



Metal-Organic Frameworks, a New Playground for Clean Energy and Environment

Hassan Abdel-Gawad ^{a*} and Reda M. Abdelhameed ^a



CrossMark

^aApplied Organic Chemistry Department, Chemical Industries Research Division, National Research Centre, 33 EL Buhouth St., Dokki, Giza 12622, Egypt.

Abstract

As a class of versatile porous materials, MOFs have shown enormous potential for adsorption for environmental remediation and fuel purification. To efficiently remove harmful gases, it is not sufficient to use MOFs of the appropriate size/shape of the pores, and other more specific interactions between harmful adsorbents and the host are desirable. Most of the harmful gases are highly reactive. The adsorption of these gases often degrades the porous structures of MOFs. However, much progress has been made in the last few years to develop very persistent organic frameworks. Certainly more and more fundamental studies will appear in this direction, which should enhance the practical application of this type of new porous material for air purification and related fields in the future. MOFs contain multiple functional groups, conjugate bonds, and metal ions that can help for understanding the interactions between MOFs and pollutants and hence increase the adsorption efficiency. MOFs suffering from relatively poor water stability and reuse potential except for some types of MOFs such as MIL, UiO and ZIF are relatively stable in water. The big challenge is converting unstable MOFs in water to stable MOFs; this will lead to high recovery and extend its application.

Keywords: Metal-organic frameworks; Synthesis; Removal; Harmful gases; Organic pollutants..

Abbreviations

Abbreviations: bdc, Benzene-1,3-dicboxylate; BTC, Benzene tricarboxylic acid; INA, Isonicotinic acid; BET, Brunauer, Emmet, Teller; btapa, 1,3,5-benzene tricarboxylic acid tris[N-(4-pyridyl)amide]; btb, 4,4',4"-benzene-1,3,5-triyl-tribenzoate; btc, Benzene-1,3,5-tricarboxylate; btt, Benzene-1,3,5-tris(1H-tetrazole); HKUST, Hong-Kong University of Science and Technology; ICP, Inductively Coupled Plasma; IRMOF, IsoReticular Metal-Organic Framework, MIL, Matériaux de l'Institut Lavoisier; MOF, Metal-Organic Framework; PSM, Post-synthetic modification; PXRD, Powder X-Ray Diffraction; SBU, Secondary Building Unit; UiO, University of Oslo; UMCM-1, University of Michigan Crystalline Material-1; XRD, X-ray diffractogram; ZIF, Zeolitic Imidazolate Framework; CR, Congo Red; MB, Methylene blue; MO, Methyl orange; RhB, Rhodamine B.

Table of Contents

1. General introduction
2. Synthesis of metal-organic frameworks
 - 2.1. Synthesis approaches
 - 2.1.1. Hydrothermal and solvothermal synthesis
 - 2.1.2. Mechanochemical synthesis
 - 2.1.3. Sonochemical synthesis
 - 2.1.4. Microwave-assisted synthesis
 - 2.1.5. Electrochemical synthesis
3. Metal-Organic Frameworks for a clean environment
 - 3.1. Removal of Harmful gas
 - 3.1.1. NH₃ removal
 - 3.1.2. Benzene removal
 - 3.1.3. NO₂ removal
 - 3.1.4. SO₂ removal
 - 3.1.5. H₂S removal
 - 3.2. Removal of organic pollutants
 - 3.2.1. Organic dyes removal
 - 3.2.2. Herbicides and pesticides removal

*Corresponding author e-mail: abdelgawadhassan@hotmail.com; (Hassan Abdel-Gawad).

Receive Date: 03 January 2021, Revise Date: 17 January 2021, Accept Date: 17 January 2021

DOI: 10.21608/EJCHEM.2021.56317.3210

©2021 National Information and Documentation Center (NIDOC)

- 3.2.3. Pharmaceutical intermediate removal
3. 3. Application of MOF for Removal other pollutants
4. Metal-Organic Frameworks for clean energy
 - 4.1. Removal of sulfur compounds
 - 4.2. Removal of nitrogenated compounds
 - 4.3. Removal of oxygenated compounds
5. Conclusion and perspective
6. References

1. General introduction

The world has seen a populace and innovation development remarkable at some other time ever. Even though: the development carries extraordinary advantages and disadvantages to people. Among the disadvantages are poisons gas evaluation, water pollution, and fuel contamination. The examination of new materials to eliminate contaminations has uncovered the presence of porous materials as one of the fundamental possibilities for purification. Some porous materials, for example, activated carbon and zeolite, have just been utilized in the poison gas expulsion. Nonetheless, these materials right now have their restrictions. Since, it is hard to make acclimations to the pores inside these materials, also low selectivity when going about as adsorbents. Besides, the low adsorption capacity of contaminant, these make zeolite and activated carbon just pragmatic for a particular scope of contamination uptake.

Metal-organic frameworks (MOFs) are one of the rising classes of porous materials, made by metallic particles or metallic groups and organic compounds. MOFs have special properties, for example, an amazingly high surface area (up to $7000 \text{ m}^2 \text{ g}^{-1}$), designable structures, permanent porosity, and controlled adsorption capacities[1]. Because of this one of a kind properties, MOFs have indicated extraordinary potential in numerous fields including gas storage, catalysis[2], detecting small organic molecule such as benzene and toluene[3], biomedical sciences, and so on. MOFs can take parts in water treatment, and improving the properties of MOFs will expand their capability to treat a wide scope of contaminations. In this review, the flow research case for MOFs in gas poison evacuation will be introduced. As well, the manufactured and post-engineered strategies that control MOFs for wastewater treatment will be clarified. Besides, using MOFs in fuel purification will be stated. A

clean environment means clean air from toxic gases and clean water from organic contaminants, also clean energy means clean fuel from sulfur, oxygen, and nitrogen compounds.

