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Metal-organic frameworks: Challenges and opportunities for ion-exchange/sorption applications

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A B S T R A C T

Exposure to common ionic pollutants, such as heavy metal ions and toxic anions, is a major concern throughout the world due to their potential impacts on human health and the environment. Recently, metal-organic frameworks (MOFs) with ion-exchange properties have attracted great interest with respect to the capture of diverse hazardous cationic and anionic species. In fact, according to the investigations on these ion exchangers, their sorption capacities are recognized to be considerably superior to conventional materials. This review focused on metal-organic materials as sorbents for ions by surveying MOFs with respect to their exchange/sorption capacities in association with their synthesis and structural characteristics. We also described the recent development in MOF composites and their practical applications toward wastewater treatment. The sorption characteristics were also evaluated among the reported MOFs and then between MOFs and other sorbents. Finally, we described the future prospects for the research and development in materials for ion-exchange based on MOF technology.

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Abbreviations: AC, activated carbon; ASA, p-arsanilic acid; CAU, Christian Albrechts-Universitat; CUSs, coordinatively unsaturated sites; DABCO, 1,8-diazabicyclooctane; DETA, diethylenetriamine; DFT, density functional theory; DMF, dimethylformamide; 1-, 2-, and 3-dimensional, 1-D, 2-D, and 3-D; ED, ethanediamine; H_2BPDC, 2,2′-bipyridine-5,5′-dicarboxylic acid; H_3BTC, 1,3,5-benzenetricarboxylic acid; HKUST, Hong Kong University of Science and Technology; IR, infrared; MIL, Matériaux de l'InstitutLavoisie; MOFs, metal-organic frameworks; MOR, metal-organic resin; MFCs, magnetic framework composites; MSIEs, metal sulfide ion exchangers; OMSs, open metal sites; LDHs, layered double hydroxides; ppm, parts per million; ppb, parts per billion; PSM, post-synthetic modification; SCSC, single-crystal-to-single-crystal; SBU, secondary building units; ROX, roxarsone; TBAI, tetrabutyl ammonium iodide; UV–Vis spectroscopy, ultraviolet–visible spectroscopy; US EPA, US Environmental Protection Agency; UiO, Universitetet i Oslo; XRD, X-ray diffraction; ZMOF, zeolite-like metal organic framework; ZIFs, zeolitic imidazolate frameworks.

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1. Introduction

1.1. Outline

The efficient decontamination of aqueous wastes, such as industrial and nuclear waste effluents, is one of the most important environmental issues that must be addressed over the next few years [1–6]. The major pollutants in these types of wastes are heavy metal ions (Hg^{2+}, Pb^{2+}, Cd^{2+}, and Tl^{+}), anionic species (CrO_4^{2-}, AsO_4^{3-}, and CN^-), and various radionuclides (^{137}Cs, ^{89}Sr, ^{235}U, ^{59}Fe, ^{57}Co, ^{65}Zn, etc.) [1,2]. Various methods have been explored for the removal of such contaminants from water. Precipitation methods are inexpensive and commonly used for the removal of metals and other species from water; however, such approaches are often ineffective in lowering the concentration of pollutants below the levels proposed by safety guidelines. They also have a tendency to generate large amounts of sludge [3]. Photocatalysis is another promising option; unfortunately, this often results in unwanted by-products (e.g., Cr^{3+} from the reduction of Cr(VI)) that must also be removed (necessitating a secondary treatment) [4]. Biological treatments, although cost-effective, have similar drawbacks to precipitation and photocatalytic methods, such as their inability to completely remove contaminants and the generation of sludge [5].

In light of the many limitations encountered by the previous approaches employed for the treatment of wastewater, sorption and ion exchange are considered to be highly effective and affordable/low-cost methods [6]. Traditionally, organic resins and inorganic materials (such as zeolites, clays, and layered double hydroxides) have been investigated for their ion-exchange properties [7–11]. Nevertheless, such conventional materials also suffered from several drawbacks such as (1) poor regeneration and reusability (organic resins), (2) slow sorption kinetics/limited selectivity (LDHs, zeolites, and clays), and (3) relatively low thermal and chemical stability (resins) [7–11]. Consequently, it is necessary to explore new sorbent materials or improve the existing ones to overcome these limitations.

Over the last decade, metal-organic frameworks (MOFs) have gained a great deal of interest due to their excellent properties including high surface area, multi-functionality, and chemical/thermal stability [12–29]. These materials are promising for wastewater treatment applications. MOFs with ion-exchange/sorption properties may be considered as next-generation ion-exchange materials through the combination of a highly-ordered porous structure (not shown by typical ion-exchange materials such as organic resins) and a large variety of binding groups (not present in traditional inorganic ion exchangers) [30–32]. Thus, MOF ion exchangers may be capable of extremely fast sorption with unprecedentedly high selectivity toward targeted ionic species. Furthermore, several MOFs have shown remarkable thermal (up to 400–500 °C) and chemical stability (resistance against acidic and/or basic conditions), unlike conventional organic and inorganic ion exchangers [33–39]. MOFs can also be cost-effective because they can be prepared in high yields via affordable and green synthetic methods (e.g., hydrothermal and mechanochemical syntheses) [31,40–42]. The recent development of ion-exchange columns of MOF composites, where efficient decontamination of industrial wastewater has been achieved, also indicates the great potential of these materials for real wastewater treatment applications [30,31]. To date, a number of review articles and monographs have been reported to describe the fundamental science behind metal-organic porous materials and their important properties [12–16,20]. Limited reviews, however, have focused on the ion-exchange chemistry of such materials [32,43,44], and these articles only briefly discuss the sorption of ionic pollutants by MOFs.