Development of metal organic framework-199 immobilized zeolite foam for adsorption of common indoor VOCs

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ABSTRACT

Reticulated foam shaped adsorbents are more efficient for the removal of volatile organic compounds (VOCs), particularly from low VOC-concentration indoor air streams. In this study composite structure of zeolite and metal organic frameworks (MOFs), referred as ZMF, has been fabricated by immobilization of fine MOF-199 powder on foam shaped Zeolite Socony Mobil-5 (ZSM-5) Zeolitic structure, referred as ZF. The ZMF possess a uniform and well-dispersed coating of MOF-199 on the porous framework of ZF. It shows higher surface area, pore volume, and VOCs adsorption capacity, as compared to ZF-structure. Post-fabrication changes in selective adsorption properties of ZMF were studied with three common indoor VOCs (benzene, n-hexane, and cyclohexane), using gravimetric adsorption technique. The adsorption capacity of ZMF with different VOCs follow the order of benzene > n-hexane > cyclohexane. In comparison with MOF-199 and ZF, the composite structure ZMF shows improvement in selectivity for benzene from other two VOCs. Further, improvement in efficiency and stability of prepared ZMF was found to be associated with its high MOF loading capacity and unique morphological and structural properties. The developed composite structure with improved VOCs removal and recyclability could be a promising material for small to limited scale air pollution treatment units.

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Therefore, to ensure industry competitiveness and growth while matching environmental regulations satisfactory, technologies for the abatement/re-use of VOCs are required. There are several methods which include physical, chemical and biological treatments to remove VOCs, either by recovery or destruction (Berenjian et al., 2012). These methods involves air-stripping (Roizard et al., 2009), oxidation by thermal combustion (Nishikawa et al., 2012), catalytic oxidation (Joung et al., 2014; Liu et al., 2013), photocatalytic oxidation (Gholami et al., 2014; Luo et al., 2014), biological treatment (Estrada et al., 2015), membrane separation (Ramaiah et al., 2013), and adsorption (Cao et al., 2015; Ion et al., 2015; Rezaee et al., 2013; Sebök et al., 2015; Tefera et al., 2014; S. Wang et al., 2014; X. Wang et al., 2014). Even though, due to complex nature and diversity of these VOCs, it is hard to find a simple and promising solution. A wide range of VOCs can, however, be removed or recovered by adsorption, at low operating and capital costs of process and with a very limited carbon footprint.

In an adsorption based process, the air stream is usually passed through a fixed bed of adsorbent (like, activated carbon, zeolite, polymeric adsorbents), where separation/purification is achieved through successive adsorption and desorption cycles (James and Ritter, 1991). The foremost challenge in this process is the packing of adsorbent bed so that an optimal flow rate can be maintained. The use of finely powdered adsorbents in these fixed beds is avoided owing to a technical limitation of pressure drop that occurs during adsorption–desorption cycles. Shaped adsorbents like beads, spheres, mesh, pellets, and extrudates are therefore preferred because they offer better adsorption efficiency and adsorption selectivity at low pressure and mechanical stability under high-pressure. For instance, an activated carbon fiber (ACF) shows higher VOC adsorption capacity when compared with powdered activated carbon (Navarrì et al., 2001). There are potential environmental and energy benefits of using ACF filters for indoor air quality improvement through Central Heating Ventilation and Air-Conditioning (HVAC) systems (Sidheswaran et al., 2012). Likewise, composite fiber material of reduced graphene oxide (RGO) and carbon has also been used for VOC removal. This composite material showed improved hydrophobicity due to the presence of RGO in fiber structure and demonstrated higher adsorption of VOCs over water vapor (Bai et al., 2013). Aerogels are also suitable materials for VOC removal due to their unique physicochemical properties such as high porosity and specific surface area. Unlike other shapes, the reticulated open cell foam structure is quite practical due to its low mass to volume ratio. The use of such foam structure in filters or fixed bed process offers important technical advantages like reasonable mass transfer dynamics and reduced pressure drop. One of the major concerns in the use of foam structures in a given application is to maintain sufficient adsorption capacity and selectivity, without compromising with structural advantages (Ghosal and Manjare, 2002). Recently, ordered macroporous ordered siliceous foam (MOSF) was synthesized by a sol–gel method using tetramethoxysilane (TMOS) as the silica source. This foam demonstrates reasonable adsorption capacity of different VOCs under static as well as dynamic adsorption conditions along with recyclability (Wang et al., 2015).

