Journal of Hazardous Materials 244–245 (2013) 444–456

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Review

Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs): A review

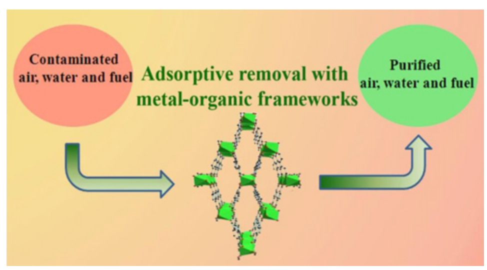
Nazmul Abedin Khan[1], Zubair Hasan[1], Sung Hwa Jhung*

Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Daegu 702-701, Republic of Korea

HIGHLIGHTS

- ► Metal-organic frameworks are very effective to remove hazardous materials.
- ► Mechanisms for adsorptive removal with MOFs were summarized.
- ► MOFs are surely regarded as potential adsorbents for clean environment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 September 2012
Received in revised form 29 October 2012
Accepted 4 November 2012
Available online 13 November 2012

Key words:
Adsorption
Adsorptive removal
Hazardous materials
Metal-organic frameworks
Review

ABSTRACT

Efficient removal of hazardous materials from the environment has become an important issue from a biological and environmental standpoint. Adsorptive removal of toxic components from fuel, wastewater or air is one of the most attractive approaches for cleaning technologies. Recently, porous metal-organic framework (MOF) materials have been very promising in the adsorption/separation of various liquids and gases due to their unique characteristics. This review summarizes the recent literatures on the adsorptive removal of various hazardous compounds mainly from fuel, water, and air by virgin or modified MOF materials. Possible interactions between the adsorbates and active adsorption sites of the MOFs will be also discussed to understand the adsorption mechanism. Most of the observed results can be explained with the following mechanisms: (1) adsorption onto a coordinatively unsaturated site, (2) adsorption via acid-base interaction, (3) adsorption via π-complex formation, (4) adsorption via hydrogen bonding, (5) adsorption via electrostatic interaction, and (6) adsorption based on the breathing properties of some MOFs and so on.

Contents

* Corresponding author. Tel.: +82 53 950 5341; fax: +82 53 950 6330.
E-mail address: sung@knu.ac.kr (S.H. Jhung).
[1] Fax: +82 53 950 6330.

0304-3894/$ – see front matter
http://dx.doi.org/10.1016/j.jhazmat.2012.11.011

1. Introduction

Presently, environmental pollution is one of the most problematic issues worldwide. There have been many trials both to reduce pollution and to eliminate the polluting materials from the environment. Common hazardous materials that exist in our environment are NO_x, SO_x, CO_x, H_2S, volatile organic compounds (VOCs), nitrogen-containing compounds (NCCs), sulfur-containing compounds (SCCs), dyes, pharmaceuticals and personal care products (PPCPs), and so on. On the other hand, porous metal-organic framework (MOF) materials are very interesting due to their versatile applications. MOFs are superior to other porous materials because of their high/tunable porosity, pore functionality, various pore architectures/compositions, open metal sites, and so on. Therefore, recently, extensive studies have been done on the adsorption/separation of various gaseous and liquid components with MOFs. In this review, the adsorptive removal of various toxic liquids and gases using virgin or modified MOFs will be discussed.

