxyanions. The in-situ immobilisation of heavy metal and oxyanions would prevent ground water contamination and also prevent uptake of heavy metals by plants.

1.3.2. SMFZ as slow release nutrient medium

Enhanced plant growth through increased nutrient retention, reduced environmental nutrient losses, and reduced fertilizer requirements is being investigated by establishing replenishable and balanced nutrient supply in the plant zone based on FAZs. The most favourable characteristic of zeolite which is attracting worldwide attention today is the fact that besides being a versatile material wherein it functions as soil conditioner, nutrients slow release medium and soil remediation agent, the composition of zeolites does not differ significantly from that of soil and is therefore not expected to alter its characteristics, thus ensuring physico-chemical stability.

1.3.3. SMFZ for immobilization of microbes

In addition to above usages, zeolite can act as host for microbes/biofertilizer which in turn is expected to provide suitable matrices for slow release of the biofertilizer. Surface modified zeolites have been used to adsorb biofertilizer namely *Azotobacter chroococcum* and other negatively charged microbes by virtue of the fact that SMFZ are positively charged and sorbs negatively charged microorganisms [27]. The sorption of these microorganisms are expected to enhance microbial activity of soil and also has applications in wastewater treatment, disinfection of water and improvement in indoor air quality.

2. Experimental

2.1 Synthesis of fly ash based zeolites (FAZs)

2.1.1. Synthesis & Characterisation of FAZ-A and FAZ-Y

The fly ash samples collected from various sources were subjected to the synthesis of zeolite-A & Y. In the

process formulated, an alkali fusion method has been suitably optimised for optimal extraction of silica & alumina from fly ash. The optimisation was carried out for caustic soda/fly ash ratio, fusion temperature & time. Several pre-treatment steps namely sieving, magnetic separation of iron were also studied for their incorporation as per the procedure reported in our earlier reports [25, 28, 29, 31–41]. The FAZ A & FAZ-Y have been thoroughly characterized for calcium binding capacity (CBC), sorption capacity and XRD analysis as per the standard procedures [42]. The samples of FAZ-Y were compared with international grade zeolite-Y samples procured from Contekka, Sweden and FAZ-A were compared with zeolite-A samples procured from Degussa, Germany.

2.1.2. Synthesis of SMFZ-Y and SMFZ-A

FAZ-A and FAZ-Y were synthesized from fly ash as per procedure detailed above. The synthesized FAZs were washed with distilled water several times. Preweighed quantity of a washed FAZs sample were then mixed with different initial concentrations of a surfactant i.e. hexadecyltrimethyl ammonium bromide solution in 1:100 (Solid:Liquid) ratio. The surfactant concentration was ranging from 100 to 800 mg/l for FAZ-Y and 200 to 1500 mg/l for FAZ-A. The solution was agitated for 7 to 8 hr at 150 rpm on a gyratory shaker at pH 8.0 to 8.5. The solution was then filtered and the solid residue was washed with double distilled water and air dried for 4 to 6 h in presence of air. The SMFZs samples synthesised as such were then mechanically ground with a mortar and pestle to fine particle size. Surface modified zeolite were also synthesised using commercial zeolite A and Y using same procedure as given above, the samples were designated as SMZ-A and SMZ-Y.

2.1.3. Synthesis of FAZ based photocatalytic materials

New photocatalytic materials were synthesised based on commercial zeolite Y and FAZ-Y to exhibit electron-hole recombination reaction. The zeolite Y and P25-TiO₂ supplied by Degussa (Germany) were used as such. A brief description of synthesis of various photocatalysts is given below:

Zeolite Y-TiO₂: 5 g zeolite-Y and 1.779 gm of titanium isopropoxide corresponding to 10%w/w loading of TiO₂ on zeolites, were mixed thoroughly resulting into a homogeneous solid mass. This mixture was calcined in air at 500 °C for 1 h followed by cooling and grinding. This material is designated as Zeo-Y/TiO₂.

Zeolite Y-TiO₂/HPA: 0.5 g of phosphomolybdic acid (HPA) was dissolved in 10 ml double distilled water. 5 g of Zeo-Y/TiO₂ was added to this solution. The slurry was stirred with a glass rod and dried at 70–80 °C on a hot plate. The catalyst was then ground to obtain a homogeneous mixture.

Zeolite Y-TiO₂/Co²⁺/HPA: Zeo-Y/TiO₂ was exchanged with Co²⁺ ion prior to incorporation of HPA. 5 g of the synthesized Zeo-Y/TiO₂ was dispersed in 100 ml double distilled water. The pH of this dispersion was maintained at 6.5–7.0. A solution of Co-Cl₂·6H₂O was prepared by dissolving 0.2319 g of salt in 250 ml double distilled water. Only 5% cation exchange capacity of zeolite-Y was used to exchange Co²⁺ ions. The pH of this solution was found to be 5.8. This solution was then mixed with the dispersion of Zeo-Y/TiO₂ in double distilled water and subjected to stirring for 40 min followed by filtration and drying at 60 °C. This Zeo-Y/TiO₂/Co²⁺ was then subjected to incorporation of heteropolyacid to enhance its photocatalytic activity in the visible range. 0.5 g of phosphomolybdic acid (HPA), which corresponds to 10% w/w on Zeo-Y/TiO₂ was dissolved in 10 ml double distilled water. To this solution was added Zeo-Y/TiO₂/Co²⁺ resulting in formation of slurry. The slurry was dried at 70–80 °C on a hot plate with constant stirring followed by grinding of the dried mass.

Fly ash zeolite based photocatalyst (FAZPC-1): Same procedure was repeated as given for synthesis of Zeolite Y-TiO₂/Co²⁺/HPA except that commercial zeolite was replaced by FAZ-Y.

3. Results and discussion

3.1 Synthesis & characterisation of FAZs & SMFZs

Fly ash with silica/alumina ratio of 3.0–3.2 results in formation of zeolite-Y. Synthesis of zeolite-A requires alumina enrichment, which was successfully achieved by addition of sodium aluminate of appropriate concentration. Several attempts made in past for similar synthesis are beset with drawbacks of low crystallinity and calcium binding capacity (CBC), bigger particle size, residual fly ash content, low yield and low reflectance values. These drawbacks have been successfully overcome by introducing several process modifications like sieving of fly ash, using sieves of mesh sizes 170 μ and 53 μ and acid treatment of fly ash as follows: 50 g of fly ash was refluxed with 250 ml of 8N HCl for 2 hours. This acid treated fly ash was then filtered and washed with double distilled water till the pH of the washing was nearly 7. The acid extract was neutralized by 50% caustic soda and filtered by using Whatman filter paper to separate the precipitate from neutralized acid extract filtrate. This filtrate was proportionately used while preparing the sodium aluminate solution required during synthesis. The magnetic iron present in fly ash as an impurity was also removed mechanically by magnetic separation. This has resulted in a breakthrough wherein residual fly ash content has significantly reduced with consequent increase in yield of zeolite. The optimisation of conditions for synthesis of highly crystalline FAZ-A and FAZ-Y has been achieved

by monitoring XRD crystallinity and are depicted in figure 1a and b. Comparison of various properties of FAZ-A and commercial zeolite are given in table 2. The results show that FAZ exhibits almost similar properties as that of commercial zeolite. Similar results were obtained for FAZ-Y.

