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Review

A review of metal organic resins for environmental applications

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HIGHLIGHTS

- A variety of new materials have been developed for their applications in diverse fields.
- Metal organic resins (MORs) have been introduced based on MOF technology.
- MORs are found to have high sorption kinetics with improved separation efficiencies.
- Environmental applications of MORs and their future prospects are reviewed here.

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ABSTRACT

In recent years, research on metal organic frameworks (MOFs) has been extended to explore various issues regarding structural flexibility, toxicity, aqueous synthesis, biodegradability, regeneration, reuse, and easy disposal. Based on such efforts, highly-ordered porous MOF structures bound to organic resins (metal organic resins or MORs) have emerged as a new generation of materials with excellent properties feasible for diverse applications. Here, we describe the excellent features of MORs and demonstrate their potential applicability in environmental as well as other relevant fields.

Contents

1. Introduction

Metal organic frameworks (MOFs) are a novel class of hybrid materials built from metal ions with well-defined coordination geometries and organic bridging ligands. Over the past decades, MOFs have gained a great deal of interest in materials science due to their unique properties, including intriguing framework architectures, topologies with tunable pore sizes (between 0.4 and 6 nm), and inherently repeating framework structures [1–7]. The potential applicability of these materials has been demonstrated from various fields of research including catalysis, nonlinear optics, and gas storage [8–12]. Despite such potential, a number of factors (e.g., the laborious synthesis and processing, aqueous insolubility, insulating nature, and high cost of the final product) still remain as barriers to a widespread use of MOFs. Consequently, many doubts still remain regarding their practicality such as real industrial applications. In order to achieve further advance in MOF technologies, it

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is important to improve their properties in a more practical sense, e.g., increasing their chemical stability and solubility in water, while lowering their dispersibility [1–12].

Recently, MOF research has focused on the development of a variety of alternative materials for different applications including: bioorganic linkers (e.g., enzymes and bacteria), graphene, carbon nanotubes (CNTs), metal nodes, integrated guest molecules (or mixing of suitable materials), redox (or catalytic) active sites as organic linkers, active guest molecules, biomolecules (e.g., enzymes and bacteria), and nanoparticles. The development of these alternative materials was sought not only to help overcome some of the limitations of MOFs but also to find ways to improve their properties (e.g., electrical conductivity) for novel industrial applications such as small molecule sensing, separation/storage of target gas, and clean energy applications (e.g., batteries, fuel cells, and capacitors) [8–12]. However, as MOFs and many conventional porous materials are usually characterized by very small particle size and insufficient mechanical strength, their use in columns has been restricted [1–8]. Therefore, the use of these materials as-prepared was not recommended in practical sense for environmental remediation applications. As such, development of an engineered form of materials was desirable to meet any specific requirements and related applications [1–8].

Based on the MOF technology, functionalized materials known as metal organic resins (MORs) have recently been introduced; the feasibility of MORs has been investigated intensively due to their advanced features like easy synthesis on a large scale with the dual benefits of both functional amorphous organic resins (with strong binding groups) and ordered porous MOF crystalline structures [3]. It is found that MORs with a functional group-based selectivity, highly porous structure, and narrow pore size distribution are advantageous in many respects. Basically, the presence of functional binding groups (e.g., conventional organic resins) with a highly-ordered porous structure has been shown to facilitate the diffusion of ions while improving sorption kinetics [5–8]. These materials have the following advantages: a) they provide a high sorption capacity, selectivity, and fast exchange kinetics for the targeted pollutant, b) they have a particle size that allows for continuous flow through the column, c) they offer sufficient mechanical strength to withstand high water pressures, and d) they allow regeneration and are reuse [5–8]. As of now, there have only been a few reports on MORs to describe sorption characteristics against target metals or pollutants such as Cr (VI), selenate, and selenite. There are also limited information regarding their applications toward biological or other fields of research [8–12].