2. Synthesis of metal-organic frameworks

The synthetic techniques of MOFs influences on structure, yield, molecule size, the morphology of prepared MOFs. Therefore, the engineered synthetic strategies lead to understanding the nature of MOFs arrangement and development [4]. In this review, we will discuss the more traditional methods for the synthesis of MOFs.

2.1. Hydrothermal and solvothermal synthesis

The most widely recognized strategy for preparing MOFs is solvo/hydro thermal, it references to responses in shut holders in watery or non-water conditions at high temperature under pressure. The temperature was utilized to conquer the initiation of vitality hindrance in the association between metal particles and natural bonds. There are numerous instances of MOFs can be prepared to utilize the solvothermal technique, for instance, MOF-5, MOF-74, Cu-BTC, ZIF-8, PCN-250 [5]. Compositional conditions, for example, metal particles, solvents, organic linkers, temperature, and weight, enormously influence the development of MOFs. Subsequently, deciding the ideal composition conditions for preparing MOFs is challenged and tedious. The presence of solvent does not just give a medium to dissolving the reactants yet besides goes as a modulator in the development of the MOFs substance. Also, a mixture of solvents has been employed to overcome the challenge of different solubilities for the starting materials. Reaction with lower temperatures are carried out in glass vials while those at temperatures higher than 400 K are carried out inside Teflon lined autoclave.

2.2. Mechanochemical synthesis

It notable that: mechanical power can be usual for the formation of the chemical bond. Mechanical science is of extraordinary monetary and natural significance because of its numerous preferences, for example, being liberated from solvents, short response times, and in any event, having moderate response conditions. In mechanical amalgamation, the mineral salt and the organic ligand were ground

together for just a couple of moments to acquire a MOFs item [6]. This method is called the dry process method, this makes the present technique is an eco-friendly method for the synthesis of MOFs. The method is simple, economical and environment friendly as it does not require the use of organic solvents which could be toxic and destructive to the environment.

2.3. Sonochemical synthesis

This strategy alludes to a response that happens in an ultrasound situation. In the ultrasound condition, little air pockets and depressions structure in the dissolvable because of the adjustment in pressure. This development of air pockets is called acoustic cavitation, which implies the arrangement, development, and breakdown of air pockets in a fluid. Cavitation empowers one of a kind connection among particles and vitality. Problem areas inside air pockets may arrive at 5000 KB and 1000 BAR with warming and cooling paces of 1010 KB and this vitality is utilized to fabricate the MOFs item [7]. The fundamental purpose behind utilizing the sonochemical strategy is to accomplish a quick, naturally amicable, and vitality sparing methodology. The first sonochemical amalgamation of MOFs was $Zn_3(BTC)_2 \cdot 12H_2O$. The nanocrystals of MOFs were prepared as follows the metal ion (zinc source, $Zn(NO_3)_2$) and organic linker (BTC, benzene tricarboxylic acid) blended under room temperature and barometrical weight in 20% ethanol in water under ultrasound illumination. The got nanocrystals ranged from 50 to 900 nm and this was adjusted by changing the time of the reaction. The advantages for this synthetic method arise from the following: speed, energy-efficient, environment friendly, reduction of crystallization time, production of fine crystallites and smaller particle size.

2.4. Microwave-assisted synthesis

Microwave radiation is a type of electromagnetic radiation with moving electrical charges. As of late, instances of microwave-helped the combination of MOFs. When all is said in done, microwave radiation expands the crystallization rate, which gives a quicker technique to combining MOFs with littler sizes with regular morphology. The main case of the microwave helped MOFs is Cr-MIL-100. This MOF was prepared at 220 °C for 4 h utilizing microwave illumination. The yield was 44%, which was like the customary solvothermal technique but solvothermal

take a 4-day reaction time. It has been discovered that microwave light quickens the cycle of nucleation instead of the crystallization cycle [8]. Some major advantages of this method are the lesser time for completion of the reaction, high efficiency, particle size reduction opportunity

2.5. Electrochemical synthesis

In the electrochemical planning, metal cations diffuse into the response medium through the anode. The organic compounds are broken up in the electrolyte, where they respond with metal cations. This method is helpful for enormous scope creation. Also, this manufactured technique is especially reasonable for the development of MOFs films and coating materials [9]. Major advantage is the rapid and continuous formation of highly pure products in large quantity.

3. Metal-Organic Frameworks for a clean environment

3.1. Removal of Harmful gas

3.1.1. NH_3 removal

Internationally, roughly 150 million tons of NH_3 is created yearly for use as a feedstock in a few enterprises, for example, composts, drugs, commercial cleaning items, and refrigerant gas. NH_3 is exceptionally poisonous and it has high dangers related to enormous scope creation and capacity. Because of the risks of NH_3 , the improvement of new materials to eliminate NH_3 from the air is vital. As of late, Cu-BTC was found to effectively ingest NH_3 in both dry and wet conditions. The instrument of ingestion is attributed to facilitating the Lewis acid/base of NH_3 atoms into open Cu (II) destinations. Dincă et al. depict the blend and assimilation properties of NH_3 for a progression of profoundly stable MOFs dependent on azoles, $M_2Cl_2(BTDD)(H_2O)_2$ ($M = Mn, Ni, \text{ and } Co$, BTDD = bis(1H-1,2,3-triazolo[4,5-b]imidazole-5-yl)dibenzo[1,4-dioxin]). The isotherm shows that the all-out NH_3 ingestion of $Mn_2Cl_2(BTDD)(H_2O)_2$, $Co_2Cl_2(BTDD)(H_2O)_2$, and $Ni_2Cl_2(BTDD)(H_2O)_2$ at 1 bar and 298 K are 15.47, 12.00, and 12.02 mmol g, respectively [10]. $Zn(INA)_2(H_2O)_4$ (INA=isonicotinate) was prepared to utilize water as a solvent at room temperature. After actuation at 100 °C for 1 h, a parchedness period of $Zn(INA)_2$ was acquired. Because of the capacity of Zn (II) to well arrange towards NH_3 , the capacity of $Zn(INA)_2$ to