3.2 FAZ/SMFZ for environmental and energy related applications

3.2.1. Air pollution control

SMFZ-Y for VOC monitoring

Active sampling was employed for monitoring VOCs in indoor and work environment using USEPA Compendium Method TO-17 [43]. The monitoring procedure involves pulling a volume of air through a sorbent packing to collect VOCs followed by a thermal desorption-capillary GC/MS analytical procedure. Prime locations were selected in residential, commercial and industrial areas. The adsorbents including activated carbon, commercial zeolite-A, zeolite-Y, SMFZ-A and

SMFZ-Y were evaluated for their efficiency. A special cartridge container was fabricated to hold the adsorbents. The adsorbent was filled in sample cartridges and subjected for degassing at 175 to 200 °C for overnight. The cartridges were then cooled in desiccators and immediately plugged with rubber seals. The degassed cartridges were then used for VOC monitoring. The monitoring schedule followed was collection of 8 hourly sampling at a flow rate of 20 ml/min. After sampling the cartridges were again plugged with rubber seal and kept below 20 °C to avoid the loss of VOCs. The sorbed VOCs were subjected to thermal desorption and collected via collection unit for analyses using gas chromatography and mass spectrometer (Model: Varian Saturn GC/MS-4D). The SMFZ-Y with optimised surfactant concentration was used for VOC monitoring in indoor air environment for residential and commercial areas. Four different locations were identified in major directions of the city i.e. north, east, south and west as sampling sites with respect to commercial and residential zone. The monitoring was carried out at a rate of 20 cc/min with the help of low volume air samplers (make: AMSH). The sampling time was selected in morning and evening hours so as to monitor the emissions during cooking process in indoor air.

Table 3 shows the comparative sorption efficiency of activated charcoal and SMFZ-Y in residential, commercial and industrial sites. The large number of VOCs adsorbed on SMFZ-Y as compared to activated carbon proves the versatility of the sorbent materials. The comparative sorption of VOCs on activated carbon and SMFZ-Y are also presented in figure 2a and b.

The study has proved that SMFZ-Y can be effectively used for VOCs monitoring since this offers advantages like low cost, selectivity for detection of VOCs in low concentration in work and indoor environment, easier regeneration, overcomes the problem of humidity interference associated with conventional adsorbents and also offers the option for thermal, chemical and photochemical destruction of VOCs.

Functionalised materials for CO₂ capture

Evaluation of various modified FAZs for their CO₂ adsorption capacities was carried out by flowing synthetic flue gas mixture through adsorbents. The weighed quantity of the adsorbent was packed in specially fabricated glass cartridges through which stream of synthetic flue gas was passed for specified durations. After exposures the cartridges were subjected to temperature programmed desorption and analysis of desorbed CO₂. Alternatively, the experiments were also performed using evolved gas analysis (EGA) in which thermogravimetric (TG) instrument is coupled with mass spectrometer (MS).

Functionalised fly ash based zeolites (FFZ) have been developed, which are to be used for separation and

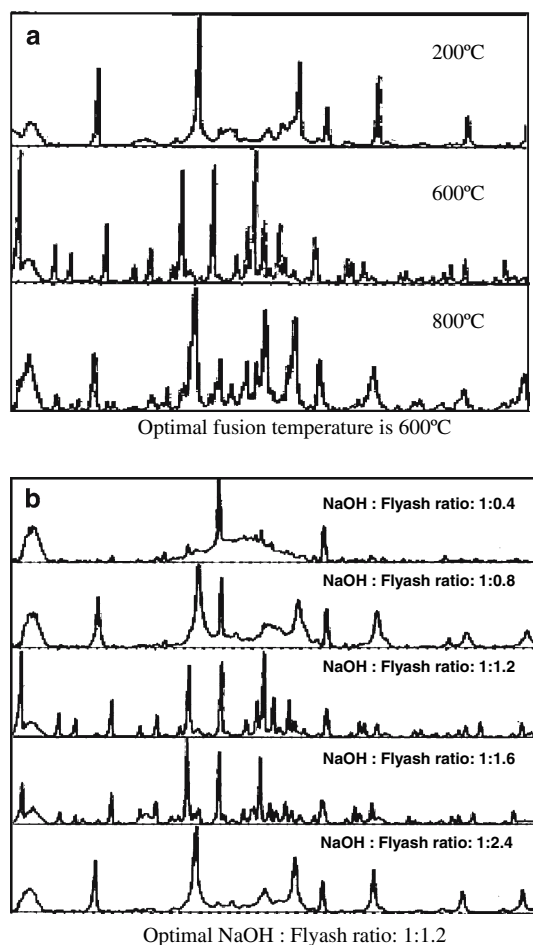


Figure 1. a: XRD patterns of FAZ-A b: XRD patterns of FAZ-Y.

Table 2
Physico-chemical characteristics of FAZ-A and FAZ-Y

Characteristic	Commercial Zeolite -Y (Contekka, Sweden)	FAZ-Y	Commercial Zeolite -A (Degussa, Germany)	FAZ-A
SiO ₂ /Al ₂ O ₃ ratio	4.18	2.33	1.93	1.86
Calcium binding capacity (CBC) (meq/100 g)	540	520	440	420
Surface area (m ² /g)	600	580	510	480
Particle size (μm)	2–3	1–3	3–4	2–3
TCLP Test*	–ve	–ve	–ve	–ve
Crystal structure	Cubic	Cubic	Cubo-octahedral	Cubo-octahedral
SiO ₂ %	49.09	29.57	32.20	30.32
Al ₂ O ₃ %	20.04	22.23	28.5	27.70
Fe ₂ O ₃ %	0.50	1.53	0.02	0.80
Na ₂ O %	6.36	11.46	14.00	14.60

*TCLP –ve: No toxic elements were leached.

capture of CO₂ from flue gases. We have developed new functionalised zeolite materials by chemically modifying the FAZs using monoethanolamine (MEA) to enhance selectivity in presence of O₂ and N₂. Results obtained from temperature programmed desorption using FAZ-Y and MEA modified FAZ-Y (FAZ-Y-MEA) are presented in figures 3a and b respectively. Figure 3a and b shows distinctly higher CO₂ selectivity in modified as compared to unmodified FAZ-Y. Similar results have been obtained for metal treated sample, however only representative figure for TPD has been included herein. Figure 3c represents results pertaining to EGA showing CO₂ adsorption on amine modified zeolite. The results clearly demonstrate high uptake of CO₂ in amine treated zeolite, almost in the temperature range of flue gas (120–150 °C). Further optimization of the conditions for synthesis of modified materials is in progress. Preliminary investigations based on modified FAZs are promising showing better adsorption capacities and selectivities. Further work is in progress to derive the adsorption capacities.

