Volatile organic carbon monitoring in indoor environment using a versatile hydrophobic flyash-based zeolite as adsorbent

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Volatile organic carbon (VOC) in indoor air is a matter of concern. The conventional adsorbents used for monitoring of VOCs are beset with drawbacks. A new class of materials, namely surface-modified zeolites (SMZ) has been synthesized from flyash as the source material. SMZ have been used for indoor monitoring of VOCs vis-à-vis conventional adsorbents. The adsorbed VOCs were desorbed at higher temperature and analysed using GC–MS technique. The VOC adsorbed on SMZ are much higher compared to activated carbon, illustrating the successful usage of SMZ as novel and versatile adsorbent for VOC monitoring.

Keywords: Hydrophobic zeolite, indoor air, sorption, surface modification, volatile organic carbon.

INDOOR air quality is degraded by emissions (of materials and products) from building materials, insulating materials, bonding resins and fabrics, cleaning materials, personal care products, pesticides, and from the combustion process of cooking, fuel heating and tobacco smoking. Human beings are exposed to elevated levels of a wide spectrum of volatile organic carbons (VOCs), many of which have been found to be potentially carcinogenic. These pollutants mostly include aromatic hydrocarbons, BTX (benzene, toluene, and xylene).

The problem is further aggravated by the fact that energy-efficient building construction has resulted in significant reduction in the outdoor–indoor air exchange rate. For example, when indoor ambient air is being kept at considerably lower temperature than outdoor air, the energy requirement for cooling is reduced by minimum exchange of hot air with cooler air and by re-circulating the indoor air only. This results in an increase in indoor contaminant levels. From the health perspective, indoor health quality is more important, as people spend most of their time indoors, such as in houses, schools, office buildings and shopping centres. Even the outdoor VOC emissions have an impact on indoor air, particularly in most of the developing countries, where due to warm climate, natural ventilation is preferred via open windows. The outdoor air quality is deteriorating due to increase in the number of industries and vehicles. Thus, the quality of indoor air depends on both indoor sources and outdoor environment. Various household activities are also responsible for emission of pollutants, as detailed in the Table 1. Therefore, it is imperative to monitor the VOC concentration in indoor and outdoor air environment.

A method for indoor air quality monitoring requires detection in a very low concentration range (ppb range) for several types of VOCs, namely aliphatic, aromatic, and halogenated hydrocarbons, alcohols, ketones and aldehydes. This necessitates sufficient sensitivity to trap the compounds of interest for subsequent analysis using appropriate chromatographic techniques. Indoor air quality monitoring employs two techniques, namely active sampling and passive sampling. Active sampling includes pumping of controlled air flow into the sampler for a specific sampling period. The air drawn-in is passed through the adsorbent for adsorption of pollutant being monitored. Whereas passive sampling is dependent on diffusion of pollutant from bulk air to the adsorbent, no pumping of air is used in passive sampling. In both the techniques adsorbents like activated carbon, resins, alumina, etc. are used to capture VOCs as much as possible for analysis with sufficient accuracy. However, many adsorbents suffer from certain limitations, e.g. resins like Tenax are very weak adsorbents suitable for compounds, less volatile than benzene; coconut charcoal causes analyte degradation on thermal desorption. Also, at sites where high ozone concentrations exist artifact generations are caused during adsorption and desorption with Tenax and Carbopack in the presence of SOx, NOx.

The artifact formation can occur by various chemical or physical phenomena on adsorbent surface such as reaction, evaporation, etc. Therefore, there is a need to identify adsorbents that could adsorb a wide array of pollutants without artifact formation. An ideal adsorbent is expected to have (i) large accessible pore volume, i.e. a large capacity of reversible adsorption; (ii) no catalytic activity; (iii) hydrophobicity; (iv) high thermal and hydrothermal stability, and (v) easy regeneration property. The several adsorbents reported for VOC monitoring include activated carbons, polymer materials, clays and zeolites. Activated carbons are most commonly used in many adsorption processes due to their higher adsorption capacity. However, their instability at higher temperatures and reactivity with several adsorbed VOCs, particularly at higher temperature which is used for desorption of adsorbed species during regeneration of adsorbents, poses a problem. Therefore, zeolites are gaining increasing importance. Hydrophobic zeolites, namely ZSM-5 and silicates have been proposed as promising VOC adsorbents, due to their selectivity for VOCs and their non-flammability.