Literature shows, that the studies carried out so far on the adsorption of VOCs by shaped adsorbents are largely focused on the activated carbon, silica, and zeolite-based materials, with primary objective of these studies being the development of an appropriate isotherm (Bai et al., 2013; Meng et al., 2013; Navarrì et al., 2001; Sidheswaran et al., 2012; Wang et al., 2015; S. Wang et al., 2014; X. Wang et al., 2014). Only limited studies on the adsorption of VOC have been carried out with metal organic framework (MOF) which comprises a new class of nanoporous materials (Barea et al., 2014; Heinke et al., 2015; Khan et al., 2013; Plantais et al., 2013; Trens et al., 2012; Xian et al., 2015; Zhao et al., 2011). MOFs are coordination network, of metal ions (clusters) coordinated to organic molecules. These materials are excellent adsorbent materials due to their high adsorption capacities for gases and vapors and also due to the possibility of modifications in their pore geometry and chemical functionalities (Llewellyn et al., 2014). The MOFs are synthesized in the form of ultra-fine particulates and therefore structuring MOFs from micro to macro level is essential for their application in an adsorption process. Although, there is very thin literature on the development of MOFs based shaped structure. In a study MIL-101(Cr) was immobilized on the monolithic structure of cordierite, by the secondary seeded growth of MOF to obtain uniform coatings of ~9 wt.% inside the monolith channels (Ramos-Fernandez et al., 2011). The other approach involves molding of MOF powder in pellets using an organic binder, like for example MIL-53(Al) tablets are prepared by using polyvinyl alcohol as an organic binder (Ferey, 2008), and tablets of MOF-199 (Cu-BTC) were made, by using Alox C and graphite as additives (Cavenati et al., 2008). It is in this context that the present study was undertaken with an objective to achieve MOFs based foam shaped structure and ascertain its selectivity for VOC adsorption. This can in principle be achieved by incorporating MOF particles in an open cell porous monolithic material.

In this study, we impregnate MOF-199 in open cellular zeolite foam of Zeolite Socony Mobil (ZSM-5) (Scheme 1) to obtain a MOF-zeolite composite material. The MOF-199 also known as HKUST-1, is a Cu based porous material \([\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]\) (Chui et al., 1999), which is easy to synthesize material and need inexpensive reagents. This collectively makes it suitable for scale-up and commercial application. The foam shape of zeolite offers ideal support due to its high surface to volume ratio (Saini and Fires, 2012). For adsorption studies, three VOCs, commonly found in the indoor environment, namely n-hexane, cyclohexane, and benzene (Scheme 1) were selected (Pittet et al., 2000). To our knowledge, this is the first study where a MOF-Zeolite composite foam material is developed and investigated for its selective adsorption properties for VOCs.

The key objectives of this study were, (1) to obtain a composite MOF-based open cell foam structure by incorporation of MOF-199 in ZSM-5; (2) to obtain static adsorption isotherms on individual and composite material with three selected VOCs; and (3) to evaluate the selectivity of composite structure for selected VOCs and compare it with constituting materials.

### 1. Materials and methods

#### 1.1. Materials

Tetrapropylammonium hydroxide (TPAOH), purity 20% in H$_2$O, was purchased from Fluka. Tetraethyl orthosilicate (TEOS),
1.3. Synthesis of MOF-199

