Mechanism and Application of Metal-Organic Framework in Wastewater Treatment

Ruiyi Gao

Beijing Huijia Private School, Beijing, 102200, China

23gaoruiyi@huijia.edu.cn

Abstract. In recent years, wastewater has been concerned to be a serious problem since it is harmful to the natural environment and toxic for animals and humans. Two major sources that create the pollutant is heavy metal ion and dyes in industry. Metal-organic frameworks with easily modified characteristics and high surface area, as a new material that performs well in wastewater treatment, have become excellent adsorbents for removing heavy metal ions and dyes through adsorption and catalysis processes. This review described the mechanism of waste material removals, such as π-π interactions, electrostatic interaction, and hydrogen bonds interaction. In addition, to further understand the mechanism, the factors such as pH, temperature change, and initial concentration of dyes are also mentioned in this review. Specific MOF for the removal of different hazardous materials is discussed. Finally, future research on MOF material is suggested, and prospecting further development of MOFs in wastewater treatment.

Keywords: MOFs, wastewater treatment, dye, heavy metal ion.

1. Introduction

The environmental problems related to chemical and biological contamination and pollution in water have become an important issue over the years. The major pollution resources come from the production of industrial waste. It would release the wastewater containing toxic materials, such as dyes and heavy metals [1]. Much effort should be paid to control and protect the water quality to create a healthy life for humans and animals.

Many techniques have been invented to remove the compound in wastewater, like heavy metal ions and dyes. The toxic molecule can be removed by enzyme, ion exchange, nanofiltration, advanced oxidation process, etc. It is noted that nano-based materials and other ways still have severe downsides, like complicated synthesis processes that lead to an expensive cost of production, limited pH ranges for applications, and being barely able to recycle and reuse [2]. The usage of enzymes could be restricted to the environmental condition since enzymes are susceptible to the temperature and pH, which would be easily denatured in impropriate conditions. However, adsorption is considered a very effective wastewater treatment for removing toxic inorganic and organic compounds and molecules because the operation is easy and highly efficient [3]. Researchers pay attention to porous materials to develop a better adsorbent with a more efficient adsorbent.

In particular, metal-organic frameworks (MOF) show an excellent ability to purify wastewater because of their high porosity, large surface area, diversity in structure, and extraordinary affinities of adsorption properties [4]. MOFs are unique porous materials that seem like crystals. It is composited by metal ions or clusters and organic ligands through coordination bonds [5]. These properties allow MOFs to be an excellent material to remove the toxic molecules discharged in wastewater and have the potential to cross the barrier of other porous materials and nanomaterials. On the one hand, MOFs have the largest BET area compared to other porous materials because of the high surface area and porosity properties [6]. On the other hand, MOFs can also undergo two processes when removing waste material, adsorption, and catalysis.

Based on previous studies, it has been suggested that the mechanisms of adsorption of organic pollutants above MOF consist primarily of electrostatic, π-π, hydrogen bond, and metallic bridge interactions [7]. All the different mechanisms suggest that the MOFs adsorption variability, which indicates that it can be applied to various aspects. In addition, to using the flexible structures, the

development of MOF composites is also exciting because they enhance water stability and higher adsorption capacity. During MOFs catalysis, it shows an excellent heterogeneous catalytic platform with reasonably well-defined good catalytic sites, which significantly benefits related activities; one particular way is photocatalysis.

Despite the several advantages of MOFs, there are still some limitations, such as poor water stability. MOFs are composed of linker and metal sites. The inclusion of heavy metal ions would present the structure, so water quality after removing hazardous pollutants in water may be questioned since the accumulation of metal or even minerals would be vital to a human being. Nonetheless, the heavy metal ion in MOFs can be replaced by others, and it is unlikely that MOFs release the metal to the environment because the linker connects it [8]. The limitation of MOFs also indicates that more research should be done to reach a more efficient adsorption capacity and more sustainable and cheaper materials.

This review mainly focuses on the mechanism and application of MOF in wastewater treatment, especially on removing heavy metal ions and dyes. Furthermore, the factors and types of MOFs in each aspect were introduced.