retain NH_3 was considered. The ingestion tests show that zinc (INA)₂ can catch NH_3 in both dry and wet conditions, the measure of NH_3 assimilation at 298 K and 1 bar is 6 mmol g⁻¹. Moreover, after three cycles, the measure of retention of NH_3 is around equivalent to that of the first example, which shows high substance strength of $\text{Zn}(\text{INA})_2$ [11]. The most encouraging methodology to create open metal site in MOFs structure is to utilize post-synthetic strategies. Walton and associates prevailing with regards to combining copper with free carboxylic acid functional groups in UiO-66 (Zr) delivering UiO-66(Zr)-(COOCu)₂, and UiO-66(Zr)-COOCu. The absorption analyses of NH_3 in dry and wet conditions (80% RH) indicated that the two materials have huge increments in the dynamic NH_3 ingestion limit and it was discovered that the new material UiO-66(Zr)-(COOCu)₂ had progressively. NH_3 has limits of more than 6 mmol g⁻¹ in dry and wet conditions and keeps up stable in water vapor just as in dry and wet NH_3 streams[12].

3.1.2. Benzene removal

Benzene and its subsidiaries can be utilized in numerous synthetic mechanical cycles. In any case, the arrival of such natural discharges will cause a ton of medical issues. Adsorption of benzene onto porous materials gives a promising strategy to the cleaning environment from these toxic pollutants. As another class of porous materials, MOFs have been read for the retention of benzene and its subordinates. For instance, the measure of benzene consumed in Cu-BTC was 9.5 mmol g⁻¹ at 298 K and 1.0 kPa[13]. The uptake of benzene on MIL-141 was ca. 2.6 mmol g⁻¹ at 303 K and 0.69 kPa. The amount of toluene absorbed on SCUTC-18 was 1.848 mmol g⁻¹ at 298 K and 3.405 kPa[14]. The stacking responses between benzene atoms and the host outline are relied upon to assume significant parts in the predominant adsorption execution of benzene for these MOFs. Kirillov and associates arranged a thermodynamically steady Zn-MOF that got from 3,5-dicarboxylic acid diphenyl with astounding auxiliary, topological, and absorbance highlights. At room temperature, the retention amounts were assessed based on ¹H NMR spectra as 1.08, 1.79, and 1.04 g g⁻¹ for benzene, p-xylene, and m-xylene, individually [15].

3.1.3. NO₂ removal

All in all, NO_2 is one of the most widely recognized poisonous contaminations, and it is likewise a typical synthetic. An assortment of sorbents containing MOFs has been created and assessed for NO_2 expulsion. Zr(IV)-based MOFs have been broadly inspected for NO_x expulsion because of their high surface area. Peterson and associates report the expulsion of NO_2 from the air with UiO-66(Zr)- NH_2 by the micro penetration strategy. The NO_2 take-up limit of UiO-66(Zr)- NH_2 is 0.9 g g⁻¹. Extra trials at 80% RH show that the NO_2 stacking of UiO-66- NH_2 is more noteworthy than 1.4 g g⁻¹ at immersion [16]. The examples were utilized as adsorbents to eliminate NO_x from dry or soggy air. It was discovered that the amine group (NH_2) or carbonyl (CHO) in urea legitimately interface with the NO_2 atoms in both wet and dry conditions, bringing about the development of surface-bound nitrates [17].

3.1.4. SO₂ removal

The produced gas resulted from the burning of coal is carbon dioxide (10-12%), sulfur dioxide (500-3000 ppm), and nitrogen oxide (10-40 ppm). Most of the sulfur dioxide can be taken out by washing with limestone slurry or a wet sulfuric acid cycle. In any case, hints of the sulfur dioxide present in the vent gas can't be taken out by these cycles. The leftover sulfur dioxide in the gas can respond with the natural amines in the carbon dioxide purging cycle, causing lasting loss of amine action and diminishing the productivity of this cycle. Subsequently, the total evacuation of hints of sulfur dioxide from the vent gas is of major significance. SO_2 ingestion onto permeable materials gives a promising way to deal with specific gas expulsion. Notwithstanding, investigations of sulfur dioxide evacuation have infrequently been accounted for utilizing MOFs as an adsorbent because of their high surface area to profoundly receptive SO_2 . Chapal et al detailed specific ingestion of sulfur dioxide in two MOFs, M (bdc)(ted)_{0.5} (M = Ni, Zn; bdc = 1,4-benzenedicarboxylate; ted = triethylene diamine). The ingestion of SO_2 in Ni (bdc)(ted)_{0.5} at room temperature and 1.13 bar is 9.97 mmol g⁻¹. The mechanism of incorporates an SO_2 onto MOFs is connected through the S and O atom from SO_2 and the metal ion in the framework. In other designing, SO_2 builds up a hydrogen bond with a CH_2 in the

