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Application of metal organic framework in wastewater treatment and detection of pollutants: Review

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Metal-organic frameworks (MOF) are strategically designed porous material with a very high surface area. Metal ions surrounded by organic linkers form a three-dimensional MOF structure with special abilities like high adsorbing capacity, excellent catalyzing behavior and photo-activity. Presently, MOFs are widely investigated as an adsorbent to remove heavy metals and xenobiotic compounds from wastewater. Several purposefully designed MOFs based on Zn, Zr, Cr and Fe are able to achieve very high (≥ 90%) dye removal efficiencies by adsorption. Because of photo-sensitive nature, MOFs act as an excellent photocatalyst for the degradation of emerging pollutants. These MOFs can also be used as sensors for the detection of antibiotics and heavy metals present in wastewater. Sulfonamide and ceftriaxone sodium antibiotics, heavy metal like Cr^{6+} can be successfully detected by MOF based sensors with minimum detection limit of 4 ppb. Another important application of MOF is as an ORR catalyst in the cathode chamber of microbial fuel cell (MFC), which was also noticed in the recent time and significant improvement in power recovery and wastewater treatment efficiency of MFC was reported. However, very less number of articles are available in this context and considerable future scope for investigation is present. This articles provides review of literature on application of MOF in wastewater treatment.

Keywords: Adsorption, advanced oxidation process, metal organic frameworks, oxygen reduction reaction, sensors.

Introduction

Increasing concentration of emerging contaminants in water body is a serious threat in present decade. The innovation of advanced materials and thorough investigation of advanced technologies are going on to face the situation. In the year 1965, a new group of material known as metal organic framework (MOF) was first time discovered. The basic molecular structure of MOF is composed of metal nodes with organic linkers connected to form one, two and three dimensional highly porous structures[1] as presented in Fig. 1.

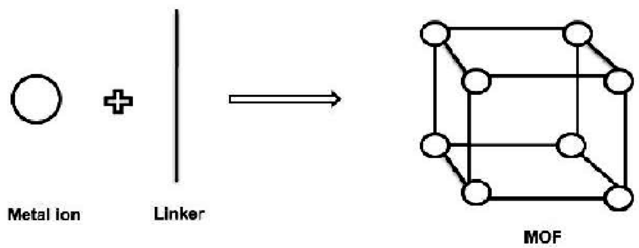

Fig. 1. Schematic representation of a MOF structure.

In a three dimensional MOF structure, metal ions and organic linkers form a polymeric structure, which is popularly known as porous coordinate polymers. Additionally, high surface area, high porosity and presence of different transition metals in polymeric nodes enable MOFs with efficient catalytic behavior. Furthermore, the physical and chemical characteristics of MOFs can be efficiently engineered by varying metal ions, organic linkers and synthesis procedure and excellent area of application can be availed[1].

Although MOFs were discovered in the previous century, during initial days researchers devoted their interest to understand the fundamental properties and structures of these group of molecules. However, after realizing the highly porous structure, excellent catalytic behaviour, a great scope of application of MOFs in wastewater treatment was emerged. High specific surface area and porous nature of MOFs allows these group of materials to be used as an excellent adsorbent to treat toxic dyes and organic contaminants from wastewater[2]. Coloured wastewater having dye contamination was efficiently treated by using Zn, Ni, Co and Cr based MOFs as adsorbent[3]. Catalytic nature and photo-sensitive behaviour empower MOFs to be used as a photocatalyst for degrading emerging contaminants and non-biodegradable aromatic compounds[4]. Additionally, MOFs are observed to have an excellent catalytic activity to reduce activation loss during oxygen reduction reaction (ORR) and can be used as efficient cathode catalysts in a microbial fuel cell (MFC) to treat wastewater with simultaneous electricity recovery[5]. Other than wastewater treatment, MOFs are also found to act as a sensor for detection and quantification of non-biodegradable emerging contaminants (EC) like antibiotics and heavy metals present in wastewater. Previously several review articles summarized the fundamental theory, synthesis process and physicochemical properties of MOFs. However, none of these reviews focused on the specific application of MOFs for detection of ECs and wastewater treatment. The main goal of this review is to understand the use of MOFs for detection and quantification of emerging contaminants and application of MOFs as innovative material as potential adsorbent, efficient photocatalyst for photo-degradation and active cathode catalyst for the bioelectrochemical system.