2. Mechanism of MOF used in wastewater

There are two ways for MOFs to remove the hazardous material in wastewater, adsorption and catalysis [9]. Adsorption of MOFs interacts with other materials in the environment, and catalysis relates to the electron.

2.1. Adsorption

One of the ways that MOFs can remove waste in the water is the process of adsorption. By interacting MOFs material with the polluted water, different MOFs would have different strategies to interact with the pollutant and adsorb them.

There are two ways to separate and adsorb the waste in water, either using the physical property or chemical property. MOFs can adsorption with their surface physical properties, such as the dipole-dipole force and their polarity. For the chemisorption of MOFs, the molecule binds with a metallic site that is not saturated yet. The adsorbate can also interact and react with the functional groups in MOFs [10].

2.1.1 Electrostatic interaction

Electrostatic interaction is a way of removing contaminants by adsorption. When MOF's charge is changed, they would be easily gone through interacting with the adsorbates that have the opposite change with MOFs. The net charge on the MOF can be modified by adding other functional groups or species; it would lead to either protonation or deprotonation [11]. Thus, the MOFs with charge can interact with adsorbates with opposite charges [12], which influences the MOF's ability of metal ion adsorption. On the other hand, the electrostatic attraction would attract cationic MOFs and anionic dye by the electrostatic forces and form chemical bonds. It will also form chemical bonds through the process of redox reaction since oxidation is losing electrons and reduction is accepting an electron. A MOF in the aqueous solution or media can modulate the net surface charge, which depends on the level of pH, for an electric charge [13]. Thus, the formation of the net charge of MOFs can efficiently adsorb the cationic or anionic adsorbates.

2.1.2 π–π interactions

π-π interactions are the interaction between two aromatic rings, which form chemical bonds. Its interaction is weaker than electrostatic attraction. Nevertheless, creating π-π stacking interaction between adsorbates and MOFs can increase the adsorption capacity of MOFs. For example, according to Abdi et al. research on ZIF-8, the aromatic ring can interact with the crew in malachite green, which through the π-π interaction and leads to a better asportation capacity [14]. Chen et al. on investigate the Congo Red adsorption mechanism through the Co-MOFs. It can open an active metal

site and create the π-π interactions between dye and Co-MOF [15]. The benzene ring present in MOF and Congo Red can create π-π interactions, as we can see from Fig.1.

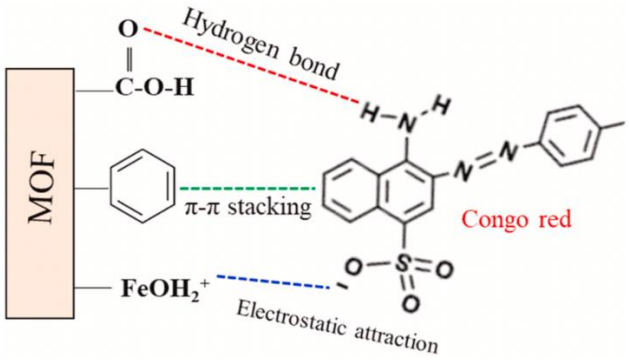


Figure 1. Mechanisms of Congo red degradation were removed by Mn-UiO-66@GO-NH_2 [16]

2.1.3 Hydrogen bonding

In MOFs adsorption, hydrogen bonds formed limited. One way to create the interaction of hydrogen bond between MOFs and dye is to the presence of the functional group. According to Wang et al., the intermolecular force created by hydrogen bonds forms between the carboxyl group in MOFs and amine groups in Congo red, as shown in Fig.1 [16]. The carboxyl group will interact with the amine group in Congo red to form a hydrogen bond. The adsorption capacity of Congo red is 1265.82mg/g by using Mn-UiO-66@GO-NH_2 [16].

2.2. Catalysis

A way to manage wastewater is the process of catalysis, such as photocatalysis. Since MOFs has a unique property, the organic linker can link various metal like transition metal, which would change the property of the material. During photocatalysis, the light should always be absorbed in order t make the electronic excitation occur with the available light source [17]. Charge separation, the second elementary stage in most catalysis processes, is also critical in photocatalysis. Light would be active in the MOFs and lead to charge separation. Then, the charge would recombine and remove dyes effectively.