Artificial photosynthesis for fixation of carbon dioxide through photo catalytically active nanostructured zeolitic materials

To evaluate methyl orange (MO) photoreduction dilute solution of MO (5 ppm) prepared in ethanol-double distilled water mixture (1:40) was taken in a tubular glass reactor fitted with a standard joint and purged with

nitrogen gas to remove the dissolved oxygen. To it, a known amount of photocatalyst (50–100 mg) was added and purging was continued further for a few minutes. The reactor was then mounted on a magnetic stirrer for keeping the catalyst in suspension during the reaction period and fitted to a water condenser. It was then illuminated with 400 W Tungsten lamps for different time intervals ranging from four to fourteen hours. After the end of the illumination period, the system was subjected to ultra-centrifugation for separation of the catalyst. The filtrate so obtained was then filtered through cellulose nitrate membrane filter to get a solution free from any catalyst, which could interfere with the spectrophotometric method of analysis. The clear filtrate obtained was then subjected to spectrophotometric analysis to determine the extent of reduction of methyl orange. A catalyst blank, similar to the above reaction system was also simultaneously run without the addition of catalyst (to account for the bleaching effect). Illumination blank consisted of a system similar to the reaction system; the only difference being that it was kept in dark to account for the adsorption etc.

The photoreduction of Methyl orange (MeOr) was carried out by observing the percentage removal of MeOr. It was observed that there was a characteristic decrease in the concentration of MeOr, which indicates the formation of hydrazine from MeOr. It has been observed that the system, which, has not been irradiated, but kept in contact with the same amount of the catalyst, did not show any photoreduction of MeOr.

Table 3
Comparative IAQ data generated from various locations in Nagpur city

Site	Adsorbed VOC's	
	Activated charcoal	SMFZ-Y
Residential	Toluene, <i>p</i> -Xylene, <i>D</i> -Limonene	2-Butanone, Benzene, 3-methylbutan-2-one, Methyl isobutyl ketone, Toluene, Pyridine, Ethylbenzene, <i>p</i> -Xylene, <i>D</i> -Limonene
Commercial	Toluene, <i>p</i> -Xylene, <i>D</i> -Limonene	Benzene, Toluene, Ethylbenzene, <i>p</i> -Xylene, <i>D</i> -Limonene, 2- Pentanone
Industrial	Toluene, <i>p</i> -Xylene	Benzene, Toluene, <i>p</i> -Xylene, <i>D</i> -Limonene

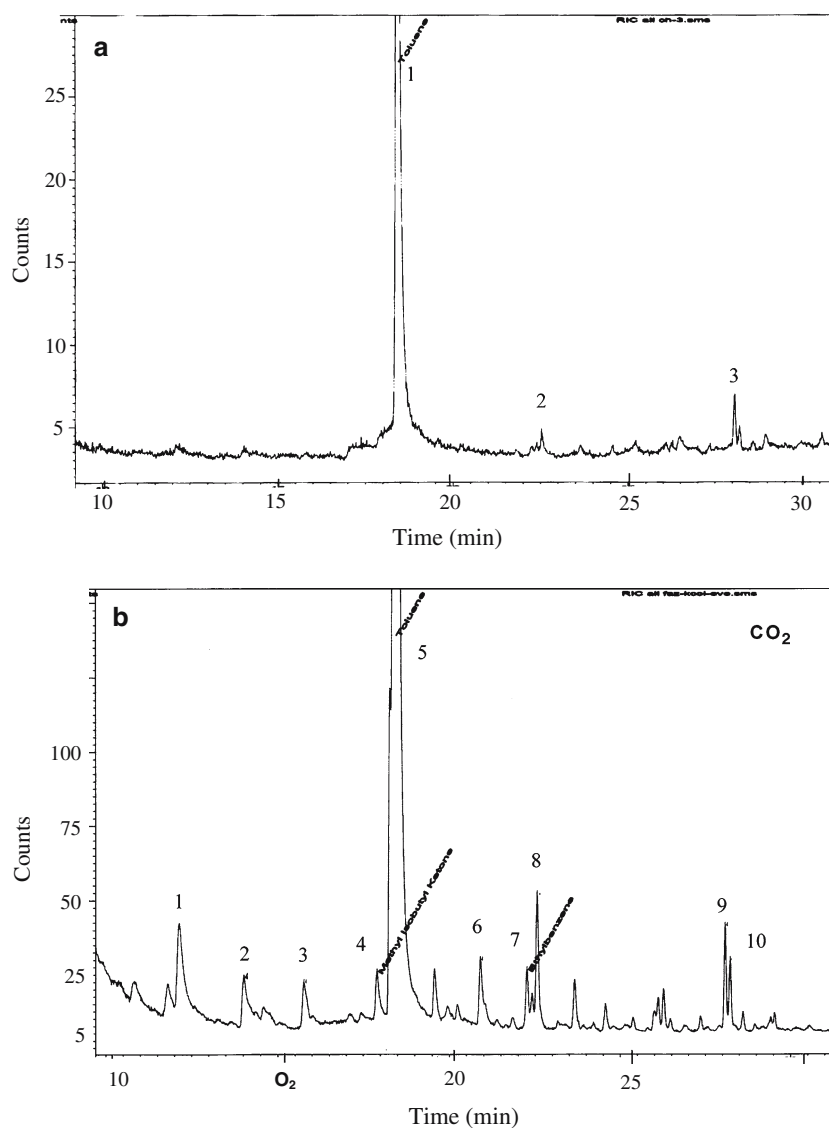


Figure 2. (a) Sorption of VOCs on activated carbon Peaks: (1) Toluene, (2) *p*-Xylene, (3) *D*-Limonene (b) Sorption of VOCs on SMFZ-Y Peaks: (1) 2-Butanone, (2) Benzene, (3) 3-methyl-butan-2-one, (4) Methyl isobutyl ketone, (5) Toluene, (6) Pyridine (7) Ethylbenzene (8) *p*-Xylene, (9) *D*-Limonene.

This confirms the photocatalytic property displayed by these catalysts. The photocatalyst FAZPC-1 is active to photoreduction of methyl orange. Undoubtedly, the zeolite matrix provides a better dispersion of active sites and free access of the MeOr molecules to these active sites, thereby facilitating photocatalytic activity. This photocatalytic activity is further enhanced by the addition of transition metals like cobalt, which delay the recombination reaction and are synergistic to the electron transfer reaction involved in the photodegradation process involved. At present, these materials are being investigated for their efficiency in catalysing water-splitting reaction to produce hydrogen energy, in our laboratory. The results are given in figure 4 for MeOr photoreduction.

However the efficiency of the FAZPC-1 is much lower as compared to photocatalysts synthesised from

commercially procured zeolite – Y (Sweden). This may be attributed to higher Si/Al ratio and alkaline nature of the sample. Further studies in this direction are in progress to improve the photocatalytic property.