framework. Schroeder et al report that sulfur dioxide can be adsorbed in In (III)-based MOF (NOTT-202a). The retention of sulfur dioxide from this natural system at 268 K and 1.0 bar is 13.6 mmol g⁻¹. In another work of a similar topic, they announced specific adsorption of sulfur dioxide in MOF, MFM-300 (In). The sulfur dioxide assimilation of MFM-300 (In) at 298 K and 1 bar is 8.28 mmol g⁻¹. The component of sulfur dioxide atoms adsorption is related to communications with free hydroxyl on the outside of the pores of MOFs, along these lines excusing the selectivity saw at the sub-atomic level. Chen et al reported SO₂ adsorption on SIFSIX-1-Cu, SIFSIX-2-Cu, SIFSIX-2-Cu-I, SIFSIX-3-Zn, and SIFSIX-3-Ni at barometrical and low weights. The outcomes demonstrated that a high limit of sulfur dioxide of 11.01 mmol g⁻¹ is accomplished at 298 K and 1.01 bar by SIFSIX-1-Cu, higher than other SIFSIX materials. At an incredibly low weight of 0.002 bar and 298 K, the assimilation of SIFSIX-2-Cu-I of sulfur dioxide is 2.31 mmol g⁻¹, and when the fractional weight increments to 0.01 bar, the retention of sulfur dioxide from SIFSIX-2-Cu-I expanded to 4.16 mmol g⁻¹, restricting destinations for anions and stacked rings in SIFSIX materials intensely retain each molecule of sulfur dioxide through S δ^+ and F δ^- electrostatic communications and O δ^- - H δ^+ dipole-dipole interaction [18].

3.1.5. H₂S removal

One testing update step in treating Refinery Off-Gas (ROG) and Natural Gas (NG) is to treat H₂S usually found in ROG and NG with different definitions extending from ppm to high levels. Expulsion of H₂S is fundamental to stay away from the harmfulness of both the sorbents utilized in the different cycles of the advancement system and the impetus engaged with the resulting utilization of H₂ and CH₄. Mohamed group has done numerous works toward this path. In ongoing work, they analyzed the specific adsorption of H₂S within the sight of streams containing CO₂ and CH₄ from soc-geography MOF, Ga-soc-MOF. The single-segment gas adsorption performed at 298 K shows that the isoquant of H₂S is more honed than that of methane and carbon dioxide at a low weight, demonstrating that H₂S displays the most noteworthy proclivity toward Ga-soc-MOF, which is attractive for H₂S Adsorbents in petroleum gas overhaul. Also, the favored selectivity to H₂S and the security of execution were affirmed by rehashed section entrance tests. Utilizing a 5/5/90 CO₂/ H₂S

/CH₄ gas blend at a stream pace of 10 cm³ min⁻¹ and 298 K, H₂S and CO₂ were held in the segment for roughly 40 and 5 min, individually. Interestingly, methane went through the section very quickly, mirroring the favored selectivity of H₂S over CH₄ and CO₂. The watched high selectivity of H₂S for Ga-soc-MOF-1a was exhibited by the favored official of H₂S in open metallic locales of Ga-soc-MOF-1a that were uncovered and generally unsaturated. Furthermore, after 5 adsorption tests, Ga-soc-MOF display repeatable H₂S and CO₂ adsorption execution. The entirety of the above outcomes affirms that Ga-soc-MOF-1a is a possible material for the resulting evacuation of H₂S and CO₂ [19]. In another work, they uncovered the appropriateness of uncommon earth-based MOFs (RE) with fcu geography for H₂S evacuation applications. Three RE-fcu-MOFs called Y-FTZB-fcu-MOF (H₂FTZB = 2-fluoro-4-(1H-tetrazol-5-yl) benzoic acid), Y-1, 4-NDC-fcu-MOF (1,4-H₂NDC=1,4-naphthalene dicarboxylic acid), and Y-fum-fcu-MOF (fum = fumaric acid) were chosen with various pore size and charge thickness dispersion inside the pore framework. Adsorption segment entrance tests were performed with a 5/5/90 CO₂/ H₂S /CH₄ gas blend at a stream pace of 10 cm³ min⁻¹. For Y-FTZB-fcu-MOF, the maintenance seasons of H₂S and CO₂ at 298 K are 42 and 10 gm minutes, individually. The relating absorbance got from the maintenance seasons of H₂S and CO₂ is 0.9 and 0.22 mmol g⁻¹, respectively. Contrasted with Y-FTZB-fcu-MOF, Y-1,4-NDC-fcu-MOF indicated an essentially higher H₂S maintenance time (70 min g⁻¹) yet with a practically identical CO₂ maintenance time (11 min g⁻¹) with similar conditions. The comparing absorbance got from the maintenance seasons of H₂S and CO₂ is 1.5 and 0.24 mmol g⁻¹, separately. The H₂S /CO₂ selectivity of Y-1,4-NDC-fcu-MOF is 6-7. Y-fum-fcu-MOF indicated comparable conduct to Y-1,4-NDC-fcu-MOF with marginally lower maintenance times for H₂S (50 min g⁻¹) and carbon dioxide (8 min g⁻¹) at 298 K. For this situation, the relating assimilation got from the H₂S and CO₂ maintenance time is 1.1 and 0.17 mmol g⁻¹, individually. Recovery tests show that Y-FTZB-fcu-MOF can be totally recovered at 323 K, and Y-1,4-NDC-fcu-MOF and Y-fum-fcu-MOF can be effortlessly recovered at 298 K. From the above trials, it was indicated that as the surface area and pore size diminished from Y-FTZB-fcu-MOF to Y-fum-fcu-MOF to Y-1,4-NDC-fcu-MOF, the take-up of