3. The application of MOFs used in wastewater

Many different pollutants will be present in wastewater, such as heavy metal ions, pharmaceutical molecules, and dyes. All these pollutants would affect the water quality, so various MOFs are designed for removal.

3.1. Removal of heavy metal ion

Industrial development is accelerating, and the pollution of heavy metal ions has become a serious global problem. It influences both environment and human health. The overdose of heavy metal ions such as cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg), poses a human health risk since they would store up by the bioaccumulation process through the food chain. Therefore, we should take action to minimize the level of heavy metal ions to an acceptable level. One of the ways that can reduce the heavy metal ion is using MOFs as adsorbents. Usually, the heavy metal ion would remove by MOFs through the adsorption process [18]. The adsorb rate depends on the net surface charge of MOFs, but the charge on the surface depends on the pH level of the solution. The optimized pH values would influence the adsorption to the waste material, such as heavy metal removal. However, the optimized pH values would change with the metal ions species' adsorbent structures and the structure of the adsorbent. The hydrogen ion would play an essential role during the adsorption process, which would affect the coordination between the metal ion in MOFs and the absorbents, depending on the metal ions species [19].

Different types of heavy metals may change the solution environment because of the heavy metal's form in the system. For example, the Cr^{6+} metal ion would exist in the form of H_2CrO_4 or $Cr_2O_7^{2-}$in acid solution, so the change of pH value would lead to the decrease of the adsorption. One type of MOF that can remove Cr ion is MOR-1-HA, which has an optimal pH between 2-8 [20]. Fig. 2 shows that 97-99.6% Cr (VI) has been removed in 2 to 8, with an initial 10.2 ppm total chromium concentration. When the pH value is 1, the removal capacity is only 82%. It indicates that pH plays a vital role in heavy metal ion removal.

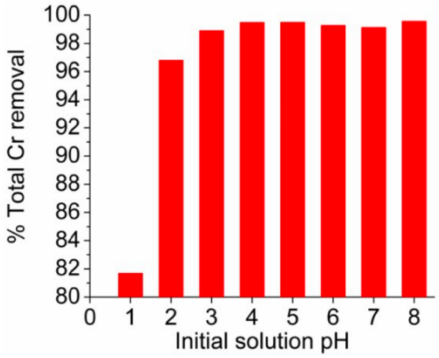


Figure 2. % Cr removal by MOR-1-HA with different initial pH value solution [19]

Additionally, Cr can also remove by the process of catalysis. The zirconium MOFs family is due to the thermal stability of easy combination of functional groups and hydrolysis or through the use of crosslinking methods. MOF composite adsorbent can further enhance the adsorption capability of MOF [21]. For example, The g-C_3N_4/NH_2-UiO-66 (Zr) ability in photocatalysis. The g-C_3N_4/NH_2-UiO-66 (Zr) is synthesized properly by constricting MOF by the routes for solvothermal and MOF deposition. As a photocatalyst, it shows elimination of hexavalent chromium with high efficiency and promotes the reduction of hexavalent chromium and the oxidation of tetracycline hydrochloride. The heterojunction structure improves carrier separation and transfer, as well as the synergistic impact, hence improving the photocatalytic effect. The removal efficiency of Cr^{6+} over CU-20 wt. was 1.86 and 3.25 times greater, respectively, than virgin NH_2-UiO-66 (Zr) and g-C_3N_4. Furthermore, CU-20 wt. % could eliminate contaminants with the hybrid system synergistically, and Cr^{6+} reduction acquired 100 percent within 90 minutes of the visible range of irradiation. According to the research, g-C_3N_4/NH_2-UiO-66 (Zr) would perform efficiently with wastewater purification [22].