MOF-199 was synthesized according to a procedure detailed elsewhere (Pöppl et al., 2008). The main reason for selecting this method is that it yields ultrafine particles of MOF-199, which is vital for its immobilization in ZF-structure. Briefly, 15.9 g (65.8 mmol) of Cu(NO₃)₂·3H₂O and 6.9 g (32.8 mmol) of trimesic acid (benzene 1,3,5 tricarboxylic acid) were dissolved in 100 mL of ethanol in a 250 mL conical flask. The solution was then heated to reflux, under constant stirring for 24 hr and then filtered to separate blue-colored precipitate. This precipitate was washed several times with ethanol, to remove unreacted traces of reagents. For each washing, the precipitate was stirred with 25 mL of ethanol for about 15 min and then filtered. The washing cycles continued until a colorless filtrate was obtained. At that point, for a final washing the sample was stirred for 4 hr in 50 mL of ethanol. After filtration, the solid was transferred to a 100 mL Schlenk tube and dried to a maximum extent under vacuum at 120°C in a sand bath, for 24 hr. In the end, a deep blue colored sample of MOF-199 was obtained which was then labeled with MOF-199 and stored under nitrogen.

1.4. Fabrication of composite structure

A dip-coating method developed by Xue et al. (2007) was adopted to incorporate MOF-199 in the porous structure of zeolite foam. Where, a fixed amount of MOF-199 sample was dispersed in predetermined volume of ethanol by ultrasonic dispersion to obtain a concentration of 5 mg/mL. Then a pre-weighted sample of ZF was completely immersed in this dispersion solution for about 15 min. The solution was placed in the ultrasonic bath to ensure maximum dispersion of fine particles to the interior of the porous structure. The sample was then removed from the solution and dried at room temperature, under N₂ flow for 6 hr which is followed by heating in an oven at 100°C, for overnight. The process of MOF-199 loading was repeated one more time and then, in the end, the composite sample was degassed at 120°C for 24 hr. The final composite sample so obtained was weighed and found to have 40.2% of ZF and 59.8% of MOF-199, by weight. This sample was labeled as ZMF (Zeolite MOF Foam) and stored in desiccators until further use.

1.5. Characterization of composite structure

The surface and structural properties of prepared materials were characterized with different instrumental techniques. For instance, open cell volume and density of PUF, ZF, and ZMF were measured with an automatic gas pycnometer (AccuPyc 1330, Micrometrics, USA). The surface area and porosity of these materials were measured with low-temperature nitrogen adsorption technique. In which, adsorption isotherms of nitrogen gas (Air Liquid, 99.999%) were obtained at –196°C using a liquid nitrogen cryogenic bath on an automatic volumetric instrument (Nova 2200e, Quantachrome USA). Before measurement, the samples (50–100 mg) were degassed for 2.5 hr under a pressure lower than 0.133 Pa and temperature 120°C. The crystal structures of MOF-199, ZF, and ZMF were observed using powder diffraction method on an X-ray diffractometer (PW 1710, Philips,
The Netherlands) using Cu-Kα radiations (λ = 1.5406 Å). This diffractometer was equipped with automatic data acquisition software (APD Phillips v.35B). The morphological characterization of these materials was made with scanning electron microscope (SEM) micrographs (JSM-5200 LV, Jeol, USA).

1.6. Adsorption experiments

The adsorption of VOCs (n-hexane, benzene, and cyclohexane) on prepared materials was studied with the help of adsorption isotherms, which were measured by gravimetric adsorption technique. This technique is particularly helpful in the study of adsorption of condensable vapor on solid materials (Rouquerol et al., 1999). A schematic diagram of the instrument setup used for obtaining isotherms is given as Scheme 2. The microbalance (from C.I. Electronics) employed in this setup permitted a precision better than 10 μg. During experiments, the pressure readings were made with a pressure transducer (CMR 262, Pfeiffer Vacuum, Germany). Before taking isotherm, each sample was degassed at 120°C for 2 hr, with a ramp of 10°C/min under a dynamic vacuum (less than 10⁻⁶ Pa). For degassing, a combined vacuum system of rotary/oil diffusion pumps was employed. The temperature of adsorption system (25 ± 0.1°C) was maintained with the help of a thermostatic water bath (GD-120, Grant Instrument, United Kingdom). During adsorption experiments, a small amounts of VOCs is successively introduced from VOC reservoir to the vacuum microbalance chamber. The amount of vapor adsorbed by the sample was monitored with a digital microbalance. Once the adsorption equilibrium is achieved, which is confirmed by constant values on microbalance as well as pressure transducers, the VOC amount was recorded as a function of equilibrium vapor pressure of VOC. To construct adsorption isotherms, this amount of VOC (in terms of mmol per gram of material) is plotted against the relative pressure of VOC. Here the relative pressure (p/p°) is the ratio of equilibrium pressure ‘p’ and vapor pressure ‘p°’ of respective VOC at adsorption temperature.

