JOURNAL OF ENVIRONMENTAL SCIENCES XX (2016) XXX–XXX

Available online at www.sciencedirect.com

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JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

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

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ARTICLE INFO

Article history:
Received 19 April 2016
Revised 9 July 2016
Accepted 7 September 2016
Available online xxxx

Keywords:
VOCs
Adsorption
Composite materials
Selectivity
Zeolite foam
MOFs
HKUST-1

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.

Introduction

A study on air quality in Europe, published by Europe European Environment Agency (EEA) in 2013, showed that air pollution with its various components reduces life expectancy in humans (8.6 months per person) (European Environment Agency, 2013). Some of the VOCs are reported to be found 2 to 5 times higher in concentration, in the indoor environment than outside regardless of whether the homes were located in rural or highly industrial areas (Clayton et al., 1993). Some of the VOCs causes respiratory illness and whereas some are classified as carcinogenic or mutagens in nature (An et al., 2014; Kay et al., 1991). Some of the VOCs react with NOx in sunlight and form ground-level ozone and carcinogenic smog, which also causes a negative impact on the environment by damaging crop, vegetation and materials (S. Wang et al., 2014; X. Wang et al., 2014). Nonetheless, VOCs have significant industrial and commercial value, due to their role in various technological applications, such as production or use of lacquers, paint, strippers, pesticides, cleaning supplies, building furnishings and materials. These compounds are also used in office supplies and equipment such as printers, copiers, correction fluids, carbonless copy paper, graphics and craft materials like glues and adhesives, permanent markers, and photographic solutions (An et al., 2014; Chen et al., 2014; Estrada et al., 2015; Tong et al., 2013; Wolkoff, 2003).

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http://dx.doi.org/10.1016/j.jes.2016.09.017

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; Sebők 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 (Navarri 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 (Ghoshal 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; Navarri 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; Planchais 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 $[Cu_3(btc)_2(H_2O)_3]$ (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 Pires, 2012). For adsorption studies, three VOCs, commonly found in the indoor environment, namely n-hexane, cyclohexane, and benzene (Scheme 1) were selected (Pitten 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_2O, was purchased from Fluka. Tetraethyl orthosilicate (TEOS),