

# EMERGING APPLICATIONS OF METAL-ORGANIC FRAMEWORKS IN THE DECONTAMINATION OF WASTEWATER

## Abstract

Due to rapid industrialization and urbanization seriously caused environmental, water pollution by producing tons of hazardous pollutants. Water is essential source for the existence of life. Metal-organic frameworks (MOFs) are porous materials with unique properties formed by metal ions connected with organic ligands through coordination bond thereby creating a three-dimensional network structure. The indispensable extraordinary properties of Metal-organic frameworks (MOFs) like adjustable porosity, large surface area, crystallinity, stability, tailorable topology makes them best alternatives for waste water treatment technologies. This review discusses the recent developments of Metal-organic frameworks in decontamination of water focusing specially on adsorption and photocatalytic approach.

**Keywords:** Metal-Organic Frameworks (MOFs) as Adsorbents Photocatalysts.

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## I. INTRODUCTION

Water is a basic source of life and all the activities of life. Of course water is considered as most abundant, cheapest and indispensable essential solvent for the existence of life. But availability of fresh water resources are limited and decreasing day by day [1-2]. As all we know industrialization, globalization and urbanization boosted the global economy while seriously caused pollution to the environment, earth and water resources. Due to rapid development in the industrial sector for meeting the demands of expanding population lead to production of tons of hazardous waste materials and toxic gases as byproducts [3-6]. Due to discharge of harmful pollutants into water, when exposure to these pollutants causes a serious threat to the human health and aquatic life [7-12]. Consequently, it is paramount important to protect, conserve water resources and find a solution for waste water treatment. In comparison to inorganic contaminants, there are vast majority of organic contaminants such as dyes, oils, pharmaceutical products and personal care products etc. Each year averagely, a world is producing around 4 billion tons of industrial and municipal waste [13-15].

Due to these untreated pollutants discharged in the water caused a water pollution and consequently, fresh water scarcity. Due to exploding population of the world enhanced the consumption of fresh water which in turn resulted in a scarcity of pure water. Hence water purification techniques have gained paramount importance and attention. There are various existing conventional techniques such as solvent extraction, ion-exchange, membrane filtration, chemical precipitation, electrochemical technologies, coagulation etc. These methods have some disadvantages such as, low efficiency, inefficient to remove completely, high energy requirement, high operational costs, expensive disposal methods etc., [16-23]. Then adsorbents and photocatalysts evolved as cost-effective innovative technologies. The existing adsorbents like zeolites, aluminophosphate etc., are found ineffective for complete adsorption of effluents. On the other hand, photocatalysts like  $\text{TiO}_2$  showed poor quantum efficiencies in the visible light spectrum. Hence, there is a rising demand for search of low-cost, efficient, effective materials for waste water treatment. Metal-organic frameworks (MOFs) are found to be indispensable alternative materials in substitution to existing materials for water treatment [24-30].

Metal-organic frameworks (MOFs) are porous materials with unique properties formed by metal ions connected with organic ligands through coordination bond thereby creating a three-dimensional network structure. The indispensable extraordinary properties of Metal-organic frameworks (MOFs) like adjustable porosity, large surface area, crystallinity, stability, tailorable topology makes them best alternatives for waste water treatment technologies. Metal-organic frameworks (MOFs) have been studied extensively and found applications in various fields such as biomedicine, catalysis, sensors, chiral separation, gas storage, opto-electronics etc [31-35]. However, application of metal-organic frameworks (MOFs) in water treatment found less in the literature. Hence, Metal-organic frameworks (MOFs) have received world wise attention. In this, review we discussed the major advancements and perspectives that driven in the utilization of Metal-organic frameworks in decontamination of water focusing on adsorption and photocatalytic approach.

The essential condition for MOFs to be followed in order to use in waste water treatment is the stability of MOFs in water. Removal of hazardous contaminants from the waste water via adsorption process and photocatalytic degradation are considered as most

prominent methods in terms of economic perspectives, simplicity, reusability and energy consideration [36-40]. The currently existing methods are less effective to remove emerging contaminants of water. Due to unique characteristics, MOFs have been emerged as challenging / prominent materials to address the current situation of decontamination of water.