2. Results and discussion

2.1. Characterization of composite structure

Structural properties are the decisive aspect of an adsorbent that eventually determines its adsorption efficiency. Therefore properties like morphology, specific surface area, porosity, and crystal structure of prepared composite structure were investigated with different techniques such as scanning electron microscopy (SEM), pycnometer, low-temperature N₂ adsorption measurements, and powder diffraction X-ray spectroscopy (XRD).

The zeolite foam (ZF) used in this study is a light weight material with its specific gravity only 68 kg/m³ (measured with a gas pycnometer). Considering, the density of ZSM-5 zeolite ‘crystals’ (825 kg/m³) the open cell volume of ZF can be calculated as, 91.75%. It clearly indicates that ZF has adequate void volume for dispersion of fine MOF particles and later for diffusion of VOCs in composite ZMF structure. The post-impregnation increase in weight from ZF to ZMF was found 59.8 ± 2%. Comparing with cordierite material which is used in an earlier study for MOF immobilization, this value appears quite high (Ramos-Fernandez et al., 2011). It is again due to the specific gravity of ZF, which is 7 to 10 times less than that of cordierite, or other similar materials that are frequently used as catalyst support. The mechanical stability of prepared composite structure in terms of compressive strength was measured to ensure its durability under different working conditions. To do so, the limit of the state of compressive stress that leads to brittle failure (rupture as the result of crack propagation) of monolithic foam scaffold was estimated. The limit of uniaxial stress, which means compressive strength (σ N/m²), was measured as;

\[ \sigma = \frac{F}{A} \]

where F [N] is the force, acting on an area A (m²). The strength of ZF and ZMF was measured 2.87 × 10⁴ N/m² and 5.82 × 10⁴ N/m², respectively. The results may be interpreted as follows; the ZF has very thin wall structures that may cause it to be more fragile. Conversely, in ZMF the structure is largely unchanged, but the thin walls here are coated with a durable MOF-199 material, that helped in the reinforcement of original structure that is why it shows higher compressive strength than ZF.

After incorporation of MOF-199 particles into zeolite structure, the white colored ZF turns into blue colored ZMF. When this ZMF is degassed at 120°C for 5 hr, its blue color turns into deep violet because of the removal of loosely coordinated water molecules that are coordinated around Cu metal in MOF-199 structure (Britt et al., 2008). The surface morphology of ZF, MOF-199, and ZMF may be compared with

Scheme 2 – Schematic of the experimental set-up for gravimetric adsorption setup for adsorption of VOCs. VOCs: volatile organic compounds.
their SEM images (Fig. 1). The image of ZF shows that the surface of its wall and struts are composed of ZSM-5 crystals with their unique elongated hexagonal plate-like structure (Lee et al., 2001). At same magnification, the MOF-199 particles can be identified as irregular structures. Similarly, ZMF image shows the presence of two different types of structure (irregular and regular hexagonal), where the irregular structure is evident as embedded structure in the interstitial sites of the hexagonal plate-like structure. These observations point toward the achievement of immobilization of MOF particles in ZF cell wall and struts.