3.1.1 Cadmium

Cadmium (Cd) is removed through a chemical adsorption process that is considerably aided by the MOF's readily accessible carboxylate groups. Cu-terephthalate MOF can be used as an absorbent to adsorb Cd. Enhancing the pH level of the solution was discovered to help with ion removal because the more anionic MOF surface produced better electrostatic interactions with the metal ions. This MOF's peak of Cd (II) removal capability was estimated to be 100mg/g [23]. We can see that Cu-terephthalate MOF will interreact with the heavy metal ion through ion exchange, which occurs in the pores of the sorbent and on the sorbent's surface, as shown in Fig.3 [23].

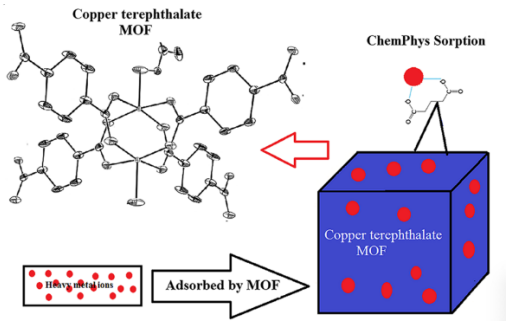


Figure 3. The adsorption process of heavy ions using the copper terephthalate MOF [23]

3.1.2 Lead

Zhang et al. demonstrate the HS-mSi@MOF-5 ability of Pb (II) removal. HS-mSi@MOF-5 is an efficient adsorbent because it has a high adsorption capacity for Pb (II), which is 312mg/g, and also the equilibrium can be reached in around 30 minutes. By raising the pH level in the solution, the process of adsorption will be faster. When the pH of the solution approaches 3, the surface of the HS-mSi@MOF-5 becomes negatively charged, and the negative charge's density grows substantially as the pH level in the solution rises. This is matched with the increased adsorption capability of HS-mSi@MOF-5 for lead ions as pH increases. Consequently, it is suggested that electrostatic attraction is the primary cause of HS-mSi@MOF-5 adsorption to lead ions [24].

3.1.3 Mercury

Chakraborty et al. created AMOF-1, a novel MOF based on zinc metal ions and tetracarboxylic linkers and evaluated it for mercury ion removal from an aqueous solution. AMOF-1 adsorption on mercury (II) ions could up to 94 percent (beginning with a concentration of 1 ppm) around 18 hours, prolonging the length and raising the adsorption rate to 99 % according to a series of time-dependent tests. The maximal absorption capacity of the substance was expected to be 78mg/g, but no pH data were provided. Ion exchange with DMA ligands arranged within rectangular MOF channels was used in the proposed adsorption procedure [25].

3.2. Removal of Dyes

With the various design of dyes that can be used in the industry, pigments are spread to different categories, such as the cloth industry, chemical indicators, and agriculture. However, the significant number of dyes used in various aspects produced considerable waste. To remove the wasted dye, MOFs can either catalyze the dye or adsorb it.

3.2.1 Factors of MOFs used in the removal of dyes

3.2.1.1 Solution temperature. The adsorbing effectiveness of the MOFs adsorbent depends mainly on the temperature of the adsorbed solution. Especially during dye removal, MOFs will go through either exothermic or endothermic reactions [26]. During the endothermic process, the temperature and the rate of adsorption will increase. Due to the increase in temperature, it would belong to the increased mobility of the dye molecule and functional adsorption sites. In the exothermic process, however, increasing the temperature reduces uptake because the equilibrium favors the endothermic reaction. The adsorbate's binding force to the active site which is on the adsorbent surface would be reduced [27].

The Gibbs equation can measure the thermodynamics of adsorption

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (1)$$

In this equation, ΔG indicates the adsorption reaction nature. With the increase of entropy (ΔS) of dye adsorption, the change of enthalpy ΔH shows the reaction nature, such as the endothermic or exothermic reaction [27]. Thus, the different temperatures can influence the efficiency of MOFs' adsorption. To reach a high efficiency of dye adsorption, an appropriate temperature is needed. The temperature is around 0-24^{o}C to maintain that ΔG is negative, which means the reaction processes spontaneously. [28]

3.2.1.2 Initial *dye concentration.* The initial concentration of dye is a vital factor in wastewater treatment. The maximum absorptance capacity depends on the adsorption area of the MOFs surface that can be accessed and the dye concentration [28]. Mohammadi et al. investigate the MOF UiO-66 to find the effect of beginning concentration on the adsorption of methylene blue (MB). They reported that increasing the concentration of MB would decrease the rate of uptake, but when the concentration of MB becomes lower, the uptake of MB rapidly increases. Fig. 4 shows that when MB concentration is 10mg L^{-1} to UiO-66 300 min. When the initial concentration of MB becomes higher, such as 20-50mg L^{-1} after 500 min, none of the concentrations has been adsorbed completely. This is because the UiO-66 surface turns to saturate [30].