3.2.2. Water/wastewater treatment

SMFZ-A for dearsenification

Metal removal studies were conducted using FAZs and SMFZs. Pre-weighed quantities of FAZs/SMFZs were mixed with 100 ml of adsorbate solutions at varying concentrations ranging from 50 to 500 mg l⁻¹. The suspension was stirred for different time periods and the final pH of the solution was recorded at the equilibrium. An aliquot was drawn for determination of metal concentration by ICP-AES/AAS

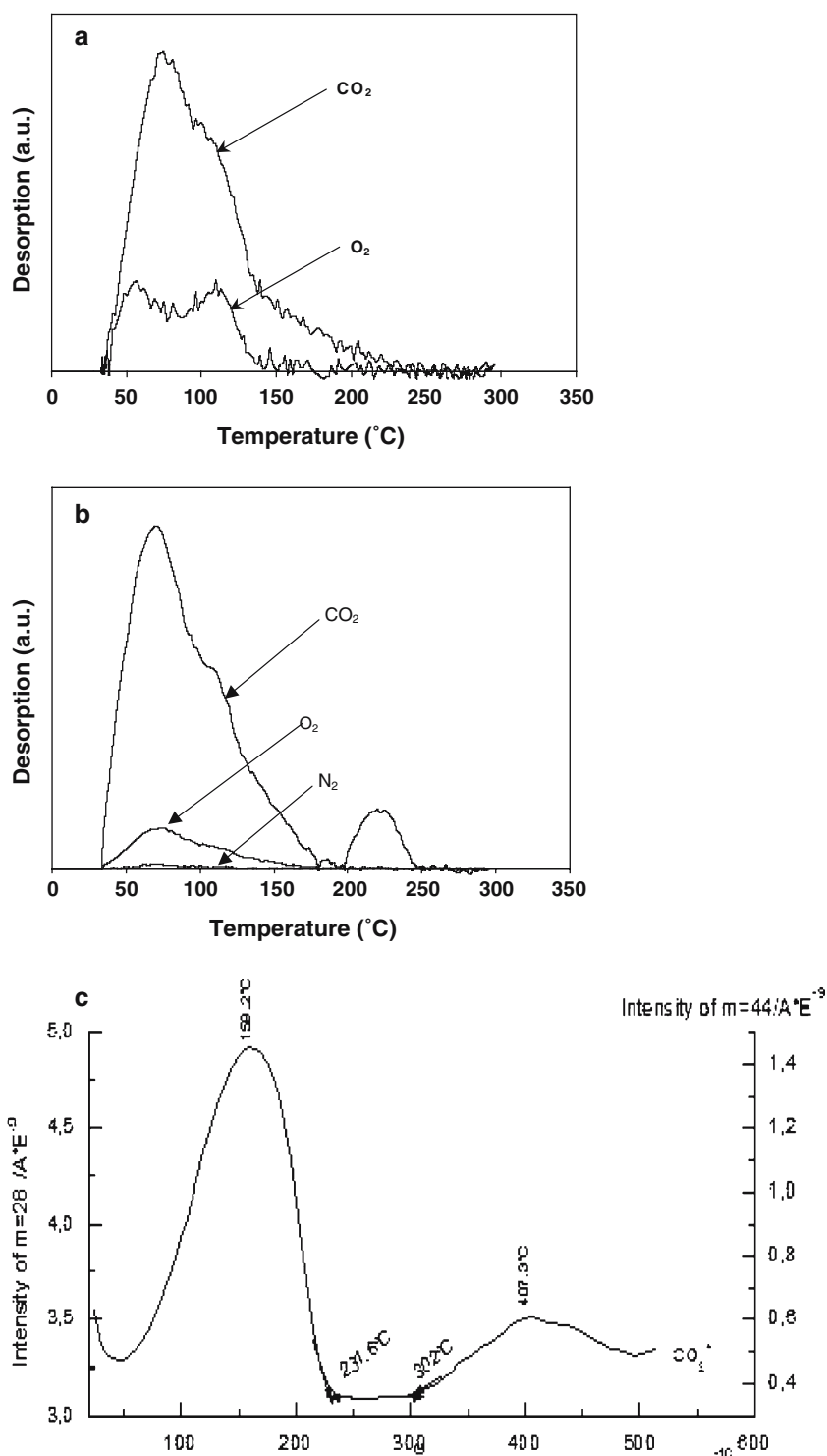


Figure 3. (a) TPD curve of CO₂ saturated FAZ-Y (b) TPD curve of CO₂ saturated FAZ-Y-MEA (c) EGA profile of CO₂ saturated FAZ-A-MEA.

The results of arsenic removal using iron treated FAZ-A and SMFZ-A are shown in figure 5a and b respectively. The results show that these SMFZ are promising low cost adsorbents for arsenic. Stringent target of arsenic concentration below 10 µg/l in drinking waters can be easily achieved using SMFZs.

The development of such innovative, versatile materials is expected to bring out major changes in the area of water and wastewater treatment since these materials offers cost attractive alternative to conventional methods and materials for arsenic removal.

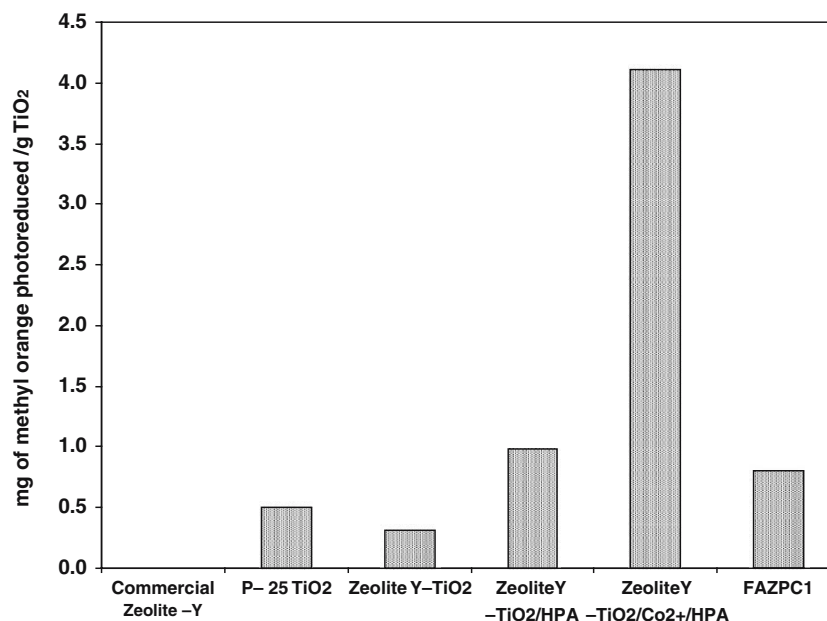


Figure 4. Comparison of photoreduction properties of various modified zeolites.