H₂S expanded at a lower fixation [20]. This shows that MOFs with little depressions are sorbents reasonable for eliminating H₂S at moderately low focuses and weights. In ongoing work, they report the blend and development of a powerfully steady MOF spongy material, kag-MOF-1. The particular auxiliary highlights of kag-MOF-1 incorporate one-dimensional channels with a little pore gap size and a profoundly accused neighborhood thickness related to the presence of tetrazolate structure blocks. Strikingly, kag-MOF-1 demonstrated generally high take-up execution towards H₂S, CO₂, and H₂O. Different investigates, for example, benzene, toluene, xylene, mono-stretched isopentane, and n-pentane was not consumed. This features the significance of this specific evacuation of H₂S, CO₂, and water from high-chain hydrocarbons containing gas streams employing sub-atomic screening, taking out the sensible rivalry between hydrocarbons, H₂S, CO₂, and water during the expulsion steps. Banduz and coauthors detailed the combination of graphite oxides (GOs) with Cu-BTC. A wide scope of logical strategies has been utilized to examine the surface area and H₂S adsorption. It was discovered that the exhibition of the new vehicles was fundamentally better than the presentation of the parent MOFs. Better elimination uptake of the mixes results from the development of new miniature porosities because of connections between sulfonic acids and amine group of GO focuses and adjusted Cu-BTC copper [21].

3.2. Removal of organic pollutants

MOFs are a good stage for adsorption of organic pollutants since the incredibly high surface area and porosity can add to the availability of adsorption and dissemination destinations through the edge. By choosing the bonds just as modifying the contact of metal particles, the MOFs porosity can be accurately changed following suit distinctive focusing on. Other than the high surface region and porosity, hydrophobic and static responses, acid/ base interaction, and the hydrogen bonding between the MOFs structure and contaminations regularly add to the retention. In this part, we will display on the utilization of MOFs to assimilate wastes deposits in the water, for example, colors from industry, herbicides and pesticides from agribusiness, and other recently developing natural contaminations. Wastes deposits are ordinarily in the water in

extremely low concentrations, and it is hard to eliminate those utilizing different strategies.

3.2.1. Organic dyes removal

Most dyes are synthetically and are not viewed as soluble in water. So that, water must be treated to eliminate an enormous part of these synthetic substances, an amazingly low convergence of colors represents an expected danger to the earth. Dyes particles are generally made out of formed chromophore mixes and auxochromes (- COOH, - OH, - NH₂, - NHR, - NR₂, and so on.), and another utilitarian group, (for example, the SO₃⁻ group to improve water dissolvability). Accordingly, the electrostatic interaction among MOFs and blended colors are a significant factor in accomplishing a high elimination capacity. It was accounted for that MIL-101(Al)-NH₂ had a watched capacity to ingest methylene blue (MB) (up to 762 mg g⁻¹) [22]. The electrostatic connection between the positive MB and the single electron sets on the amino group in the metal edge adds to the high capacitance. Likewise, the electrostatic response will prompt special retention when numerous colors are available. A case of MB adsorption and isatin adsorption has been accounted for by MIL-100 (Fe) [23]. MOF just indicated adsorption towards MB because of electrostatic connections among host and color. Examination of the adsorption of MB, MO, RhB, and Congo Red (CR) utilizing MOF: [Zn(bdc)(tib)].3H₂O (tib=1,3,5-tri (1H-imidazol-1-yl) benzene and bdc=1,4-dicarboxybenzene) [24]. It showed an exclusive affinity for CR over three other dyes. The selectivity was expected to be due to pore size and interactions between the open metal site and CR. Recently, methylene blue (MB) and rhodamine B (RhB) was removed from water using MIL-125-NH₂@cotton, Ag₂WO₄@MIL-125-NH₂@cotton, and Ag₃VO₄@MIL-125-NH₂@cotton. The novel composite was used to adsorb the dyes and underexposed to visible light the formed electron-hole pairs oxidized the colored dye to colorless fragments (Figure 1) [25]. MIL-125-NH₂ has good photocatalytic properties because it absorbs light in the visible region and its bandgap is small compared with pure titanium dioxide. A lot of researches were done to minimize the bandgap of MIL-125-NH₂ using post-synthetic modification of free amino group with organic reagents. On the other hand, some research use nanoparticles to doped MOFs to

minimize its bandgap. The photocatalysis represented the more suitable techniques for the removal of organic pollutants from water, from the best photocatalysts; MOFs come over all the catalysts due to their advantages and regeneration without loss of their activity [26-28].

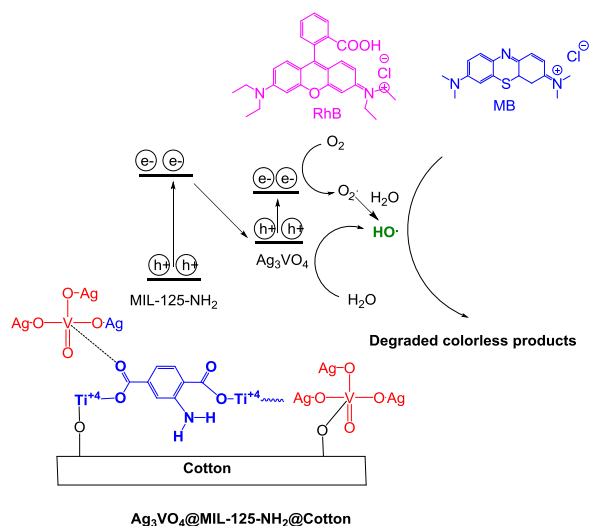


Fig.1. Mechanism of photocatalytic degradation of MB and RhB dyes by $\text{Ag}_3\text{VO}_4@\text{MIL-125-NH}_2@\text{cotton}$ and $\text{Ag}_3\text{VO}_4@\text{MIL-125-NH}_2@\text{cotton}$ composites

