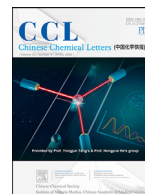




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Editorial

MOFs for water purification



Metal-organic frameworks (MOFs), as emerging porous crystalline materials, were constructed from metal ions or clusters as nodes and organic ligands as linkers. Due to the superior features like diverse structure, abundant functional groups, tunable pore channels, large specific surface area and so on, MOFs have received increasing attentions in various fields like gas separation & storage, catalysis/photocatalysis, adsorption, sensor, electrochemistry as well as biochemistry.

Heavy metals and organic pollutants like organic dyes, pharmaceutical and personal care products (PPCPs) and industrial chemicals in aquatic environment can damage ecological balance and threaten human health. Detecting and removing these pollutants from water is of great significance for environmental and health concerns. MOFs, as emerging functional environment remediation materials, were adopted to accomplish efficient sensing and removal of different hazardous pollutants. In this Editorial, the development of MOFs for pollutant detection in water and water purification reported in *Chinese Chemical Letters* in the past five years were summarized.

Luminescent MOFs as fluorescent probes to detect pollutants from aqueous solution exhibit promising potential in environmental monitoring due to the fast response, easy operation and real-time detection. The interactions between luminescent MOFs and target pollutants like metals and organic compounds lead to the change of fluorescence intensity by fluorescence quenching or enhancement. The luminescent MOFs, especially the lanthanide-based MOFs, displayed strong fluorescent emission. Wang *et al.* constructed a water-stable Tb-based MOF ($[\text{Tb}(\text{L})(\text{HL})(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}]_n$, $\text{H}_2\text{L} = 5\text{-(4H-1,2,4-triazol-4-yl)benzene-1,3-dicarboxylic acid}$), namely NKU-115, with the design concept of hardness and softness of acids and bases principle, which exhibited selective detection of Fe^{3+} in aqueous solution through emission quenching effect caused by Fe^{3+} adsorption [1]. Li *et al.* prepared a Tb-based MOF ($\text{Tb}_4(\text{paip})_6\cdot 1.2\text{H}_2\text{O}$, $\text{paip} = 5\text{-(1H-pyrazole-4-yl)isophthalate}$), namely NKU-130, with fluorescent emission to achieve selective and sensitive detection of picric acid in aqueous solution [2]. Luminescent MOFs can also be constructed using specific organic ligands rather than luminescent metal ions. Pang *et al.* reported a Tb-based MOF ($\{\text{H}_3\text{O}\cdot [\text{Tb}(\text{H}_2\text{O})_2(\text{ETTC})]\}$, $\text{H}_4\text{ETTC} = 4',4''',4''''',4''''''\text{-(ethene-1,1,2,2-tetra-yl)tetrakis}([1,10\text{-biphenyl-4-carboxylic acid})$) using an active ligand with the characteristic of aggregation-induced emission. The emitted fluorescence of the as-prepared Tb-based MOF was ascribed to the active ligand rather than Tb^{3+} , which exhibited superior fluorescence sensing performances toward Cr(VI) and Fe(III) ions