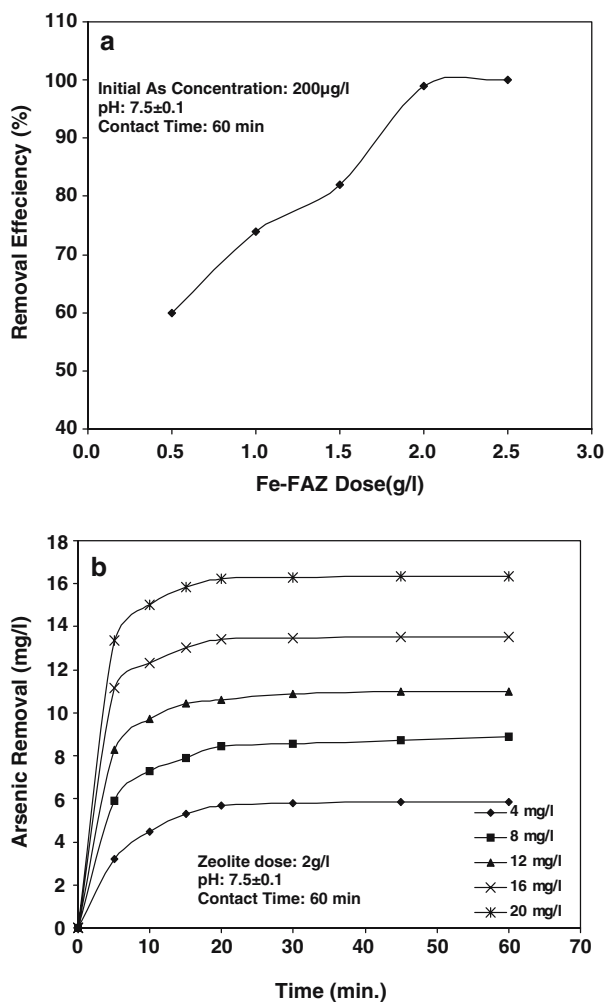


Figure 5. (a) Arsenic removal using iron treated FAZ-A (b) Arsenic removal using different doses of SMFZ-A.

Surface modified zeolites for removal of phenolics

To study removal of phenol pre-weighed quantities of FAZs/SMFZs were mixed with 100 ml of phenol solutions at varying concentrations ranging from 10 to 50 mg/l. The suspension was stirred for different time periods and an aliquot was drawn for determination of phenol by UV-Visible spectrophotometric method. The removal of phenol using SMFZ-Y is presented in figure 6a. The removal efficiencies has also been compared with FAZ-Y, SMFZ-A and SMZ-Y (commercial zeolite) and are shown in figure 6b. SMZ-Y showed enhanced adsorption for 2-chlorophenol as compared to phenol and may be attributed to higher hydrophobicity of 2-chlorophenol as compared to phenol. These materials appear to be promising for adsorption of phenolics and have been reported elsewhere [33]. Further studies are in progress to improve the efficiency of SMFZ-Y for removal of phenolics.

Fly ash based zeolites for removal of heavy metals

The metal removal studies were conducted by following the same procedure as described in section 3.2.2.1 for arsenic removal studies. The cation uptake is attributed to different mechanism of ion exchange process as well as to adsorption process. During ion exchange, the metal ion has to move through the pores of the zeolite mass, and through the channels of the lattice, and they have to replace exchangeable cation (sodium). The uptake of lead, cadmium and copper is mainly attributed to the ion-exchange reaction in the zeolitic materials. FAZ-A exhibits good sorption potential for lead, cadmium and copper. The equilibrium data fits well in the Langmuir model of sorption showing the formation of monolayer coverage at concentration of 500 mg/l with

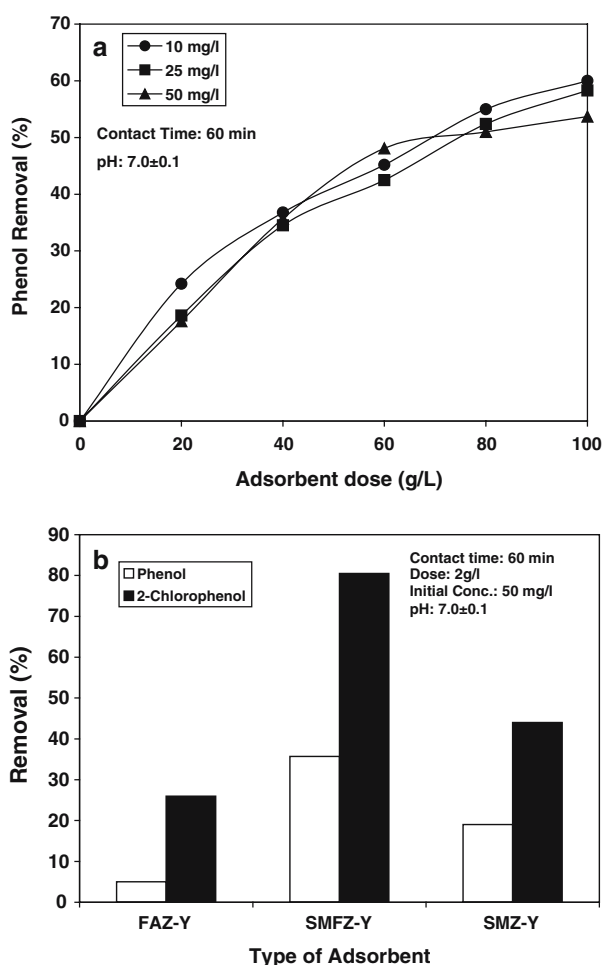


Figure 6. (a) Phenol removal using different doses of SMFZ-Y (b) Comparison of phenol uptake by FAZ-Y, SMFZ-Y and SMZ-Y(Commercial).

maximum adsorption capacity of 270.27 mg/g for cadmium. The rate constants have been derived using Lagergren equation:

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} t$$

Where q_e and q (both in mg/l) are the amount of metal sorbed at equilibrium and at time t (min), respectively, and K_{ad} (min^{-1}) is the rate constant for sorption of metal ions. The values of K_{ad} at different concentration were calculated from the slopes of the respective linear plot of $\log(q_e - q)$ versus t .

The mass transfer analysis carried out using McKay's equation indicates that pore diffusion is the rate-limiting step above a concentration of 500 mg/l. The pore diffusion co-efficient at higher concentration of 800 & 1000 mg/l is 2.83 and $4.89 \times 10^{-11} \text{ cm}^2/\text{s}$ which is comparable with that reported in literature for other heavy metals. To summarize, it may be mentioned that the exchange process in zeolite is governed by two mechanisms namely mass transfer of the sorbate for exchange

on surface of zeolite and diffusion within the pores of zeolite for exchange with the mobile ions in the pores. Mass transfer for exchange on the surface of the zeolite is the rate limiting step at lower concentration and at higher concentration the predominant rate limiting step is pore diffusion but it is not the only one. Similar studies have been carried out for lead and copper. Some of the results pertaining to removal of Pb(II), Cu(II) and Cd(II) using FAZ-A are presented in figures 7a. The removal efficiency of FAZ-A was also compared with its commercial counterpart procured from Degussa (Germany) and the results are shown in figure 7b. The results indicate that the FAZ-A has almost similar efficiency as that of Degussa zeolite. The plots of $\log(q_e - q)$ for Pb, Cd, and Cu are shown in figure 7c. The rate constants for sorption of Pb(II), Cd(II) and Cu(II) from Lagergren's Equation at different concentrations were calculated and are given in table 4. It may be concluded from the values of K_{ad} that the reaction taking place is of the first order. The cation binding capacities (CBC) of FAZ-A is approximately 500 meq/100 g. The results show that the exchange capacities in terms of Pb, Cd, and Cu are 47.6, 43.7 and 44.3 % of CBC respectively under the experimental conditions.