3.2.2. Herbicides and pesticides removal

Nowadays, the problem of pesticide residue removal from water has a great challenge [29]. From the best efforts on this hard topic, our group put our hand on the best adsorber of pesticide, from this adsorber, low-cost agricultural adsorber [30], polymeric materials [31] and MOFs [32]. Six different types of mechanisms have been proposed [33, 34] for the connection of MOFs with pesticide: (1) complex formation; (2) acid/ base cooperation; (3) π - π collaborations; (4) hydrogen bonding; (5) electrostatic interactions; and (6) adsorption dependent on hydrophobic nature. Contrasted with customary adsorbents, for example, zeolite and activated carbon, the half and half, organic and inorganic nature of MOFs are especially good for the ingestion of herbicides and pesticides. Examination of the adsorption of methylchlorophenoxypropionic acid (MCP) onto UiO-66 (Zr) [35] demonstrated quicker and higher MCP adsorption than activated carbon (AC) with 7.5 occasions higher retention limit at low concentrations of MCP (1 ppm), and a dynamic steady multiple times higher than that of AC. This fast and high assimilation of UiO-66 (Zr) has been credited to electrostatic responses at low pH

and π/π stacking responses at high pH. UiO-66 (Zr) can be recovered well in water/ethanol mixture. MIL-53 (Cr) was used for the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) [36]. The study found that the pH could impact 2,4-D uptake. At the point when the pH is low the purpose of isoelectricity in the MOF, the decidedly charged MOF spongy indicated a solid bond with 2,4-D. Conversely, when the pH esteem expanded, just the beta responses added to adsorption. UiO-67 (Zr) was found to show the adsorption towards glyphosate (GP) and glucosinate (GF) [37]. Zr-OH moieties in the UiO-67 (Zr) permeable can respond with organophosphorous pesticides (GP and GF), hence framing edifices. In this way, synthetic retention as opposed to electrostatic adsorption is the principle adsorption instrument. The adsorption of pentazone, cloperalid, and isoproturon were concentrated on a progression of MOFs (MIL-100 (Fe), Cu-BTC, MIL-53(Al), MIL-53(Al)- NH_2 , $-(\text{OH})_2$ -MIL-53(Al), DUT-5(Al), $(\text{OH})_2$ -CAU-1(Al), NH_2 -CAU-1(Al), MIL-125 (Ti) and MOF-235 (Fe)), CAU-1(Al) and MOF-235(Fe) demonstrated the most noteworthy ingestion limit and fantastic adaptability after different retention cycles. The adsorption instruments of MOFs were not surely known, yet markers, for example, pore size, hydrophobicity, and bond quality were proposed to impact the take-up of pesticides [38]. Cu-BTC shows high affinity toward adsorption of 14C-ethion pesticide (Figure 2). The mechanism of adsorption is related to P-O of ethion with free electrons, and copper atom in Cu-BTC that presents an open (unsaturated) metal coordination site. Cu-BTC contains channels ca. 0.9 nm [39] across, while the ethion molecule measures ca. 0.7 nm from oxygen to oxygen in the two phosphoryl groups. If one considers also a typical Cu-O bond length of ca. 0.18 nm [40] the ethion particle can undoubtedly connect across two Cu (II) ions over the MOF channel. Accordingly, this work proves that 14C-ethion can significantly remove using Cu-BTC [41].

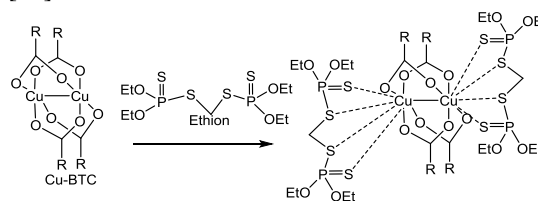


Fig. 2. Mechanism of ethion insecticide adsorption by Cu-BTC

Cu-BTC@Cotton composite is used for removal of ethion pesticide from water, the results clear that the composite has high adsorption capacity due to the porosity structure of the MOF (Cu-BTC) and functional group of cellulose in the composite. Adsorption of ethion onto Cu-BTC@Cotton could be brought out through two primary ways; physical adsorption or chemical adsorption. Pores of Cu-BTC can catch ethion atoms through pore of Cu-BTC@Cotton composite, this way called the physisorption pathway. Another pathway is the connection of ethion with Cu-BTC@Cotton composite through Coordination linkage between sulfur of ethion with the copper of Cu-BTC or hydrogen bonding between the oxygen of ethion and function groups of cellulose (Figure 3) [42].

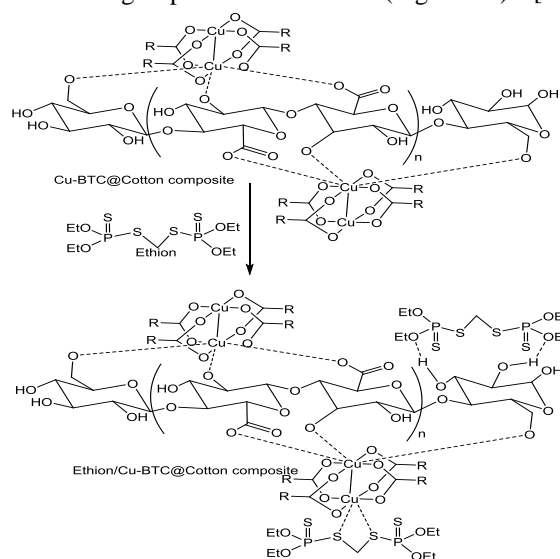


Fig. 3. Mechanism of the interaction of ethion insecticide with Cu-BTC@Cotton composite