[3]. Qian *et al.* designed a new Zn-based MOF with embedded pyridine tetrazolium unit as fluorophore for the detection of Fe^{3+} and Cu^{2+} through host-guest ion exchange between the Zn-O chains of the MOF and target metal ions [4]. Wang *et al.* developed a Cd-based MOF ($\{[\text{Cd}_3(\text{L})_2(\text{H}_2\text{O})_6]\cdot 1.5\text{DMF}\}$, $\text{H}_3\text{L} = 4,4',4'\text{-(methylsilyl)tribenzoic acid}$) with fluorescent emission of ligand for Fe^{3+} and acetone sensing via fluorescence quenching mechanism [5]. Wu *et al.* reported a turn-on fluorescence sensor based on a new Zn-based MOF ($\{[\text{Zn}_2(\text{BBIP})_2(\text{NDC})_2]\cdot \text{H}_2\text{O}\}_n$, $\text{BBIP} = 3,5\text{-bis}(\text{benzimidazol-1-yl})\text{pyridine}$, $\text{H}_2\text{NDC} = 1,4\text{-naphthalenedicarboxylic acid}$), namely JXUST-5, which was used to detect Al^{3+} and Ga^{3+} through fluorescence enhancement mechanism resulting from the interaction between target metal ions and framework of the MOF [6]. Wang *et al.* reported a Cd-based MOF ($[\text{Cd}_2(\text{TB})(\text{H}_2\text{O})_4]\cdot 3\text{DMF}\cdot \text{H}_2\text{O}$) constructed by chromophore organic ligands of H_4TB (3,3',5,5'-tetra(4-carboxyphenyl)bimesityl) to recognize Fe^{3+} and nitroaromatic compounds like 4-nitrophenol, 4-nitroaniline and (4-nitrophenyl)-hydrazine [7]. The flexibility, regulatability and modifiability facilitate MOFs as an ideal platform to construct highly selective and sensitive sensor with the help of the specific interaction between detected pollutant and the functional group. Wang *et al.* demonstrated hydroxyl group modified Zr-based MOF, UiO-66-(OH)₂, as a fluorescence sensor to selectively detect Fe^{3+} due to the complexing actions between hydroxyl group and Fe^{3+} [8]. Li *et al.* designed two Co-based MOFs modified by alkynyl group for selective detection of Fe^{3+} and nitroaromatic compounds especially like 2,4-dinitrophenylhydrazine [9]. Recently, Chen *et al.* reviewed the recent advances on fluorescent sensor based on MOFs with dual-emission centers for detection of organic pollutants [10].

Electrochemical sensors based on MOFs also have gained widespread attentions due to the advantages like easy operation, low cost, rapid response, and so on. Li reported an aptamer modified PCN-222(Zr)/GO composite to improve working electrode to detect trace chloramphenicol via responsive signal of electrochemical impedance spectroscopy. A large amount of aptamer was immobilized on the composite thanks to the abundant pore channels and numerous metal sites of PCN-222(Zr), leading to the low detection limit of 7.04 pg/mL [11]. Zhang *et al.* fabricated an electrochemical immunosensor based on Au@MIL-101(Cr) for the detection of microcystins by the changes of current signal using chronoamperometry [12].

Colorimetric method to detect pollutants by naked eye demonstrated a broad perspective application. Zhou *et al.* employed a CuFe-MOF as metalloenzyme for colorimetric detection of H_2S

in industrial wastewater. The CuFe-MOF behaved like peroxidase mimic to induce the color change of the substrate (3,3',5,5'-tetramethylbenzidine) in the presence of H₂O₂. The above-mentioned color reaction was inhibited by H₂S, which can be used to detect H₂S by naked eyes [13].