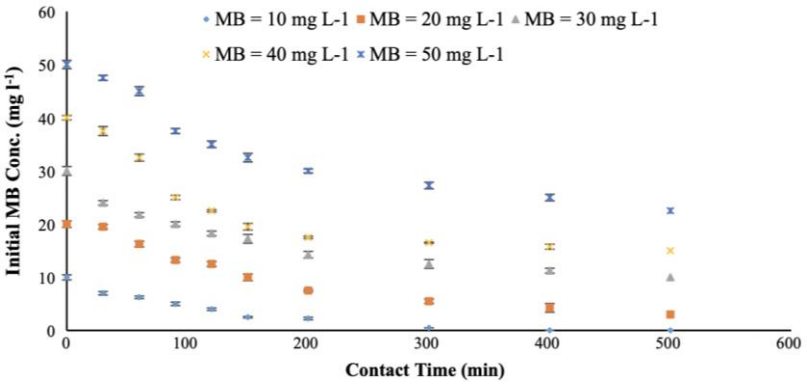


Figure 4. The relationship between initial methylene blue concentration and contact time that conducts in 25°C [30]

3.2.2 Methane orange/Methane blue Removal

Zubair et al. investigate the adsorption of methane orange (MO) and Methane blue (MB) by using UiO-66. When the temperature is increased, the adsorption capacity of MO/MB decreases, which can be related to the unique character of the dye-adsorbent interaction. MO adsorption on UiO-66 is an exothermic process, whereas MB adsorption on UiO-66 is an endothermic process, as previously indicated. As a result, increasing the temperature favors the MB adsorption with the use of UiO-66 while decreasing the adsorption capacity of MO, resulting in a decrease in MO's adsorption selectivity over MB. The graph (Fig.5) Freundlich model parameters acquired through curve fitting. According to Fig.5, At the temperatures that are investigated in this research, from 25°C to 45°C, the values for both dyes are greater than one, indicating that both MB and MO adsorption on UiO-66 can be favored. The n values that refer to the Freundlich model of MO, on the other hand, are higher than those of MB, showing that UiO-66 prefers anionic MO dyes over cationic MB dyes. It was discovered that UiO-66 absorbed MO more readily as an anionic dye than MB did as a cationic dye [31].

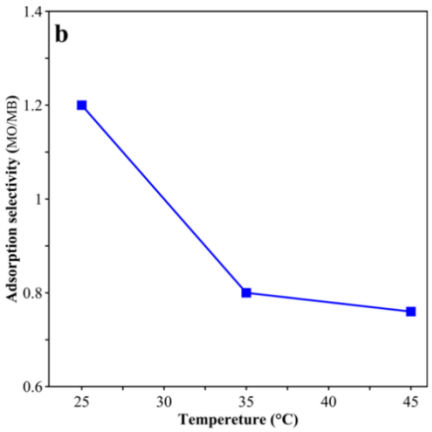


Figure 5. The selectivity index of adsorption of MO/MB in 25°C to 45°C, [31]

4. Conclusion

In conclusion, MOFs are very prospective materials for wastewater treatment. The recent progress in the field of MOFs for wastewater treatment is introduced in this article. MOFs play an essential role in heavy metal ions such as cadmium, chromium, lead, mercury, and removal and dyes, such as methyl blue and methyl orange through adsorption and catalysis. By modifying the environmental condition, such as temperature, pH, and initial concentration, MOFs can remove all the waste materials in the quantic environment. The temperature would influence adsorption efficiency depending on whether the reaction is endothermic or exothermic. pH level would influence the charge on the surface of MOFs because it would provide hydrogen ions or carboxyl groups. The initial dye concentration will affect the efficiency of dye removal since researchers aim for the lowest dye

concentration at the end of the adsorption. However, it is harsh for the researcher to modify the natural environment to reach an ideal situation. It is also essential to find carious MOFs that fit different conditions, such as having different pH tolerance. The various aspects that can be further developed suggest MOFs' colossal potential. It is expected to see the further investigation of MOFs, which the rapid development of new inventions in wastewater treatment material.