Alternatively, fascinating zeolites can be modified to achieve the required characteristics for VOC monitoring, i.e. modifying the surface of the zeolite with surfactant. Treatment with surfactant imparts hydrophobic characteristics to zeolites. These hydrophobic zeolites can adsorb a wide array of VOCs.
Table 1. Types of volatile organic compounds and potential indoor sources

<table>
<thead>
<tr>
<th>Pollutant type</th>
<th>Example</th>
<th>Indoor source</th>
</tr>
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<tbody>
<tr>
<td>Aliphatic hydrocarbon</td>
<td>Propane, butane, hexane, decane, limonene, octane, and naphthalene</td>
<td>Cooking and heating fuels, aerosol propellants, cleaning compounds, refrigerants, lubricants, flavouring agents, perfume bases</td>
</tr>
<tr>
<td>Halogenated hydrocarbon</td>
<td>Chloroform, methylene chloride, PCBs</td>
<td>Aerosol propellants, fumigants, pesticides, refrigerants, degreasing, dewaxing and dry-cleaning solvents</td>
</tr>
<tr>
<td>Aromatic hydrocarbon</td>
<td>Benzene, toluene, xylene and their alkyl-substituted derivatives</td>
<td>Paints, varnishes, wood polish, glues, enamel, lacquers and cleansers</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Ethanol, methanol</td>
<td>Window cleaners, paint thinners, cosmetics, adhesives and human breath</td>
</tr>
<tr>
<td>Ketones and aldehydes</td>
<td>Acetone, MBK, formaldehyde, nonanal, nonanone</td>
<td>Nail polish, polish remover, adhesives, fungicides, germicides, disinfectants, cosmetics, flavouring agents</td>
</tr>
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</table>

Figure 1. Volatile organic carbon monitoring locations in Nagpur city.

of VOCs. Faujasitic zeolites are basically hydrophilic in nature and can adsorb organic compounds of kinetic diameter of 7–8 Å, by virtue of their molecular sieving ability. Their pore size is 7–8 Å. To enhance the efficiency for adsorption of VOCs, they are subjected to treatment using a surfactant, namely hexadecyltrimethylammonium bromide (HDTMA-Br) to incorporate hydrophobicity. Here we report a novel adsorbent, namely surface-modified flyash-based zeolite having a better adsorption capacity, for a wide range of VOCs, which may be present in air, in small concentrations.

Flyash-based zeolite-Y (FAZ-Y) having silica/alumina ratio of 2.0 to 2.25 and cation exchange capacity of 400 to 425 meq/100 g, was synthesized from flyash using the procedure detailed elsewhere.\(^{16,17}\) The first step in the synthesis procedure was fusing flyash with sodium hydroxide in a ratio of 1:1.2 at 550°C for about 1–2 h. The resultant fused mass was cooled, milled and mixed thoroughly in distilled water. This slurry was then subjected to aging for 8 h. This amorphous alumino-silicate gel was then subjected to crystallization between 90 and 110°C for about 2–24 h. The solid crystalline product was recovered by filtration and washed thoroughly until the filtrate pH was 10–11, and dried at 50–60°C. The surface-modified zeolite was synthesized by subjecting FAZ-Y to modification using surface-modifiers like HDTMA-Br. The synthesized flyash-based zeolite-Y was washed with distilled water several times till its pH reached 10.0 to 10.5. A pre-weighed quantity of washed FAZ-Y sample was then mixed with different initial concentrations of surfactant, i.e., HDTMA-Br solution in 1:100 (solid: liquid) ratio. The surfactant concentration ranged from 100 to 800 mg l\(^{-1}\) for 10 g of FAZ-Y. The solution at pH 8.0 to 8.5 was agitated for 7 to 8 h at 150 rpm on a gyratory shaker. The solution was then filtered and the solid residue was washed with double-distilled water and oven-dried for 4 to 6 h. The surfactant loading on FAZ-Y was monitored using total organic carbon (TOC) analyser and was around 30–32 mg g\(^{-1}\). In terms of surfactant to CEC ratio, the loading ranges between 6.5 and 8 mg-g/meg. The synthesized SMZ-Y sample was then mechanically ground and sieved for uniform particle size of zeolites. The adsorbents used in this study, FAZ-Y and SMZ-Y were characterized using XRD, SEM, FTIR, BET, surface area estimation and Hg porosimetry.

