Perspective

Mining resources from wastes to produce high value-added MOFs

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Since Yaghi et al. proposed the concept of MOFs in 1995 (Yaghi et al., 1995), Metal-organic frameworks (MOFs) have been developed as a new class of porous inorganic-organic hybrid materials, which arose the wide interests from many scientists in various research fields (Wang and Ho, 2016). In the past two decades, tens of thousands of MOFs have been prepared and applied in many fields, due to their merits like high specific surface area, large pore volume, tunable structure and abundant active sites in adsorption/separation, catalysis, photoreduction, sensing, supercapacitors, energy storage, food safety and other fields. To better realize large-scale applications in various fields, the production cost of MOFs must be considered. However, traditional synthesis approaches of MOFs usually require expensive either chemicals and solvents with high purification or the complicated or harsh synthesis conditions and operational steps. Under the strategy of reduction of pollution and carbon emissions, the metal ions and organic ligands as the components of MOFs can be obtained by recycling various wastes. Recycling and converting waste plastics and different wastes containing metals into MOFs products with high value-added are emerging and feasible ways and means.

The plastics are widely used in large quantities in various applications such as plastic bottles, cups, packaging and textiles. It was well known that the natural degradation of most waste plastic products can take up to decades or even hundreds of years, which primarily resulted into the wide distribution of microplastics in the environment. It has been found that polyethylene terephthalate (PET) in refractory plastic waste contains up to 85 wt% terephthalic acid (i.e. 1,4-benzenedicarbocylate, BDC), which is one of the most used organic linkers to construct different MOFs including but not limited to MIL-88B, MIL-101, MIL-53, MIL-125 and UiO-66. Therefore, using PET plastic waste as a source of BDC linker to synthesize MOFs can not only eliminate PET waste in the environment, but also reduce the consumption of new reagent grade raw BDC. However, it has been reported that PET can be depolymerized into terephthalic acid (BDC) in the presence of acid or alkali at high temperature and pressure. The environmental threat of the large amount of wasted waste acid/base generated in the PET depolymerization may

outweigh the economic and environmental benefits of the cost savings from recycling PET to H_2BDC. Fortunately, the recent findings reported that some new PET hydrolases can depolymerize PET into H_2BDC monomer at ca. 50 °C (Lu et al., 2022), which offers a feasible approach to yield H_2BDC ligand from used PET plastics under mild condition for MOFs production. Besides PET, polybutylene terephthalate (PBT) and polylactic acid (PLA) in the plastic waste can also be used to provide organic ligands (terephthalate and lactic acid) for the synthesis of MOFs (Shanmugam et al., 2022).

Similarly, as shown in Fig. 1, the metal templates (Fe, Cu, Al, Cr, V, Ca) of MOFs can also be obtained by recycling metal-containing wastes discharged from various industries. MIL-53(Cr) can be synthesized by using Cr-containing electroplating sludge with a Cr content of about 63% as a metal source. Nickel electroplating sludge and PET were used as metal and linker sources to prepare Ni-MOF. Vanadium in carbon black waste leachate from oil refineries can replace commercial vanadium chemicals to prepare V-MOF. Waste egg shells can replace commercial $CaCO_3$ as a Ca(II) source for the preparation of Ca-based MOFs. High-alumina fly ash waste and discarded aluminum foil/cans in life are also available aluminum sources for the preparation of MIL-53(Al), and metal-rich Li-ion batteries can also be successfully used as metal sources to synthesize MOFs such as MIL-96, CuBTC and MIL-53. However, in fact, most of these metal ion-containing wastes contain other impurities, which will influence the purity of the as-obtained MOFs and even lead to some structural defects in the synthesized MOFs.

Either waste polymer or scrap metal sources or both as sources were adopted to accomplish the synthesis of MOFs, in which the as-prepared MOFs exhibited comparable performance to their commercially-sourced counterparts in adsorption, catalysis, sensing, and other fields. However, up to now, both the waste PET hydrolysis process and the MOFs synthesis process consume a large amount of acid, alkali and/or some toxic organic solvent. As well, the purity of the obtained MOFs may not be ideal due to the impact of the coexisting substances in the waste. Therefore, one of the main challenges of waste-to-MOFs conversion is to be proceeded under greener reaction conditions. It is necessary to

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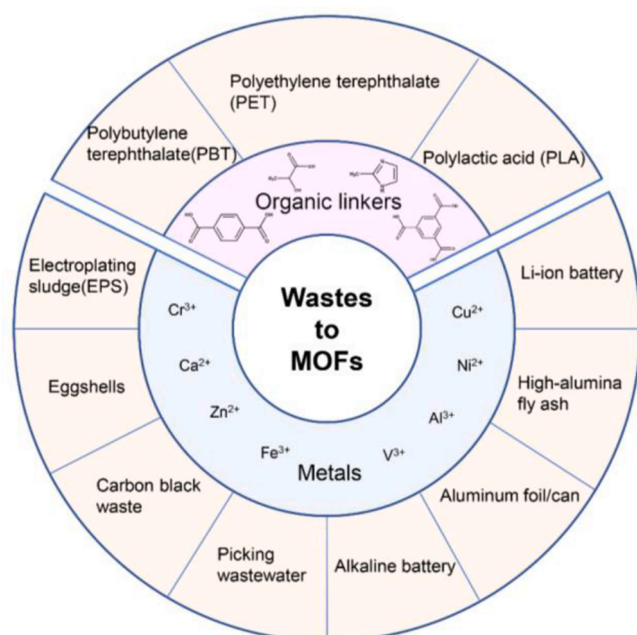*E-mail address:* wangchongchen@bucea.edu.cn (C.-C. Wang).

Fig. 1. Organic ligands and metal sources for waste-to-MOFs.

consider how the recycling and conversion of wastes into MOFs with the purpose of resource saving can be achieved without introduction of additional toxic chemicals.

It was well known that the wastewater generated in the process of cleaning stainless steel oxide skin contains both rich metal ions (30–40 g/L Fe^{3+}, 7–10 g/L Cr^{3+} and 5–8 g/L Ni^{2+}) and strong acidity (180 g/L HNO_3 and 55 g/L HF, pH≈−0.3∼−0.2), which provides all MOF raw materials (metal source, and acidic reaction condition) except organic ligands. Fe/Cr-MIL-100 was successfully prepared from Fe^{3+} and Cr^{3+} in stainless steel pickling wastewater with the presence of H_3BTC ligand, in which the Ni^{2+} could also be purified for further utilization. The as-obtained Fe/Cr-MIL-100 demonstrated the adsorption capacity toward dyes, heavy metal ions, and drugs in the aqueous phase, comparable to that of MIL-100 prepared by commercial reagents (Zhao et al., 2023). This method of recycling pollutants in the environment into high value-added products took environmental conditions into account,

which not only solves the problems of high energy consumption and waste of resources in traditional treatment methods, but also eliminates the waste generated in the reuse process, accomplishing economical and efficient realization of waste recycling.

In all, it is "killing two birds with one stone" approach to convert waste materials into useful ones like high value-added MOFs based on the strategies of 3Rs (reduce, recycle and reuse) along with the carbon peak and neutrality goals. However, it was not feasible to convert wastes to MOFs heavily relying on excessive energy and chemical inputs, especially exceeding the economic and environmental cost of MOFs production with new chemical precursors. From this point, producing MOFs from wastes at low cost should consider both the actual waste compositions and MOFs production conditions, which should be in the line of the approach of recycling economy, sustainable development, carbon peak and carbon neutrality.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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