The low-temperature nitrogen adsorption isotherms of ZF, MOF-199, and ZMF are compared (Fig. 2). The shape of all the three isotherms is of type-I, which is particularly characterized by a steep adsorption at low relative pressure. According to the IUPAC (International Union of Pure and Applied Chemistry) categorization (Sing et al., 2008), it signifies the presence of microporosity in all of these materials. This property is particularly vital for their adsorptive applications under low relative pressure condition, where higher adsorption is desired from adsorbents. It is important to mention here, that the VOCs are sufficiently noxious even at very low concentrations, and hence their removal, even at low concentration, is indispensable. The specific surface area and pore volume of these materials were calculated from nitrogen isotherms and are listed in Table 1. MOF-199 has quite high 1558 m²/g as compared to ZF, 363 m²/g. Both the values are in agreement with earlier reports (Pöppl et al., 2008; Saini and Pires, 2012). The surface area of ZMF was 957 m²/g, which is justified in the view of its composition. A similar trend in total pore volume and micropore volume has also been observed, where composite material has higher pore volume than ZF, but less than MOF-199.

The powdered X-ray diffraction patterns obtained for ZF, MOF-199 and ZMF are compared (Fig. 3). The diffraction pattern for both ZF (ZSM-5) and MOF-199 are found in agreement with their respective patterns in other reports (Lee et al., 2001; Pöppl et al., 2008). In the case of MOF-199, some minor deviation were however observed in the relative intensities at certain angles, which could be due to variations in the degree of hydration (Schlichte et al., 2004). The diffraction pattern of ZMF sample confirms most of the major peaks of both ZF (ZSM-5) and MOF-199, indicating that impregnation of the MOF in zeolite foam takes place without any loss of crystal structure in either of the constituting material.

2.2. Adsorption of VOCs

The adsorption isotherms of VOCs (n-hexane, benzene, and cyclohexane) on ZF, MOF-199, and ZMF are obtained at 25°C (Fig. 4). The figure indicates that the adsorption capacity of these materials are different from each other and are in order of their specific surface area, MOF-199 > ZMF > ZF. Every material shows different adsorption capacity for different VOC. This behavior is of main concern particularly for to make

Fig. 1 – Graphical as well as SEM images of materials, before and after, impregnation of MOF-199 on the surface of the zeolite. ZMF stands for the composite MOF-199 material. SEM: scanning electron microscope; MOF: metal organic framework; ZMF: Zeolite MOF Foam.
use of their ‘selective adsorption properties’ and transfer it to the composite structure. It is important to highlight here that all the three VOCs molecules have six carbon atoms structure with no finite dipole moment, but still with different structural and electronic properties. For instance, n-hexane is a linear alkane molecule with a kinetic diameter of 4.3 Å, the kinetic diameter of cyclohexane is 6 Å, whereas the benzene has planar π-electronic structure, with 5.85 Å of kinetic diameter (Barcia et al., 2007).

In the case of ZF, only n-hexane shows maximum adsorption at low pressure (Fig. 4a), whereas, with benzene and cyclohexane, the adsorption takes place at relatively higher partial pressure. Besides, the isotherms of benzene and cyclohexane show a ‘step’ at relative pressures near 0.1 or less, which can also be noticed in nitrogen adsorption isotherm of ZF. Similar behavior of ZSM-5, has been observed by Rudziński et al. (1997) during adsorption of hydrocarbon where this step was interpreted as the result of cooperative redistribution of the adsorbed molecules. On ZF, the comparative adsorption of VOCs follow a trend n-hexane > benzene > cyclohexane, which is in order of their kinetic diameter. It suggests that diffusion of molecules in the ZSM-5 channel is a critical aspect of their adsorption in ZF. In MOF-199 (Fig. 4b) most of the adsorption, with each VOC, takes place at low partial pressure, <0.05 and the adsorption capacity follow a trend of benzene ≫ n-hexane > cyclohexane. The higher adsorption of benzene is due to the presence of open Cu metal sites (Lewis acid) in an MOF-199 structure that preferentially interact with π electron cloud of benzene (Britt et al., 2008). In rest of the VOC (alkanes), the n-hexane shows relatively higher adsorption capacity than cyclohexane due to its low kinetic diameter and linear structure, which allows more favorable packing of adsorbed molecules. In contrast to this, ZMF (Fig. 4c) shows synergetic effects of MOF-199 and ZF adsorption properties. For instance, due to the presence of MOF-199 in structure, the maximum adsorption in ZMF takes place at low pressures. Further, the adsorption capacity of this material follows an order benzene > n-hexane > cyclohexane. The ZMF clearly shows more difference in adsorption capacity for n-hexane and cyclohexane as compared to MOF-199 (Fig. 4b). It is probably due to the presence of ZF-structure that has a maximum difference in adsorption capacity, for n-hexane and cyclohexane.