Conventionally, ambient air quality monitoring in India is carried out in industrial, commercial, residential/sensitive areas to meet the regulatory requirements. We have chosen sites in each area type in Nagpur city. The city is located at the centre of India (lat. 21°06′ long. 79°03′) with moderate industrialization and a population of about 2 million. A map of Nagpur city locating various indoor monitoring sites in residential, commercial and industrial
areas is shown in Figure 1. Active sampling was employed for monitoring VOCs in indoor and work environment using Compendium TO-17 USEPA method\textsuperscript{18}. Standard low volume samplers were used for monitoring indoor air. The adsorbent materials were filled in a glass tube open at one end, and the other end of the glass tube was attached to the sampler in such a way that air was drawn though the adsorbent-filled tube. Sampling was conducted for 8 h using air throughput rate of 1200 ml h\textsuperscript{-1}. After 8 h, the tube was carefully closed at both ends. The adsorbents used included activated carbon and SMZ-Y. The adsorbed benzene, toluene and xylene on the adsorbent were subjected to thermal desorption and collected using a collection unit. The gas sample was analysed using gas chromatograph and mass spectrometer.

Zeolite structure stability was monitored during characterization of the materials. Powder XRD analysis using CuK\textsubscript{α} as the source for X-rays, and the sum total of relative intensities of $d$-spacing values of standard zeolite-Y were compared to FAZ-Y and SMZ-Y to determine per cent crystallinity. The $d$-spacing values used for reference are as follows: 14.15, 8.73, 7.46, 5.69, 4.78, 4.39, 3.79, 2.87 and 2.65 Å. The closely matching $d$-spacing values of all these zeolites prove that the structure has been retained. The surface morphology of FAZ-Y and SMZ-Y was examined by SEM. It was observed that the orthorhombic geometry
of the zeolites has not changed much, probably there are changes in sharp edges and corners, which may be due to deposition of surfactant molecules. FTIR spectra obtained using KBr pellets of FAZ-Y and SMZ-Y are shown in Figure 2. The IR patterns confirm that in SMZ-Y, characteristic peaks at wavenumbers 3419, 2922, 2854, 1377 and 721 cm⁻¹ are observed. These are similar to FAZ-Y. There is a slight shift in peaks at wavenumbers 1458 and 983 cm⁻¹; however, both the patterns are nearly the same. This further substantiates the structural stability of zeolite after surface modifications. FTIR pattern of HDTMA-Br was obtained separately. The three most intense peaks in case of HDTMA-Br are observed at 725, 3427 and 964 cm⁻¹. Peaks at 3427 and 964 cm⁻¹ are coincident with those observed in FAZ-Y. The peaks may be overlapping. However, the most intense peak at 721 cm⁻¹ is observed distinctly. This confirms the loading of HDTMA-Br on zeolite.

The surfactant loading was confirmed using TOC analysis, as mentioned earlier. Substantial changes in specific surface area and micropore volume were observed in the case of SMZ-Y. Micropore volume, micropore surface area estimated using nitrogen adsorption for FAZ-Y were 0.337 cc g⁻¹, 868.8 m² g⁻¹ and 34.4 m² g⁻¹ respectively. These were reduced to micropore volume of 0.283 cc g⁻¹, micropore area of 728.4 m² g⁻¹ and external surface area of 28.08 m² g⁻¹ for SMZ-Y. The surfactant molecules (head size of about 6 Å) have probably entered into the micropores of FAZ-Y and some of the molecules may be present at the pore openings.

Indoor monitoring of VOCs carried out at three types of activity areas (four sites in each activity type) revealed that at all the sites, VOCs exist in air. Most of the aromatic hydrocarbons are released from indoor sources like paints, varnishes, wood polish, glue enamel and cleaners, etc. Unless there is some specific activity, the concentrations of these pollutants are not expected to vary with change in the monitoring period. However, difference in VOC concentration was observed at three out of the four residential sites, between monitoring conducted during morning and evening, as depicted in Table 2. This indicates that outdoor activities such as change in traffic may be the probable reason for variations observed in BTX indoor concentrations. This is also evident when concentrations of VOCs are compared between residential and commercial sites. At commercial sites, where vehicle movement is relatively high, the VOC concentrations are generally observed to be higher compared to residential sites. In the case of industrial sites, higher concentrations compared to residential sites are observed only for toluene, whereas concentrations of benzene and xylene are in the same range.