FAZ-Y for ammonium ion removal

To evaluate the FAZ-Y for removal of ammonium ion pre-weighed quantities of FAZ-Y was stirred with solutions of ammonium ion solution (81 mg/l) for 15 min. The solution was filtered and the ammonium ion removal efficiencies were determined by determining the ammonium ion concentrations in the initial and final solutions using standard procedure [43]. The influence of zeolite dose and contact time on percentage removal of ammonia is presented in figure 8a and b respectively. The results obtained are encouraging. The optimal dose appears to be 3 g/l for maximum adsorption with contact time of 15 min. It can be inferred from the results that FAZ-Y offers an excellent ammonia recovery process, which is environmentally benign, cost-effective and has tremendous potential for fertilizer industries.

3.2.3. Soil remediation

FAZ-A/SMFZ-A for heavy metal and oxyanion immobilisation

Soil samples were collected by grab sampling and were contaminated by mixing with 1000 mg/l of metal solutions. The suspension was shaken overnight (12–18 h) at 120–150 rpm. It was then filtered followed by washing (2–3 times) with deionised water. The filtered soil was then thoroughly dried at room temperature and homogenized well before use. The mixture of contaminated soil and FAZ-A were set up in batches with the different amount of FAZ-A. Proper mixing of the

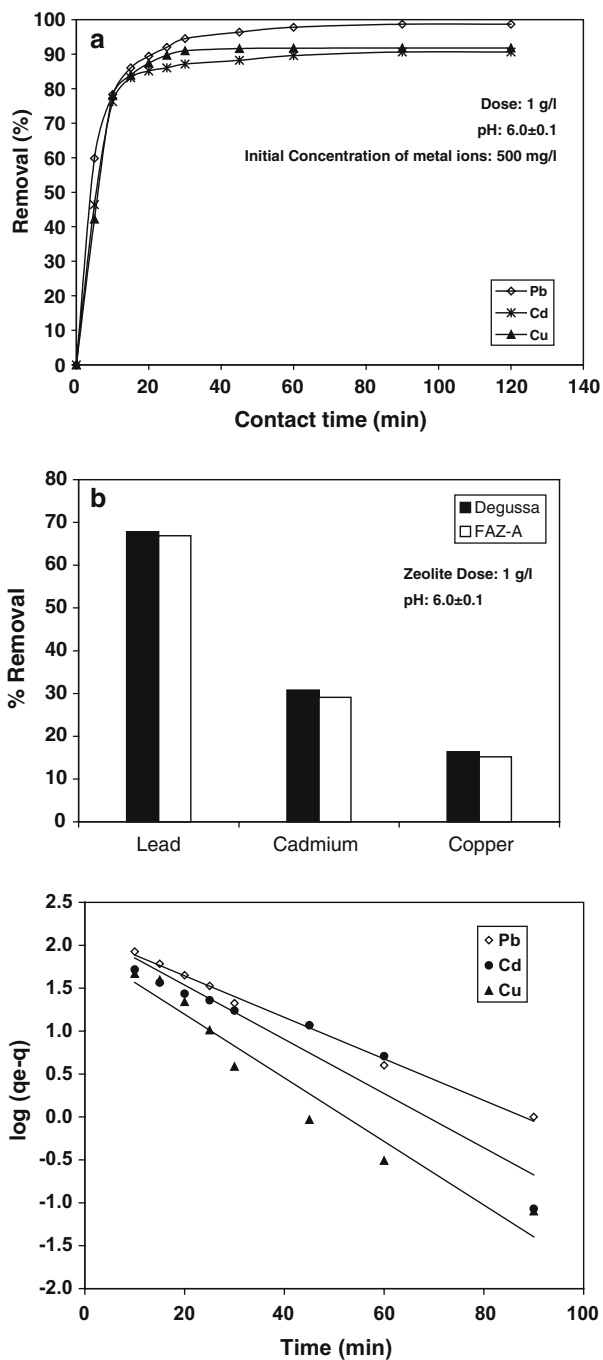


Figure 7. (a) Removal of Pb, Cd and Cu using FAZ-A (b) Comparison of commercial zeolite and FAZ-A for sorption of heavy metals (c) Linear plot of $\log(q_e - q)$ versus t to obtain rate constants.

FAZ-A with the contaminated soil was ensured by the wet and dry process wherein each set was sprayed with a little water to moisten it and thoroughly mixed by repeatedly turning over the mixture. This procedure was repeated three to four times for thorough mixing of the FAZ-A with the Cd contaminated soil to simulate actual field conditions. Each set of metal immobilized soil sample was subjected to leaching studies by shaking 20 g of immobilized soil sample with 100 ml of leaching

Table 4
Rate constant for sorption of Pb(II), Cd(II) and Cu(II) calculated from Lagergren's equation

Initial Concentration (mg/l)	K_{ad} (min^{-1})		
	Pb	Cd	Cu
500	6.72×10^{-2}	7.39×10^{-2}	8.52×10^{-2}
800	6.19×10^{-2}	7.00×10^{-2}	7.99×10^{-2}
1000	5.89×10^{-2}	6.84×10^{-2}	7.65×10^{-2}

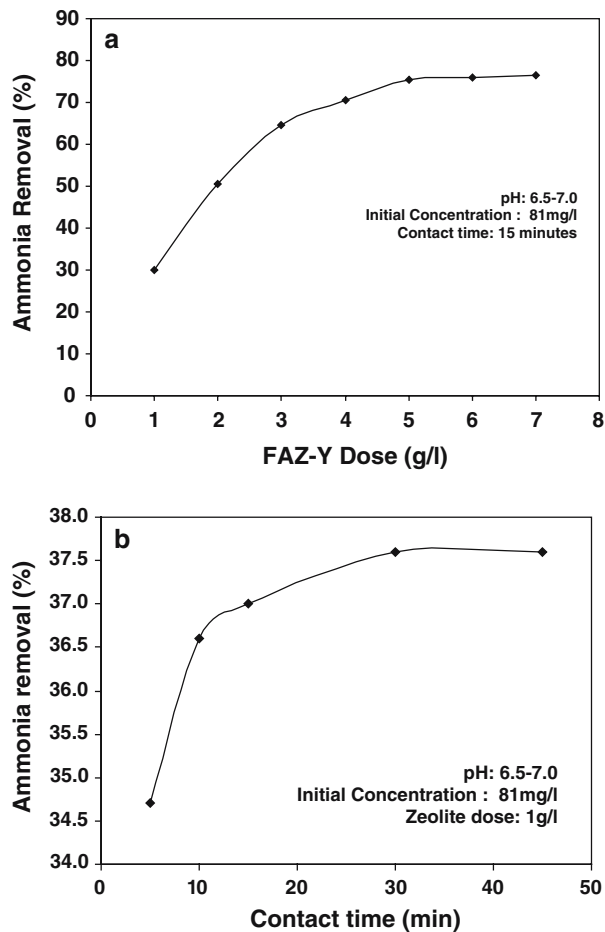


Figure 8. (a) Effect of zeolite dose on ammonia removal (b) Effect of contact time on ammonia removal.

solutions for an hour. The filtrates obtained after filtration of these samples were analysed for their metal content using Perkin-Elmer Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) Model Optima 4100 DV.