The adsorption affinity of material cannot be compared on the basis of maximum adsorption capacity but with ‘normalized adsorption capacity’ in terms of amount adsorbed on per unit area of adsorbent. This comparison is given in Supplementary information Fig. SI-1, which shows that for n-hexane the ZF has maximum affinity followed by ZMF and MOF-199. For cyclohexane, the MOF-199 has higher affinity at low pressure whereas ZMF shows affinity at higher pressure, followed by ZF. Interestingly the adsorption affinity for benzene was found maximum in ZMF followed by MOF-199 and ZF. These results clearly indicate the difference in adsorption properties of constituting materials (MOF-199 and ZF) and their harmonious influence in the adsorption properties of composite zeolite structure, ZMF. The influence of impregnation on adsorption selectivity was further analyzed by modeling of the adsorption data in terms of their separation factor.

### 2.3. Separation factor (selectivity) of materials

The selective adsorption property of prepared composite structure was analyzed with the help of a selectivity model based on Dubinin-Radushkevich (D-R) expression (Dobruskin,
With this expression (Eq. (3)), the separation factor or selectivity \((S)\) of each material was calculated for a given binary VOC mixture. This model employs the theory of volume filling in micropores and is thus appropriate for adsorption of multicomponent mixtures in micropores. Briefly, according to D-R equation,

\[
\theta = \exp \left[ -\frac{A}{\beta E_0} \right] \tag{1}
\]

where \(\theta\) is a degree of filling, \(E_0\) (kJ/mol) is an adsorbent-related constant, and \(\beta\) is the similarity coefficient. This coefficient is defined in relation to a standard adsorbent and suggests the differences among the various adsorbents. Following a previous work, the molar polarizations of the pure components were used to estimate the values of \(\beta\) (Pires et al., 2003). \(A\) is the adsorption potential (kJ/mol) which is

\[
A = RT \ln \left( \frac{p^0}{p} \right) \tag{2}
\]

where \(p\) (mbar) is the partial pressure and \(p^0\) (mbar) the saturated pressure of the liquid adsorbate. This methodology leads to an expression for the separation factor \((S)\) for binary mixtures:

\[
S = \left( \frac{n_1}{\theta} \right) \exp(\beta) \left[ \exp \left[ \left( \ln \frac{n_1}{\theta} - \frac{\Delta H}{RT} \right)^2 \right] + \exp \left( \ln \frac{n_1}{\theta} - \frac{\Delta H}{RT} \right) \right]
\]

where \(\beta = \Delta H/2RT\). Using this equation the separation factor, for all the three possible binary mixtures of VOCs were calculated and their variations along with surface coverage are presented (Fig. 5).

For benzene/cyclohexane mixture (Fig. 5a), ZF shows lower and constant selectivity compared to other materials. It is because both these molecules have comparable and larger size and considering the small pore size of ZSM-5 (~6 Å) none of them is preferentially adsorbed (Rudziński et al., 1997). The MOF-199 shows higher selectivity for benzene that decreases gradually along with surface coverage. At low coverage the higher selectivity is attributed to a preferential interaction of benzene with Cu metal sites and its gradual decrease with coverage is probably due to less and less availability of vacant metal sites. This phenomenon highlights the role electron density on a molecule in determining its adsorption selectivity. The composite zeolite foam ZMF shows slightly improved selectivity than the constituting materials, particularly at low surface coverage. This slight increase in selectivity is probably a result of easy access of molecules to adsorbent surface in ZMF structure, as compared to powdered sample of MOF-199. The separation of benzene and n-hexane (Fig. 5b) shows the role of both molecule size and electron density on selectivity. For this binary mixture, all the three materials demonstrate preferred adsorption of benzene over n-hexane, even though the latter has a smaller kinetic diameter. It shows that the presence of electron density on the molecule is more critical for this particular separation. The composite zeolite ZMF shows higher selectivity for this separation, compared to ZF and MOF-199. This increase in selectivity of ZMF is a result of incorporation of MOF-199 in zeolite foam structure. It is again important to highlight here that for this separation the selectivity values are always higher than 3, which is considered as a reference value for an adsorbent to be used in the industrial