Applications of MOFs

(A) Adsorption:

Adsorption is the most prominent application of MOFs for removal of emerging contaminants from wastewater. High specific surface area and porosity of MOFs enhances the ability to adsorb persistent pollutants and heavy metals from aqueous media. Almost ten times higher adsorbing capacity of a manganese metal based MOF was observed for organic dye removal (1393 mg/g) as compared to a conventional activated carbon (129 mg/g)[6,7]. Excellent antibiotics, pesticides and dye removal efficiency were also reported (90%) from wastewater by utilizing MOFs as an adsorbent[8,10].

(i) Dye:

Uncontrolled discharge of coloured dyes without adequate treatment and removal from aqueous environment can raise potential threat to the ecology of water-bodies. Persistent nature of these toxic dyes bring them in contact with potable water sources and causes health hazards. Nickel based MOF (SCNU-Z1-Cl) having very high active surface area (1636 m^2/g) was used as an adsorbent by Deng *et al.* (2019) for treatment and removal of a group of dyes from water and excellent dye treatment efficiency was achieved. Almost complete elimination of methyl orange, acridine orange, congo red and methylene blue was observed within an hour. Very high adsorption capacities of 285, 180, 582 and 262 mg/g were noticed during treatment of methyl orange, acridine orange, congo red and methylene blue, respectively. Additionally, SCNU-Z1-Cl was also used for the treatment of toxic oxo-anions and proficient treatment efficiency was noticed[11].

Cobalt-based MOFs are specifically engineered by Wu *et al.* (2019) and two different types of porous polymers $\{[Co_{0.5}(TBC)]\cdot 2DMF\}_n$ and $\{[Co(TBC)Cl_{0.5}(CH_3OH)]\cdot 0.5Cl\}_n$ were synthesized by solvothermal process using a chemical combination of cobalt(II) salts and 3,5-bis(1*H*-1,2,4-triazol-1-yl)benzene carboxylic acid. Among these two MOFs $\{[Co(TBC)\text{-}Cl_{0.5}(CH_3OH)]\cdot 0.5Cl\}_n$ was observed to have higher selective dye methyl orange (MO^-) adsorption properties than that of other because of microspores structure and suitable charge properties[3]. Similar other purposefully designed MOFs based on Zn, Zr and Cr were also synthesized and complete elimination of dyes from the wastewater (Table 1) was reported in laboratory scale[6,12]. However, bulk synthesis procedure of MOFs is required for successful application in field scale and further research is desired on the bulk production of it.

Table 1. Application of MOFs for adsorption of dyes

MOF	Pollutant	Removal efficiency (%)	Adsorption capacities (mg/g)	Ref.
Zn-MOF	Methylene blue	94	180	12
Zr-MOF	Direct red 2B	76	10	36
Cr-MOF	Reactive yellow 15	99	397	37
Mn-MOF	Congo red	98	1393	6
P2W18@Cr-MOF	Rhodamine B	100	146.1	38

(ii) Pesticides:

Pesticides are persistent pollutant majorly detected in agricultural runoff. Toxic behaviour of pesticides even at a low concentration is a major concern for mankind and commonly adopted wastewater treatment plants are incapable of degrading these contaminants present in wastewater. Quite a few research articles are being found on the adsorption of pesticides by MOFs in laboratory scale. Excellent atrazine removal efficiency was observed by using highly stable and porous Zirconium-MOF (UiO-67) and Zeolite Imidazole

Framework-8 (ZIF-8) as adsorbent. Almost 98% of atrazine removal efficiency within two minutes was observed by using UiO-67 as adsorbent. However, ZIF-8 took almost 40 min to remove 98% of atrazine from water solution. Atrazine treatment efficiency of MOFs was compared with commercial activated carbon (F400) and almost 50 min was required to achieve 98% atrazine removal efficiency by F400, which is 25 times higher than the time required by UiO-67 and slightly higher than the time required by ZiF-8[13]. Almost 96% removal of diazinon organophosphorus insecticide having an initial concentration of 40 mg/L was observed within 64 min by adopting highly porous (2600 m^2/g) 0.74 g/L of Chromium terephthalate MOF (MIL-101)[14]. However, around 10% lower removal efficiency of diazinon organophosphorus insecticide was observed by using bentonite as an adsorbent having almost four times higher dosing (3 g/L) with a contact time of 69 min[15].