MORs have the potential to overcome several drawbacks of conventional/advanced porous materials, including (1) low water solubility and stability, (2) low conductivity, (3) poor regeneration and reusability (organic resins), (4) slow sorption kinetics/limited selectivity and (5) low thermal and chemical stability (resins). Research on MOR-based materials is currently in its infancy and is needed to focus on realizing the full potential of these materials. In this article, we summarize the synthesis and structural characteristics of MORs that can be tailored for applications in environmental, biomedical, and ceramic materials. In light of recent advances achieved in MORs, our discussion has been extended to assess their performance in relation to MOFs. Finally, the potential of MOR-based materials in environmental applications is also discussed to describe various aspects of this emerging research field.

2. Advantages of MORs over MOFs

Currently, zeolites, activated carbon, clays, layered double hydroxides (LDHs), and organic resins are considered to be effective sorbents materials for diverse applications in storage, separation, and catalysis. These materials suffer from a number of drawbacks discussed above. Recent advancements in the development of novel sorbent materials (including MOFs and their composites) seem to be promising routes to address these problems [5–7]. Fundamentally, these materials combine a highly porous ordered structure (not realized by conventional organic resins) with a variety of binding groups not available in inorganic materials. Hence, they are capable of exhibiting exceptionally fast and selective sorption properties.

In the following sections, we provide a detailed comparison of MORs with various sorbents in terms of sorption capacities, selectivity, and regeneration capacity. It was apparent that MORs, although yet limited to a few cases, showed significant advantages (e.g., higher sorption capability, selectivity, and regeneration/reuse) over a number of known sorbents. Therefore, research on MORs deserves to be expanded to areas of diverse fields of research.

In real world applications, questions may arise about the chemical and thermal stability of MORs as well as their preparation costs. These are critical parameters for any sorbent if used in real applications such as environmental remediation. Several MORs are stable in water and may have high structural stability under harsh treatment conditions (e.g., highly acidic or alkaline conditions) [5–13]. These features make them superior candidates in comparison to MOFs (Fig. 1). In addition, the cost-effective preparation of MORs has been realized through the development of rapid/green methods like hydrothermal and mechanochemical synthesis [6,7]. Thus, MORs seem to meet the requirements of practical ion exchange materials. As such, they are expected to play a central role in diverse applications in the near future, as discussed in the next section.

3. Performance of MORs in environmental applications

An overview of the available literature indicates that solvothermal and hydrothermal methods are the most common routes used for the synthesis of MORs. However, methods for synthesizing MORs in the laboratory are not yet well established. The following issues must be taken into account before synthesizing MORs: (1) selection of metal ion type, (2) type of organic resin linkers, (3) synthesis medium, and (4) solvent used during the synthesis. The synthetic process to fabricate MORs should also be selected by considering the solvent medium (aqueous, non-aqueous, and a combination of aqueous/non-aqueous media in a particular ratio) used for the targeted applications. The selection of these factors will also affect the desired properties of MORs for their fields of applications. In the next section, we will discuss the synthesis as well as performance of 1-D, 2-D, and 3-D MORs compared to MOFs in environmental, biomedical, and ceramics applications.

In the literature, MORs have been explored most commonly for environmental applications, especially as ion exchange column materials [5–7,13]. MOR sorbents have some excellent features that can benefit from such application: (a) high selectivity and fast sorption kinetics for targeted toxic ions, (b) a particle size that allows for continuous flow of wastewater through a column, and (c) sufficient mechanical strength to withstand high water pressures [5–7]. Tokalioglu et al. [14] used atomic absorption spectrometry to investigate how a polystyrene divinylbenzene-copolymer known as Amberlite XAD-16 (and other copolymers including XAD-2, −4, −7, −8, and −16) performed in the sorption of heavy metals such as Cr, Ni, Cu, Cd, and Pb from lake water samples. A flame- and graphite furnace-atomic absorption spectrometry technique optimized with sodium tetraborate reagent was used in determining the free metal ions with detection limits (DL, $\mu g\,L^{-1}$) of 2 (Cd) to 54 (Ni) ($n = 20$, $3s$) [14]. An Amberlite XAD-16 resin packed col-