References

[1] Crini, G., Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. Environ Chem Lett 17 (2019) 145–155.

[2] Kumar, P., Bansal, V., Kim, K.-H., & Kwon, E. E' Metal-organic frameworks (MOFs) as futuristic options for wastewater treatment. Journal of Industrial and Engineering Chemistry, 62, (2018) 130–145.

[3] Akpinar, I., Yazaydin, A.O. Rapid and efficient removal of carbamazepine from water by UiO-67. Ind. Eng. Chem. Res. 56 (2017) 15122–15130.

[4] Kreno, L. E., Leong, K., Farha, O. K., Allendorf, M., Van Duyne, R. P., & Hupp, J. T. Metal-Organic framework materials as chemical sensors. Chemical Reviews, 112 (2) (2011) 1105–1125.

[5] Li, H.-Y., Zhao, S.-N., Zang, S.-Q.; Li, J, Functional metal-organic frameworks as effective sensors of gases and volatile compounds. Chemical Society Reviews, 49 (17), (2020) 6364–6401.

[6] Kobielska, P. A., Howarth, A. J., Farha, O. K., & Nayak, S. Metal-organic frameworks for heavy metal removal from water. Coordination Chemistry Reviews, 358 (2018) 92–107.

[7] Hasan, Z., Khan, N.A., Jhung, S.H. Adsorptive removal of diclofenac sodium from

[8] water with Zr-based metal-organic frameworks. Chem. Eng. J. 284 (2016) 1406–1413.

[9] khan, N.A., Hasan, Z., Jhung, S.H., Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs): a review. J. Hazard Mater. 244–245 (2013) 444–456.

[10] Russo V, Hmoudah M, Broccoli F, Iesce M, Jung O and Di_serio M, Applications of MOFs in Wastewater Treatment: A Review on Adsorption and Photodegradation. Front. Chem. Eng. 2:15 (2020)

[11] Petit, C., Present and future of MOF research in the field of adsorption and molecular separation. Current Opinion in Chemical Engineering, 20 (2018) 132-142.

[12] E. Haque, J.E. Lee, I.T. Jang, Y.K. Hwang, J.-S. Chang, J. Jegal, S.H. Jhung, Adsorptive removal of methyl orange from aqueous solution with metal-organic frameworks, porous chromium-benzenedicarboxylates, J. Hazard. Mater. 181 (2010) 535-542.

[13] Hasan, Z., & Jhung, S. H. Removal of hazardous organics from water using metal-organic frameworks (MOFs): Plausible mechanisms for selective adsorptions. Journal of Hazardous Materials, 283, (2015) 329-339.

[14] Au, V.K.M. Recent advances in the use of metal-organic frameworks for dye adsorption. Front. Chem. (2020)

[15] Abdi, J., Vossoughi, M., Mahmoodi, N.M., Alemzadeh, I., Synthesis of metal-organic framework hybrid nanocomposites based on GO and CNT with high adsorption capacity for dye removal. Chem. Eng. J. 326, (2017) 1145-1158.

[16] Chen, D., Feng, P., Fei, Wei, Hua, F. Preparation of Fe (III)-MOFs by microwave-assisted ball for efficiently removing organic dyes in aqueous solutions under natural light. Chem. Eng. Process. - Process Intensif. 135, (2019) 63–67.

[17] Eltaweil, A.S., Elshishini, H.M., Ghatass, Z.F., Elsubruiti, G.M., Ultra-high adsorption capacity and selective removal of Congo red over aminated graphene oxide modified Mn-doped UiO-66 MOF. Powder Technol. 379 (2021) 407-416.