(iii) Antibiotics:

Antibiotic contamination is a serious concern and consumption of antibiotic rich water can cause disruption of endocrine system of human health. Presence of very low antibiotic concentration in natural water bodies can genetically modify pathogens and cause serious concern for future. Conventional wastewater treatment technologies are incapable to manage this pollution and development of advanced treatment technologies are necessary. Antibiotics can be efficiently removed from wastewater by adsorption and MOF was found as an excellent adsorbent for removal of antibiotics. Commonly prescribed antibiotics, tetracycline (TC) and oxytetracycline hydrochloride (OTC) were effectively eliminated from wastewater by using ZIF-8 (0.5 g/L) and 89.9% and 68.2% removal efficiency was observed with corresponding maximum adsorption capacity of 303.0 and 312.5 mg/g, respectively[16]. This research was further advanced to evaluate the removal efficiency of two mixed antibiotics simultaneously from water. Surprisingly, an increase in TC (90.7%) and OTC (82.5%) removal efficiency was observed because of a π-π synergetic interaction between both pollutants. The adsorption kinetic for removal of TC and OTC was also investigated and pseudo-second order rate kinetics following Langmuir isotherm was observed[16].

During another investigation, adsorption of TC and Cr(VI) was evaluated by Mn-doped zirconium metal-organic framework (UiO-66) and maximum adsorption capacity of 184.493 mg/g and 32.773 mg/g was observed, respectively. Doping of Mn in UiO-66 structure enhanced almost 4.9 and 3.1 times maximum adsorption capacity of UiO-66. Additionally, similar to previous investigation here also Mn-UiO-66 demonstrated higher removal of TC-Cr(VI) mix sample as compared to removal of pollutants separately[17]. In an another research, aluminum based MOF (CAU-1) was synthesized by Yang *et al.* (2018) to eliminate the tinidazole antibiotic from aqueous solution and excellent saturated adsorption capacity of 450 mg/g was achieved[8].

(iv) Heavy metal pollutant:

Contamination of water bodies because of the presence of toxic heavy metals causes serious impact on human health and environment. A water-stable triazine-based MOF (CAU-7-TATB) was effectively synthesized and used for removal of Pb(II) from water and almost 80.6% removal of Pb(II) was achieved, demonstrating adsorption capacity of 63 mg/g within 20 min in presence of interfering ions Cr(III), Co(II), Ni(II), Mn(II), Zn(II), Mg(II) and Ca(II)[18]. However, almost two hours duration was required by activated carbon to remove about 90% of Pb(II) from aqueous solution[19]. Several other articles are also reporting adsorption of heavy metals by MOF in laboratory scale (Table 2). However, lack of large scale synthesis options of MOFs restraints for efficient real-life use of this group of material.

Table 2. Heavy metal adsorption by MOFs

MOF	Pollutant	Removal efficiency (%)	Adsorption capacities (mg/g)	Ref.
Fe-Co MOF	As(V)	80	292.29	39
Al-MOF-GO	As(III)	94.8	65	40
Zr-MOF	Uranium	87	1217	41
Zn-MOF	Uranium(VI)	95	129.36	42
Zr-MOF	As(III)	91.83	205.0	43

(B) Photocatalyst:

Transition metal-based MOFs having high specific surface area are observed to have high photo-active nature and can be used as a promising photocatalyst for degradation of persisting contaminants. Zinc based 3D MOF was strategically designed to utilize as a photocatalyst to decompose methyl violet and around 98% decomposition of methyl violet (MV) was noticed within 40 min[20]. However, almost 78% degradation of MV was observed within 20 min by titanium oxide supported platinum (TiO_2/Pt) photocatalyst[21]. To efficiently degrade the organic dyes from aqueous solution, Pan *et al.* (2019) proposed a new 3D Zinc(II)-MOF. The photocatalytic properties of MOF were investigated by degrading organic dyes MV and rhodamine B (RhB) and 78.3% and 56.8% degradation efficiency was reported within 45 min, respectively[22].

A new 3D Cu(II) based visible light photocatalytic MOF was effectively synthesized by solvothermal method and successful degradation of crystal violet (CV), rhodamine 6G (R6G), congo red (CR) and basic red 2 (BR2) was achieved in presence of H_2O_2[23]. This newly synthesized MOF exhibited high chemical robustness in acidic and basic solution. Almost complete degradation of CV and R6G was found, whereas 87.8% and 70.2% of CR and BR2 degradation was achieved by using this MOF. Other MOFs having Ti-Zr, Ni, In, Ln and Ag-based metal centre were also investigated in-depth for efficiently degrading persistent pollutants and very high degradation efficiency was observed in most of these scenarios (Table 3).