Recently, ZIF MOFs was applied for the removal of pesticide from water. The results show the high adsorption uptake of prothiofos and ethion in ZIF MOF. The mechanism of adsorption is principally focused on the cooperate prothiofos with Zn atom in the framework through $(-P=S\cdots\cdots Zn)$ and a $(Cl\cdots\cdots Zn)$. The chlorine particle was likewise shaped hydrogen bond with an imidazolium's hydrogen. Prothiofos was additionally interfaced with ZIF-8 through $(-P-S\cdots\cdots Zn)$ and $(-P=S\cdots\cdots Zn)$. This cooperation was settled by three intermolecular hydrogen connections between a chlorine particle and imidazolium's hydrogens, just as a $\pi-\pi$ stacking between the prothiofos benzene ring and an imidazolium ring. Then again, ethion pesticide can

connect with ZIF MOFs through both $(-P=S\cdots\cdots Zn)$ bond (Figure 4) [43].

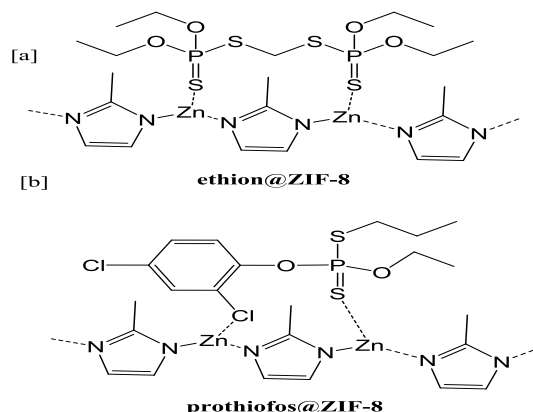


Fig. 4. The interactions of ethion and prothiofos molecules with ZIF-8 surface

3.3. Pharmaceutical intermediate removal

The adsorption of pharmaceutical intermediate has been generally concentrated with customary, multi-walled carbon nanotubes, activated carbon, zeolites, MOFs, and so on were used to eliminate such intermediates from water. In 2010, the elimination of sulfasalazine over MOF-177, MOF-5, Cu-BTC and MIL-100 were first detailed with various water steadinesses. All the more as of late, Wang et al. report the adsorption of a sulfonamide, sulfachloropyridazine from the water with Cu-BTC. Cu-BTC indicated a noteworthy elimination capacity of 384 mg g^{-1} at room temperature, outperforming the past examined sorbents, for example, dynamic carbon powder (4.5 mg g^{-1}), Faujasite Y zeolite (280 mg g^{-1}), and HSZ-690HOA zeolite (151 mg g^{-1}). The amazing presentation is credited to the high surface area, enormous pore size, and a huge measure of unsaturated metal sites of Cu-BTC. The electrostatic response, hydrogen bonding, and $\pi-\pi$ stacking have been proposed as the main impetus for eliminating sulfachloropyridazine. Cu-BTC likewise indicated fast energy to eliminate most sulfachloropyridazine in wastewater in 15 min, reliable with a pseudo-second-order model. In any case, the recovery of Cu-BTC is sketchy because of helpless water dependability. The vital plan of fluidly stable MOFs is urgent in a genuine watery arrangement based application [44]. The adsorption of nitrofurazone (NZF) and nitrofurantoin (NFT) was accounted for by Zhou et al., utilizing two recently stable artificially stable Zr based MOFs, $Zr_6O_4(OH)_8(H_2O)_4(CTTA)_8$ (BUT-12, H3CTTA = 5-(4-carboxyphenyl)-2',4,6'-trimethyl-(1,1:3',1''-terphenyl)-4,4-dicarboxylic acid) and $Zr_6O_4(OH)_8(H_2O)_4(TTNA)_8$ (BUT-13, H3TTNA =

6,6,6-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(2-naphthoic acid)). Both MOFs show a high elimination capacity for explicit nitrofurazone and nitrofurantoin from water. Likewise, the hydrophobic methyl bunches acquainted with the BUT-12 and -13 bonds improved the nitrofurantoin take-up, showing that the hydrophobicity of the MOFs decidedly influences the absorbable elimination of the nitrofurantoin from the water. Among the chose anti-infection agents, BUT-12 demonstrated a high elimination rate for NZF and NFT drugs, while BUT-13 had a high elimination rate for NZF, NFT, ODZ (ornidazole), SAM (sulbactam-ampicillin), and CAP (chloramphenicol), which was identified with various pore size 13 and 21 degrees for BUT-12, 14 and 28 degrees for BUT-13)[45].

Recently, ZIF@wool fabric composites [46] can be used in the removal of 2-naphthol as pharmaceutical intermediates from water. The physisorption idea of adsorption mirrors that the adsorption of 2-naphthol onto composites is overwhelmingly helped out through feeble communications spoke to in van der Waals interaction, hydrophobic bonding, particle dipole connections, dipole-dipole interaction, hydrogen bonding, and coordination bonding [47-49]. The mechanism of adsorption is mainly framed between the functional groups of the entire composites (OH, NH, SH) and OH in the 2-naphthol. Besides, cooperation between the two rings (phenyl in 2-naphthol and imidazolium ring in composite) could be communicated as π - π connection [50, 51]. The more interesting factor affected on the adsorption of 2-naphthol onto ZIF is the pores inside the textures of MOFs, this leading physical catching of 2-naphthol atoms onto pores supporting the physisorption hypothesis (Figure 5) [42, 52, 53].