In-situ immobilization studies have been conducted for immobilization of heavy metals like lead and cadmium using FAZ and SMFZ-A. Efficiencies have also been compared with commercially available zeolite-A. The results for immobilization studies for

lead and cadmium are shown in figures 9a and b respectively. As evident from the results that FAZ-A and SMFZ-A provides up to 98% immobilization for lead and cadmium even at very small doses of 1.5 g/50 g soil. The metal leachability is dependent on several factors like soil pH, complexation stability, organic functional group, solution ionic strength and presence of other cations, which influence the metal partitioning between solid and liquid phase. The metal ion concentration in leachate is expected to be higher at lower pH values, which is observed distinctly in the present investigation also. The metal exchangeable and adsorptive capabilities increase with decreasing pH in the soil samples. pH, therefore appears to play a major role in affecting metal leachability. The addition of FAZ-A to the soil results in increase in pH and CEC. In addition, of the increased cation exchange capacity (CEC) of the soil mixture, the increased pH of the soil mixture also contributes favourably towards lower metal leachability.

Surface modified zeolites having anionic characteristic are expected to sorb toxic oxyanions like arsenate, arsenite, chromate etc. In-situ immobilization of arsenate has been studied using SMFZ-A and very encouraging results were obtained as shown in figure 9c. Up to 90% immobilization has been achieved with SMFZ dose of 1.5 g/50 g of soil.

SMFZ-A as slow release nutrient medium

The experimental set up for leaching experiments consisted of constant flow chemical reactor which includes glass columns of internal diameter 1 cm and height 30 cm. The columns were filled with 10 g of sieved soil and overlaid with 0.5 g of fertilizers. The column was then filled with deionised water while maintaining a constant water head. The leachates were collected at different time intervals and the phosphate concentrations were determined spectrophotometrically at $\lambda_{\max} = 570 \text{ nm}$. Zeolites have been reported to induce favourable effects when applied to agricultural soils, such as the increase of water-stable microaggregates, a more advantageous moisture holding capacity, better availability of plant nutrients and higher crop yields, especially in coarse-textured soils. Various nutrient loaded zeolites have also been reported as slow release fertilizers. A constant flow chemical reactor was designed to study the slow release of nutrients from various fertilizer loaded FAZs. The results for slow release of phosphate are shown in figure 10a. As evident from the results, the phosphate loaded SMFZ-A shows much higher activities than normal zeolite and pure fertilizer. The release of PO_4^{3-} from pure KH_2PO_4 was completed in 9 days; however, the PO_4^{3-} loaded SMFZ-A continues to release even after 30 days. These initial studies have proved that the SMFZ-A can be effectively used for slow release of various nutrients.

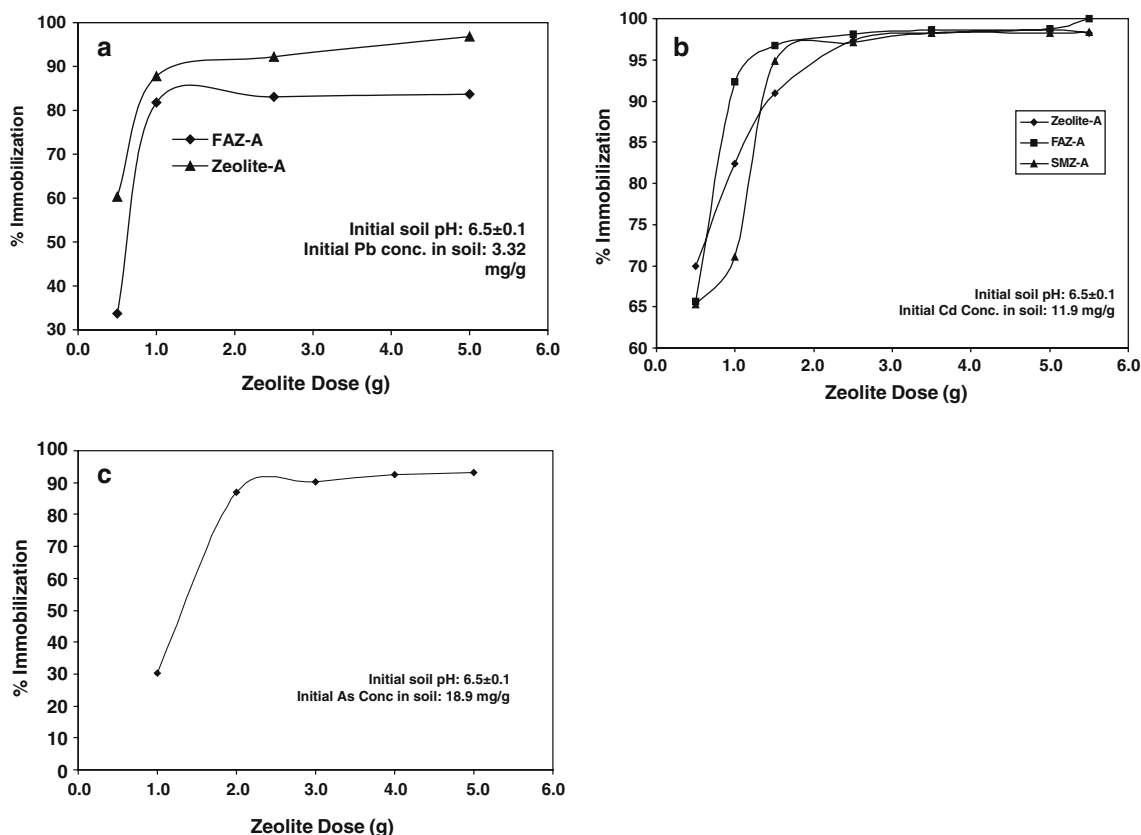


Figure 9. (a) In-situ immobilization of lead (b) In-situ immobilization of cadmium (c) In-situ immobilization of arsenic.