Various adsorbents used in this study include SMZ-A, SMZ-Y, FAZ and activated charcoal. Based on a few initial runs it was observed that SMZ-Y is more suitable for monitoring a range of VOCs and was used in further experiments. The adsorption capacity and selectivity of adsorbent towards different organic compounds govern the monitoring efficiency, in terms of ability to monitor a range of VOCs at low concentrations. A comparison of SMZ-Y and conventional activated charcoal was made for the identification of various VOCs. Both the adsorbents were used under similar conditions. The desorbed VOCs were analysed using GC-MS and patterns for both the adsorbents are compared in Figure 3. In the case of monitoring at residential areas, the compounds identified using activated charcoal (Figure 3a) are toluene, p-xylene, d-limonene and benzene, 1-methyl-4-(1-methylethyl). In the case of SMZ-Y (Figure 3b), compounds identified included benzene, 2-pentanone, methyl isobutyl ketone, toluene, 1-nonane, p-xylene, 1-decane, benzene, 1,2,4-bimethyl, d-limonene and benzene, 1-methyl-4-(1-methylethyl) and 1-undecane. Similarly, it is revealed from a comparison of both the
adsorbents at commercial and industrial areas, that SMZ-Y is able to adsorb more VOCs. Conventional adsorbents like activated carbon adsorb VOCs with relatively low volatility and below a threshold concentration. Most of the VOCs that might be present in small concentrations, are not adsorbed on activated charcoal. However, several VOCs are adsorbed on SMZ-Y. The adsorption capacity of the adsorbent and its affinity towards various VOCs are improved, if the surface of the adsorbent is made hydrophobic. Surface modification using a particular surfactant introduced hydrophobicity to zeolite-Y, as in the case of SMZ-Y. The increased hydrophobicity increases the wettability of the adsorbent surface by VOCs, thus increasing the adsorption capacity for compounds with a varied range of volatilities. The surface-modified zeolite-Y is identified as an effective adsorbent for VOC monitoring, even at low concentrations in indoor environment. Synthesis of SMZ offers a cost-effective alternative to conventional adsorbent by virtue of a single treatment for a wide range of VOCs.

SMZ was exposed to known concentrations of benzene and subsequently regenerated using He gas at 20 ml min⁻¹ at a temperature of 150°C. A benzene recovery in the
range of 99.46 to 99.74% from SMZ was obtained. In a separate experiment at one site, simultaneous monitoring was conducted using fresh SMZ and regenerated SMZ for comparison. The GC–MS peaks for desorbed gases show similar patterns for VOCs, as shown in Figure 4. This confirms that the regenerated SMZ material is reusable.

The VOC-adsorbed SMZ was heated up to 200°C and desorbed gases were collected in a collection chamber. Samples were drawn from a gas collection chamber through a septum arrangement. The samples were then analysed. No catalytic oxidation products such as CO or CO₂ were observed. This indicates that the SMZ, used as adsorbent in this study, has no catalytic activity for oxidation of adsorbed VOCs, under monitoring and desorption temperatures. Thermal stability study of surfactant loading, using TG-DTA, confirms that the material is stable up to a temperature of 250°C, well above the temperature used for desorption.

The surface-modified zeolite-Y as such synthesized was identified as an effective adsorbent for VOCs even at
low concentrations in indoor air. The synthesis procedure offers cost-effective alternative to conventional adsorbent by virtue of single treatment for a wide range of VOCs. Also, it overcomes the problems associated with commercial adsorbents, namely activated carbon and Tenax, like regeneration, analyte catalytic degradation and polymerization of VOCs. The adsorption efficiency of SMZ was compared with activated carbon. This revealed that SMZ is more selective for adsorption of VOCs having a wide range of volatilities. Thus, with enhanced adsorption capacity for several VOCs, better stability and regeneration possibility, the use of SMZ-Y as adsorbent is an advancement for VOC monitoring.

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Aerobic granular biomass: a novel biomaterial for efficient uranium removal

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Aerobic microbial granules, self-immobilized microbial consortia cultured in aerobically operated bioreactors, primarily consist of mixed species of bacteria ensconced in an extracellular polymeric matrix of their own creation. Such aerobically grown microbial granules have attracted considerable research interest in environmental biotechnology. In recent times, it has been demonstrated that the granules could be used for efficient degradation of recalcitrant organic compounds and for the treatment of a growing number of wastes. The objective of this study was to investigate whether aerobic granules could be used as novel biomass material for biosorption of uranium from aqueous solutions. The granular biomass for biosorption experiments was cultivated in a laboratory-scale sequencing batch reactor by feeding with synthetic wastewater. Biosorption of uranium [U(VI)] was studied at different initial pH values (1 to 8) and different initial uranium concentrations (6 to 750 mg L⁻¹). Biosorption was observed to be rapid (<1 h) in acidic pH range (1 to 6) compared to that at pH 7.0 or above. Almost complete removal of uranium was observed in the range 6–100 mg L⁻¹ in less than 1 h. Redlich–Peterson model gave the best fit when the experimental data were analysed using different adsorption isotherm equations. The maximum biosorption capacity of U(VI) was determined to be 218 ± 2 mg g⁻¹ dry granular biomass. Further, it was

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