Table 3. Photocatalytic application of MOFs

MOF	Pollutant	Degradation efficiency (%)	Ref.
Ag-MOF	Methylene blue	99	44
In-MOF	Benzylamine and thioanisole	99	45
Ni-MOF	4-Nitrophenol	74	46
Ti-Zr-MOF	Acetaminophen	90	47
AC/Fe-MOF	Reactive Red 198	99	48
Ln-MOFs	Rhodamine B	96	49

(C) MOF as cathode catalyst in microbial fuel cell:

The MFC is a wastewater treatment technology having potential to generate simultaneous electricity[24]. Carbon sequestration[25] and ability to remove emerging contaminants[26] from wastewater by hybridization of this technology with other advanced technology are some added advantages. Activation loss during ORR in cathodic chamber of MFC causes significant voltage reduction and simultaneously decrease wastewater treatment efficiency[27]. Conventional ORR catalysts are very costly and not suitable for large scale applications[28]. High specific surface area, excellent catalytic activity of MOFs allow its application as cathode catalyst in MFC. Porous ZIF-8 type of MOF was successfully synthesized by Xue *et al.* (2019) and used as a cathode catalyst in an air cathode MFC. The porous structure of ZIF-8 having high active surface area of 1416 m^2/g reduced activation loss and increased the power recovery from MFC. Power density of the MFC having ZIF-8 coated on cathode surface was observed to have optimal power density of 2103.4 mW/m^2, which was 1.62 times the power produced by a MFC having Pt/C coated cathode[29]. Pyrolysed Cu based MOF was synthesized by Zhang *et al.* (2018) and used as an cathode catalyst in MFC and performance was compared with a MFC having Pt/C coated on cathode surface and a comparable power recovery was observed (326±11.2 mW/m^2)[5]. Highly porous Co-MOF derived dual metal and nitrogen doped carbon (M/CoNC) was investigated as a cathode catalyst to enhance the power production of MFC. Almost two times increase in power density was achieved by using M/CoNC catalyst (4335.6 mW/m^2) as compared to Pt/C cathode catalyst (2520.8 mW/m^2)[30]. Again, Cu-MOF was also observed as an excellent cathode catalyst and a maximum power density of 2229±10 mW/m^2 was reported[31].

(D) Sensor:

Detection of the concentration of emerging contaminants is important to estimate emerging contaminants removal efficiency in a MFC or any other treatment system. Sensor based application is a popular area of application for MOFs and efficient detection of antibiotics and heavy metals is possible by using MOFs. Zicn(II)-based fluorescent MOF $\{[Zn_3(\mu_3\text{-}OH)(HL)\text{-}L(H_2O)_3]\cdot H_2O\}_n$ (FCS-1,H_3L = 5-(4-carboxy-phenoxymethyl) isophthalic acid) was observed to have high sensitivity for detection of antibiotics from wastewater within a wide pH range of 3 to 9[32]. Another fluorescent Cd based MOF was synthesized for detecting ceftriaxone sodium antibiotic from water and very low limit of detection (LOD; 50 ppb) was reported within 20 s in the pH range of 4 to 1133. Microporous Zr^{4+}-terephthalate MOF was synthesized by Sofia *et al.* (2017) for detecting hexavalent chromium concentration in water. Very low LOD of 4 ppb and limits of quantification (LOQ) of 13 ppb were observed within an very short time period of one min[34]. Aluminium (III)-based luminescent MOF, named CAU-10-CHO was capable to detect dichromate ($Cr_2O_7^{2-}$) ion in water in a pH range of 2-12[35]. Many other articles are also addressing the application of Zr, Tb, Co, Eu, Ce and Fe based MOFs for successful and efficient detection of the toxic compounds in aqueous medium (Table 4).

Table 4. MOFs as sensors

MOF	Pollutant	LOD	Ref.
Ce-MOF	Ochratoxin A	0.067 ng/L	50
Tb(III)-MOF	2-Thiazolidinethione-4-carboxylic acid	1 mg/L	51
Co(II)-MOF	MnO_4^-	200 μmol/L	52
Zr-MOF	4-Nitrobenzaldehyde	4.7 μmol/L	53
Eu-MOF	Uranyl	309.2 μg/L	54
Fe-MOF	Chlorogenic acid	10 μmol/L	55

Conclusions

Adsorption of emerging contaminants from wastewater is the most popularly used application of MOFs. However, absence of bulk synthesis procedure of most of the MOFs is the major constraint for real life use of MOFs. Photocatalytic activity of MOFs has great scope of application and excellent removal efficiency of organic dyes was observed by using very small amount of MOFs. Application of MOFs for photodegradation of emerging contaminates is feasible to scale-up, however very limited research was found in this context. Application of MOFs as a cathode catalyst of MFC can exhibit excellent power recovery and wastewater treatment efficiency, however till now MOF was not tested in any liter scale MFCs. Sensor based application for detection of emerging pollutants like antibiotics by florescent MOFs is another wide application area of MOFs and very low antibiotic concentration can be efficiently detected.

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