## II. METAL-ORGANIC FRAMEWORKS (MOFS) AS ADSORBENTS

Hermes et al., first synthesized macroscopic MOF followed by Liu et al., prepared MOF-5 membrane [41]. Then rapid developments of MOFs like ZIF-8 membrane which showed excellent mechanical stability and UiO-66 fibers which showed potential for desalination capacity due to outstanding physico-chemical properties such as thermodynamic robustness and structural robustness and stability in various solvent [42-43]. Then the researchers focused on development of MOFs which can be tunable to change the porosity, shape and size. In 2018, Valizadeh et al., reported MOF-based beads of different sizes. In 2022, Wang et al. [44] prepared MIL-88a (Fe) cotton fibers fixed bed reactor. Nicholas Prasetya et al [45] studied three free-base porphyrine Zr-metal organic frameworks namely MIF-525, MIF-545 & NU-902 for adsorption of diclofenac. Interestingly it is observed that their adsorption affinity towards diclofenac different from one another due to hydrogen bonding occurred between MOF and diclofenac. MOF-525 found to be efficient adsorbent of diclofenac, followed by MIF-545 & NU-902.

One of the extensively studied MOFs by the process adsorption is MIL-53 (Al) prepared by solvothermal method due to its potential chemical and mechanical stability. In hydrothermal process, temperature of the reaction plays an important role and has significant effect on the properties of materials. Recently removal of dyes using MOFs has gained a significant interest. It is observed that by the use of specific MOFs it is possible to adsorb single or set of dyes. But still, there exists a challenge that removes cationic and anionic dyes simultaneously from the mixture. Li et al 2017 demonstrated the extraordinary adsorption capability of MOF-545 to adsorption capability of MOF-545 to the simultaneous adsorption of cationic and anionic dyes from the mixture.

To investigate the adsorptive separation of CO<sub>2</sub> / CH<sub>4</sub> mixture Ferreira et al., used MIL-53 (Al) tablets in a fixed bed reactor [46]. Also, to hydrolyze carboxymethyl cellulose to 5-hydroxy methyl-furaldehyde MIL-53 (Al) used as a catalyst by Zi et al [47] and also MIL-53 (Al) was used as an adsorbent to remove various pollutants like nitrobenzene, methylene blue, methylene orange and mixture etc.. Moreover, it is reported that the adsorptive capacity of MIL-53 (Al) increased several folds by the incorporation of [BMIM] PF<sub>6</sub> [48]. Finally it is concluded that many factors such as structural morphology, pore size and functional groups present on the Metal organic-frameworks etc., affects the adsorption property of MOFs [49].

## III. METAL-ORGANIC FRAMEWORKS (MOFS) AS PHOTOCATALYSTS

In spite of several adsorbents have increasingly reported in the waste water treatment but the major drawback is the formation of secondary waste. To overcome the drawbacks, photocatalytic degradation emerged as efficient method to treat various wide varieties of pollutants. As a result, various research groups have designed and synthesized varieties of

photo catalysts to application in decontamination of water. In the reported literature TiO<sub>2</sub> considered as a potential photocatalyst due to its stability, availability, oxidation capacity, non-toxicity etc [50]. But it is observed that the photocatalytic yield of TiO<sub>2</sub> is low. To overcome this limitation, the alternate method is coupling of photoactive semiconductors with MOFs to enhance photocatalytic activity.

Chang et al., [51] synthesized TiO<sub>2</sub>@MIL-53 core shell composite by combining two materials TiO<sub>2</sub> and MIL-53 which enhanced the photocatalytic yields of TiO<sub>2</sub> due to synergistic effect. Ning Fu et al [52] synthesized double shell hollow TiO<sub>2</sub>@ZIF-8 nanocomposites which showed a photocatalytic efficiency of 99.1 % towards methylene blue in comparison with TiO<sub>2</sub>. Yu Zhu et al [53] synthesized novel hollow BiOI/TiO<sub>2</sub>/ZIF-8 heterojunction which showed enhanced photocatalytic activity in the removal of Norflaxacin. Zahra Pouramini et al reviewed the adsorption and photocatalytic applications of ZIF-8 & ZIF-67 which reported as potential candidates in waste water treatment.

#### IV. CONCLUSION

Metal organic frameworks are porous materials possessing distinct properties such as adjustable porosity, large surface area, crystallinity, stability, tailorable topology which made them best alternatives for waste water treatment technologies. This review mainly focused the recent developments in MOFs in application of waste water treatment by adsorption and photocatalytic approach. Application of MOFs in the decontamination of water need to be explored and improved. Water soluble, water stable, different functionalized MOFs need to be developed.

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