SMFZ-A for immobilization of microbes

For immobilisation of *Azotobacter chroococcum* onto SMFZ-A Jensen's broth was prepared, sterilized by autoclaving and inoculated with a loopful culture of *Azotobacter chroococcum*. The flask was then kept in a shaker-cum-incubator with the speed adjusted at 150 RPM and temperature 30.5 °C for 5 days. This broth culture was then centrifuged. The supernatant was discarded. The biomass settled at the bottom of the centrifuge tube was collected using phosphate buffer of pH 7. The set, biomass plus phosphate buffer (pH 7) was prepared in duplicate. Initial cell count in both the flasks using standard plate count method was done. Zeolite A was added (5 g/l) to one of the sets and another set was run as blank i.e. without zeolite. Both the flasks were kept in shaker cum incubator for 24 h. The final cell count was performed after 24 hr for both the flasks using standard plate count method.

Attempts have also been made to immobilize microorganisms to impart microbial activities in zeolites. The results of immobilization of *Azotobacter chroococcum* on FAZ-A and SMFZ-A are shown in figure 10b. The results show up to 100% immobilisation with zeolite dose of 0.7 g/l. FAZ-A carrying positively charged replaceable ion i.e. cation could not show good adsorption of *Azotobacter chroococcum* cells whereas SMFZ-A having hydrophobic and positively charged surface shows 100% adsorption. The nitrogen fixing capacity of the *Azotobacter chroococcum* cells adsorbed on SMZ was also demonstrated in the nitrogen free Jensen's medium, using Kjeldahl method and the organism showed fixation of atmospheric nitrogen efficiently during its growth.

4. Future perspectives and conclusions

4.1 Enhanced carbon sequestration through surface functionalised materials for capture and long term safe storage of carbon dioxide

Carbon capture is one of the most significant aspects of the entire carbon sequestration process. Conventional

adsorbents in vogue are beset with drawbacks of lack of selectivity, which in turn has implications on cost of carbon capture. To overcome this problem it is proposed to develop materials with enhanced selectivity and affinity, which would increase the capacity for carbon capture in turn reducing the cost of treatment of flue gases.

4.2 Zeolite as storage materials for hydrogen

NEERI has initiated work on production of hydrogen as clean fuel using photocatalytic approaches. Efforts are now being focused on storage of hydrogen, which is the crucial step for its safe transportation. Amongst other materials like metals hydride, liquid organic hydride (LOH) etc. zeolites are also being prepared to be evaluated for their potential as hydrogen storage materials.

4.3 Innovative monitoring and control technologies for indoor air quality using nanostructured materials

Indoor air quality is influenced due to emission of VOCs from new materials and products of building materials, insulation, bonding resins, fabrics, cleaning materials, personal care products, pesticides, and in addition, from the combustion process of cooking, fuel heating and tobacco smoking. The exposure of human beings to toxins from these incredible varieties of sources causes typical disease known as "sick building syndrome". To address this problem of environmental significance, the proposed work is to be carried as follows:

- Development of sensory materials for detection of VOCs
- Development of functionalised materials for indoor air quality monitoring and
- Development of photocatalytic materials for indoor air quality control.

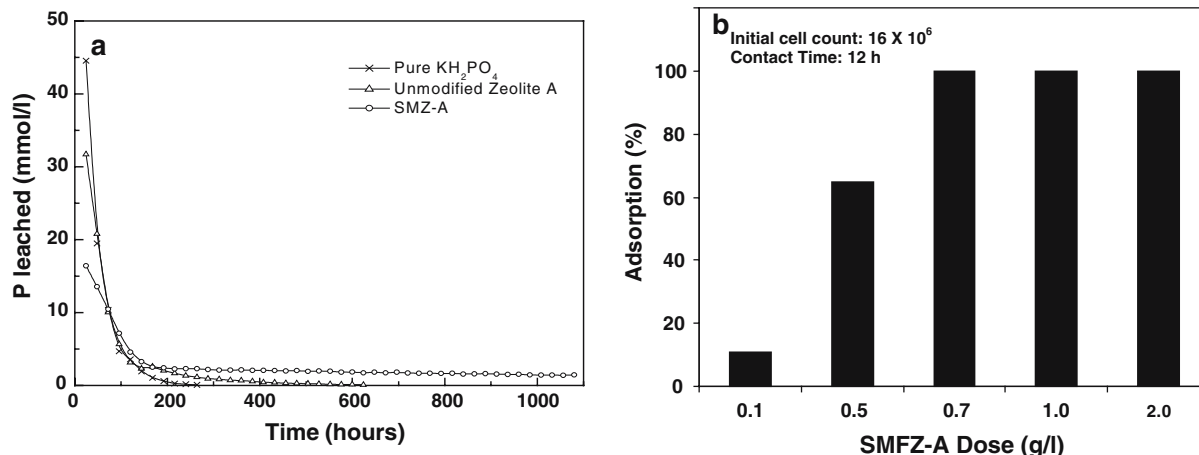


Figure 10. (a) Slow release of nutrients from FAZ and SMFZ (b) Adsorption of *Azotobacter chroococcum* on SMZ-A-200.

4.4 Molecular imprinting techniques for detection of hazardous pollutants

An important area of research is to overcome the problems of monitoring of highly toxic and carcinogenic compounds through molecular imprinting. Molecular imprinting is a technique to incorporate specific recognition into a substrate. These sites display affinity and selectivity. Molecular imprinting aims to create solid materials containing chemical functionalities that are spatially organized by covalent or non-covalent interaction with imprint molecules during synthesis process. Preliminary work has been carried out at NEERI and encouraging results have been obtained using functionalised zeolitic materials for detection of arsenic and VOCs.

5. Conclusions

Fly ash with its high content of SiO₂ and Al₂O₃ has successfully been used for production of a wide array of zeolites. The process formulated for production of fly ash based zeolites has the following advantages:

- Cost effective production of zeolites
- Commercially feasible substitute for synthetic zeolites
- Economically viable, technically convenient and non-tedious process
- High value utilization of fly ash
- Environmentally benign process
- Concomitant resolution of fly ash disposal problem.

The FAZ process offers several advantages over the conventional processes, viz.; conservation of raw materials (sodium silicate/aluminate), reduction in production time, and energy conservations

Despite low volume utilization of fly ash in FAZ process compared to other medium/low value utilization, FAZ production process has advantages of value addition with concomitant conservation of conventional raw materials, offering an edge over other fly ash utilization technologies in vogue.

The FAZ production has the potential to serve as a co-generation commodity to power generation rather than a waste.

SMZs are showing affinity for cationic, anionic and hydrophobic pollutants, and therefore may prove to be versatile hybrid material for water and wastewater treatment wherein a single unit may be employed for multicomponent pollutants in wastewater vis-à-vis multiple units required for treatment of wastewater.

Fly ash based zeolites have tremendous potential for environment and energy conservation, in specific for the following:

- Hybrid materials for soil remediation and enhancement of plant growth
- Adsorption and in-situ destruction of VOCs in indoor air

- Selective adsorption of CO₂ from flue gases
- Selective adsorption of arsenic at low concentrations
- Single unit in water and wastewater treatment vis-à-vis multiple units in conventional process
- Air pollution control with specific reference to VOC adsorption and in-situ destruction, vehicular emission control and NO_x reduction.

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