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Fig. 4 – Adsorption isotherms of n-hexane, cyclohexane, and benzene, at 25°C on (a MOF-199, b) ZF and (c) ZMF materials. MOF: metal organic framework; ZF: Zeolite Foam; ZMF: Zeolite MOF Foam.
separation process (Yang, 2003). Unlike other binary mixtures, the separation of n-hexane and cyclohexane (Fig. 5c) is based on the relative size of VOC molecule. Being smaller, n-hexane is always preferentially adsorbed over cyclohexane on these materials. The results show that all the three materials show similar variation in selectivity (with less mutual difference) along with surface coverage. Due to the absence of clear electronic effect in the case of cyclohexane and n-hexane, the selectivity of MOF-199 is lower than other two materials.

The above comparison shows that incorporation of MOF-199 in zeolite structure has resulted in improvement in its adsorption selectivity, particularly for adsorptive separation of benzene/cyclohexane and benzene/n-hexane binary mixtures. In the case of benzene/n-hexane separation, its selectivity surpass the selectivity of MOF-199, which clearly indicates the synergistic influence of present immobilization approach.

2.4. Reusability

The reusability of any new adsorbent material is important for its sustainable application in a given adsorption process. In general, the reusability of adsorbent is determined by retentions of its adsorption capacity after a desorption process. In this study, the reusability of these materials is compared with the help of adsorption–desorption study with n-hexane. For desorption, the exhausted material (after achieving maximum adsorption) is heated up to 120°C under vacuum (less than 10⁻² Pa), for 2 hr. For the sake of comparison, the first adsorption capacity of each material is considered as 100%. The change percentage in this is recorded up to three consecutive adsorption–desorption cycles. The results (Fig. 6) show a gradual decrease in adsorption capacity with every material after each cycle. This decrease is steeper in the case of MOF-199 whereas less and comparable in ZF and ZMF. It shows that under similar desorption conditions the foam shaped materials can achieve better desorption as compared to fine particulate materials. These observations clearly point toward the structural advantages of materials in ascertaining its reusability.

3. Conclusions

In this work, it was shown that it is possible to incorporate MOF-199 (post-synthetically), in monolithic zeolite (ZSM-5) foam, by an ultrasonication assisted dispersion method. The

Fig. 5 – Variation of separation factor (selectivity) in different materials, as a function of surface coverage, for the mixtures of (a) benzene/cyclohexane, (b) benzene/n-hexane, and (c) cyclohexane/n-hexane.

Fig. 6 – Change in n-hexane adsorption capacity of ZF, MOF-199, and ZMF after adsorption–desorption cycles. MOF: metal organic framework; ZF: Zeolite Foam; ZMF: Zeolite MOF Foam.
impregnation enhances the handling and adsorptive properties of powdered MOF-199 material, by introducing it to a surface of porous zeolite structure. The amount of MOF-199 in composite zeolite foam structure (ZMF) can be controlled by varying the numbers of dispersion cycles. In present study composite zeolite, with 59.8% MOF-199, enhanced the adsorption capacity of zeolite foam for n-hexane, benzene, and cyclohexane by 150%, 283%, and 468% respectively. It was related to increase in surface area (1635%), total pore volume (155%), and micropore volume (160%) of ZMF after incorporation of MOF-199. The blending of two different materials in a structure brings in synergetic effect in terms of selectivity for binary mixtures of VOCs. Enhancement of adsorption selectivity of composite zeolite particularly for benzene/cyclohexane and benzene/cyclohexane mixture is attributed to ease of access of VOCs molecules to the surface of MOF-199 entrenched in zeolite structure. In other words, the physical and surface properties of the zeolite foam were changed upon MOF-199 introduction. These changes can be used to improve the performance of the materials, for instance as adsorbents for the selective separation of vapors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.09.017.

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