1.1. Common hazardous materials

The most abundant hazardous components that exist in the environment can be classified into two categories based on their sources; these are naturally occurring hazardous materials and anthropogenic. A considerable amount of naturally occurring pollutants is present in the air, minerals, water, and soil. On the other hand, the anthropogenic pollutants generally originate from combustion, chemical reactions or from the unsecured effluent of toxic materials. The global energy demand is being supplied mainly by natural gas, coal, and crude oil. The burning of these energy sources emits huge amounts of toxic gases into the atmosphere. Generally, the emissions with the greatest concern for environmental air pollution are NO_x, SO_x, CO_2, VOCs, H_2S, NH_3, and other hydrocarbons [1,2]. Emissions of N_2O, SO_2, O_3, and CH_4 enlarge the ozone levels in the troposphere and are also considered as greenhouse gases. Vehicle-related pollutants like SO_2, NO_2, CO, CH_4, and black carbon contribute to global warming [1]. The carbon balance of the world is one of the most important environmental issues currently; therefore, reducing anthropogenic CO_2 emissions has become a great challenge for humanity. NH_3, one of the most widely used chemicals in laboratories and various industries including agricultural, manufacturing, refrigeration, etc., is responsible partly for the nitrogen containing pollutants in the atmosphere [3–5]. The American Conference Governmental Industrial Hygienists (ACGIH) has specified the allowable NH_3 concentration as up to 25 ppm as the time-weighted average and 35 ppm as short-term exposure [5]. Recently, adsorption has been regarded as one of the most successful techniques for NH_3 capture [5–8]. H_2S, another toxic and odorous air pollutant has also been removed through sorption [9–11]. VOCs are chemicals with high vapor pressure, generally emitted from solvents, resins, paints, adhesives, etc. [12,13]. The common hazardous VOCs are benzene, naphthalene, toluene, phenolics, xylenes, and so on. VOCs are considered hazardous materials since they are harmful to the environment and human health.

Organic compounds containing sulfur or nitrogen are naturally occurring species that are present in fossil fuels and oils like crude oil, gasoline, diesel, jet fuel, and heating oil. More than 85% of the global energy has originated from fossil fuels [14]. The combustion of a huge amount of fossil fuel is the major source of toxic emissions that account for the dangerous air pollution, greenhouse effect, and global warming as well as the harmful impact on living organisms [2]. Therefore, recently, it has become a great challenge to remove these harmful compounds from crude oils before utilization. For example, based on EU and US guidelines, the sulfur level in fuels should be less than 10 ppmw and 15 ppmw, respectively [1,15–17].

The most abundant pollutant of water is dye materials. Dyes are widely used in the textile, leather, paper, painting, and plastic industries. Around 100,000 commercially available dyes are produced at a rate of 7×10^5 tons per year [18] with 2% of the produced dyes being discharged into aquatic systems as effluent [18]. Removal of these materials from waste water is very important because water quality is highly influenced by color [18] and even a small amount of dye is highly visible and considered to be toxic and extremely hazardous to aquatic living organisms [18–20].

PPCPs include a class of chemical contaminants that exist in water even after these products are utilized for medicines, cosmetics, fragrances, veterinary drugs, fungicides, disinfectants, and agricultural practices [21–23]. The presence of these kinds of PPCPs in the effluent of wastewater treatment plants, rivers, lakes and occasionally, in groundwater, has been demonstrated by the recent research [24]. Moreover, it is reported that, a class of PPCPs is unsafe for living organisms and may cause endocrine disruptions changing hormonal actions [25,26].

The disposal of heavy metal ions in processed water is still a considerable amount. Some metals like lead (Pb), arsenic (As), copper (Cu), mercury (Hg), antimony (Sb), chromium (Cr), manganese (Mn), and cadmium (Cd) are significantly toxic to ecological systems and human beings [27–31]. The recovery of those harmful metal ions from environment has been a global concern for the last few decades [27–31].

1.2. Adsorptive removal of hazardous materials

Adsorption has been considered to be superior to other techniques for decontamination in view of its comparatively low cost, wide range of applications, simplicity of design, easy operation, low harmful secondary products and facile regeneration of the adsorbents. Adsorptive removal is based on the ability of a porous adsorbent to selectively adsorb some specific compounds from the atmosphere or refinery streams. The compounds, which have a suitable size and shape, can be removed via adsorption since these compounds have easy access to the pores of the solid sorbents. Based on the types of interactions between an adsorbate and a porous sorbent, the adsorption can be categorized as a physical or chemical one [1,32]. Physical adsorption is usually called adsorptive adsorption, whereas chemical adsorption is called reactive adsorption. In the case of adsorptive removal, the adsorbates are generally trapped with weak (van der Waals) forces inside the pores of the solid adsorbents. Therefore, the adsorbent can be easily