For water purification, MOFs with large specific surface area and abundant pore channels are demonstrated potential candidates for the adsorption of pollutants. Zhang *et al.* explored the electrochemical preparation of Fe-based porous coordination polymer Fe(BTC) (H₃BTC = 1,3,5-benzenetricarboxylic acid) using scrap iron as raw material. The as-prepared Fe(BTC) was proved to be a good adsorbent for the removal of inorganic and organic arsenic [14]. The tunable framework structure and functional designability of MOFs provide convenience for the rapid and selective adsorption of pollutants. He *et al.* reported a new Zn-based MOF ($\{[Zn_8(BTA)_6(L)_5Cl_2] \cdot (NO_3)_3\} \cdot 5DMF$, H₂LCl = 1,3-bis-(4-carboxyphenyl)imidazolium chloride, HBTA = 1H-benzotriazolate) with cationic framework that selectively adsorbed anionic dyes [15]. Yang *et al.* constructed an anionic In-based MOF (In(PBPTTBA))[(CH₃)₂NH₂], H₄PBPTTBA = 4,4',4'',4'''-(4,4'-(1,4-phenylene)bis(pyridine-6,4,2-triyl))tetrabenzoic acid), which was used for the selective removal of cationic dyes [16]. Hu *et al.* fabricated two new MOFs with Ni and Co as nodes ($\{[M_3(L)_2(bpb)_3(H_2O)_4] \cdot 2DMF \cdot 2H_2O\}_n$, H₃L = 2',6'-dimethyl-[1,1'biphenyl]-3,4',5-tricarboxylic acid, bpb = 1,4-bis(pyrid-4-yl)benzene), respectively, which displayed good and selective adsorption toward methyl orange [17]. The introduction of defects into MOFs endows them to demonstrate improved textural features. Feng *et al.* selected salicylic acid as a defect-generation molecule to prepare hierarchically porous MIL-53 with exposed coordination unsaturated sites (CUS), which was used as a promising adsorbent for the removal of an azo dye Orange G (OG) relying on the hierarchical pores and electrostatic interactions between CUS and OG [18]. Membrane-based materials are beneficial to the realization of long-term continuous removal of pollutants, which displayed great potential in actual wastewater treatment. Membrane modified by MOFs provides more active sites originated from the functional groups and porous characteristics for the boosted removal efficiency. Zhu *et al.* fabricated a membrane based on partially reduced graphene oxide (prGO) and MOF (HKUST-1). Considering that HKUST-1 could be inserted into the inter-layer of prGO to form larger prGO interlayer spacing and more active sites, the rejection of dye with ultrahigh flux and good adsorption performance was achieved. Besides, the oil-water separation was successfully accomplished using the prGO/MOF membrane [19]. Meteku *et al.* reported a magnetic nanostirrer Fe₃O₄@MIL-100(Fe)-Au to capture bacteria like *Salmonella*. In addition, the nanostirrer exhibited a good catalytic reduction activity toward 4-nitrophenol in the presence of NaBH₄ [20].

Some MOFs can also be applied for catalytic reduction of nitrophenol to weaken its toxicity. Huang *et al.* synthesized a new Ag-based MOF ($[Ag_2(H_3ddcba)(dpp)_2]$, H₅ddcba = 3,5-(di(2',5'-dicarboxylphenyl)benzoic acid, dpp = 1,3-di(4-pyridyl)propane) under the guidance of mixed-ligand tactic, which presented catalytic reduction activity toward nitrophenol [21]. Photocatalysis is considered as a sustainable, green and environmental-friendly technology since sufficient solar light can be used as driving force. Therefore, various MOFs-based photocatalysts are developed, which can oxidize or reduce the toxic pollutants into less toxic or non-toxic forms through photocatalysis. Zhou *et al.* prepared a ternary composite Ag/Ag₃PO₄/NH₂-MIL-125 with Z-scheme heterojunction to accomplish photocatalytic Cr(VI) reduction under visible light irradiation. The Ag nanoparticles accelerated the electron transfer to improve the separation efficiency of photogenerated carriers, leading to the excellent photocatalytic Cr(VI) reduction performance [22]. Photocatalyst in the form of powder is

detrimental to practical application owing to the difficulty in separation and recycle, so immobilization of MOFs is needed. Shi *et al.* loaded UiO-66, a classical Zr-based MOF, on wood via one-step method to prepare a supported photocatalyst, which was used to achieve photocatalytic degradation toward antibiotic ofloxacin under sunlight irradiation [23]. Besides, Xia *et al.* summarized the recent development of MOF-based photocatalysts for degradation of organic pollutants from wastewater [24].

Applications of MOFs in pollutants detection and removal in aqueous solution exhibit extensive prospective. However, there are some huge challenges to develop MOF-based sensors with high selectivity and sensitivity. As well, MOF-based adsorbents with large capacity and MOF-based catalysts with high catalytic activity should also be considered in the future. Especially, the investigation of MOFs in advanced oxidation processes (AOPs) like Fenton-like reaction and sulfate radical-based AOPs, as research hotspots, should be strengthened. This Editorial provides peers new advances of MOFs in pollutant detection and removal in water, and we hope that it will bring some inspirations to our worldwide readers.

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Declaration of competing interest

The authors report no declarations of interest.

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