[18] Pournara, A. D., Margariti, A., Tarlas, G. D., Kourtelaris, A., Petkov, V., Kokkinos, C., Manos, M. J. A Ca2+ MOF combining highly efficient sorption and capability for voltammetric determination of heavy metal ions in aqueous media. Journal of Materials Chemistry A, 7 (25), (2019) 15432-15443.

[19] Dhakshinamoorthy, A., Asiri, A. M., & García, H, Metal-Organic Framework (MOF) compounds: Photocatalysts for redox reactions and solar fuel production. Angewandte Chemie International Edition, 55 (18) (2016) 5414-5445.

[20] Xu, G.-R., An, Z.-H., Xu, K., Liu, Q., Das, R., & Zhao, H.-L. Metal-organic framework (MOF)-based micro/nanoscaled materials for heavy metal ions removal: The cutting-edge study on designs, synthesis, and applications. Coordination Chemistry Reviews, 427 (2021) 213554.

[21] S. Rapti, A. Pournara, D. Sarma, I.T. Papadas, G.S. Armatas, Y.S. Hassan, M.H. Alkordi, M.G. Kanatzidis, M.J. Manos, Inorg. Chem. Front. 3 (2016) 635–644.

[22] Qasem, N.A.A, Mohammed, R.H., & Lawal, D.U. Removal of heavy metal ions from wastewater: a comprehensive and critical review. Npj Clean Water, 4 (1) (2021)

[23] Ren, J., Lv, S., Wang, S., Bao, M., Zhang, X., Gao, Y., Liu, Y., Zhang, Z., Zeng, L., & Ke, J,Construction of efficient g-C3N4/NH2-UiO-66 (Zr) heterojunction photocatalysts for wastewater purification. Separation and Purification Technology, 274 (2021)118973.

[24] Rahimi, E., & Mohaghegh, N, Removal of Toxic Metal Ions from Sungun Acid Rock Drainage Using Mordenite Zeolite, Graphene Nanosheets, and a Novel Metal-Organic Framework. Mine Water and the Environment, 35 (1) (2015) 18–28.

[25] Zhang, J., Xiong, Z., Li, C., & Wu, C, Exploring a thiol-functionalized MOF for elimination of lead and cadmium from aqueous solution. Journal of Molecular Liquids, 221 (2016) 43–50.

[26] Chakraborty, A., Bhattacharyya, S., Hazra, A., Ghosh, A. C., & Maji, T. K, Post-synthetic metalation in an anionic MOF for efficient catalytic activity and removal of heavy metal ions from aqueous solution. Chemical Communications, 52 (13) (2016) 2831–2834.

[27] Uddin, M. J., Ampiaw, R. E., & Lee, W. (2021). Adsorptive removal of dyes from wastewater using a metal-organic framework: A review. Chemosphere, 284, 131314.

[28] Salleh, M.A.M., Mahmoud, D.K., Karim, W.A.W.A., Idris, A., 2011. Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. Desalination 280, 1–13.

[29] Lin, S., Song, Z., Che, G., Ren, A., Li, P., Liu, C., Zhang, J. Adsorption behavior of metal-organic frameworks for methylene blue from aqueous solution. Microporous Mesoporous Mater. 193, (2014) 27–34.

[30] Katheresan, V., Kansedo, J., Lau, S.Y, The efficiency of various recent wastewater dye removal methods: a review. J. Environ. Chem. Eng. 2018.

[31] Mohammadi, A.A., Alinejad, A., Kamarehie, B., Javan, S., Ghaderpoury, A., Ahmadpour, M., Ghaderpoori, M., Metal-organic framework Uio-66 for adsorption of methylene blue dye from aqueous solutions. Int. J. Environ. Sci. Technol. 14 (2017) 1959–1968.

[32] Molavi, H., Hakimian, A., Shojaei, A., Raeiszadeh, M, Selective dye adsorption by highly water-stable metal-organic framework: long term stability analysis in aqueous media. Appl. Surf. Sci. 445 (2018) 424–436.