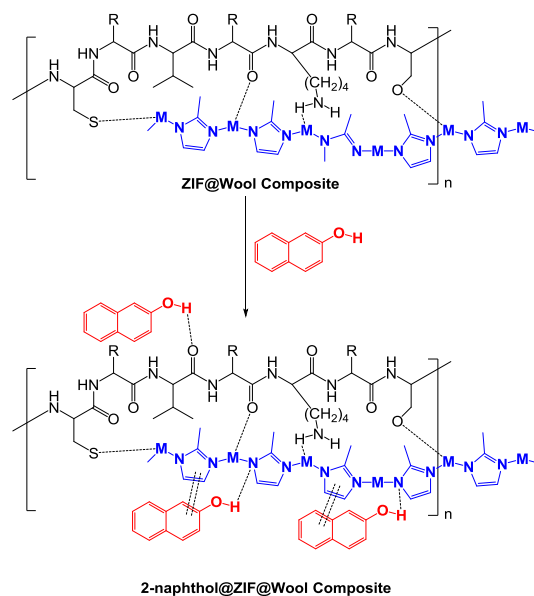


Fig. 5. Mechanism of adsorption of 2-naphthol by ZIFs@wool composites

3.4. Application of MOF for Removal other pollutants

The removal of toxic metal ions continues to pose a crucial problem for health safety and preservation of the environment. In recent times, metal organic frameworks (MOFs) have introduced a new pathway to the act of adsorbing the numerous classes of heavy metals due to their effective chemical stability and numerous functional groups[54-56]. El-Shahat et al in 2020 development of MOFs with cross linked chitosan as a promising adsorbent material for the remediation of environmental water polluted by iodine. Due to the drawbacks of current adsorbents such as low uptake capacity, highcost, and non-recyclability; a novel cross-linked chitosan-MOF composite was synthesized and used in the adsorptive removal of iodine from wastewater. The novel composite shows high iodine removal capacity 399.68 mg g⁻¹at room temperature. The cross-linked chitosan-MOF composite shows chemical and thermalstability, high removal efficiency for capture of iodine from wastewater and furthermore good recyclability[57].

4. Metal-Organic Frameworks for clean energy

Given the expansion in vitality request, new and eccentric wellsprings of vitality must be researched in the following decade. Until this point in time, the fundamental wellspring of vitality is petroleum derivatives. Non-renewable energy sources are

flammable gas, coal, and oil/oil. The non-renewable energy source most utilized is oil, while 40% of the world's power created for a huge scope is through coal. The utilization of petroleum products antagonistically influences nature by spreading unsafe synthetic compounds upon ignition. These defer increments with the expansion in vitality request. Whimsical petroleum derivatives contain enormous measures of undesirable poisons. Consequently, the expansion in the utilization of non-renewable energy sources can be communicated as an unnerving circumstance. The fundamental kinds of these toxins are sulfur, nitrogen, and oxygen-containing contaminations (SCCs and OCCs, individually).

In fossil-inferred powers, for instance, fly fuel, diesel, raw petroleum, gas, heater oil, and so on, upon burning, sulfur oxides, nitrogen oxides, and carbon dioxide are created, causing numerous natural perils including extreme water and air contamination. Global warming through the presentation to ozone harming substances in the air, and ecological insecurity. Furthermore, when these unsafe gases blend in with water, these mixes produce what is called acid downpour, which effectively affects human-made structures and the earth. Adsorption is the most well-known and best strategy for eliminating toxins from fluid fills, and adsorbents have been predominantly picked by their capacity to collaborate with poisons.

4.1. Removal of sulfur compounds

Sulfur-containing contaminations (SCCs) in petroleum products are known as thiophene and its derivatives, for instance, dibenzothiophene, benzothiophene, 4-methylbenzothiophene, 3,7-dimethyldibenzothiophene, 4,6-dimethyldibenzothiophene and 2,8-dimethyldibenzothiophene. There are numerous vaporous of sulfur compounds emitted when consuming fuel products such as SO₃, H₂S, and SO₂. These vaporous is very dangerous for humans and animals, therefore it must be removed from the source. Pre-burning and post-ignition techniques are two distinct cycles that can be embraced to decrease the discharge of SO_x. The pre-ignition measure is more favored because the post-burning cycle is described by a significant expense and presence of hot destructive effluents. The oxidative and desulfurization measures have demonstrated great potential in eliminating S-containing mixes, yet they are acted in the fluid stage and the oxidizing items must be extricated which

restricts their applications. Hydrogen disulfide expulsion requires a high temperature and requires pressure and an impetus to happen, which is reflected in the high treatment cost. Adsorption in the fluid stage is the better technique to eliminate sulfur-containing mixes due to its moderate working conditions, without the requirement for oxidizing or lessening specialists, and can be utilized in the mechanical scale. The most adsorbing materials applied to eliminate sulfur from fuel in the fluid stage are activated carbon, trailed by zeolite. What are more, different porous materials such as MOFs, (for example, Y-BTC, Ni-BTC, Cu-BTC, ZIF-8, ZIF-67, CPO-27, MIL-101, MIL-53 and UiO-66(Zr)), MOF-functionalities (for example UiO-66(Zr)-NH₂, UiO-66(Zr)-COOH), and MOF-containing composites (for example graphite oxide/Cu-BTC, Fe₃O₄/Cu-BTC, Cu/MIL-100, MIL-53-NH₂/textile) altogether expanded the adsorption of thiophene, benzothiophene, and dibenzothiophene. Instead of the previously mentioned adsorbents, the utilization of MOFs demonstrated a critical improvement in the adsorption capacity because of their permeable gem structures. Cu²⁺ based MOFs with and without open metallic site spoke to by Cu-BTC and Cu-JAST-1, individually, was as of late combined and applied in eliminating sulfur compounds.

Four different MOFs structures (Cu-BTC, Cr-BTC, Cu-BDC, and Cr-BDC) were applied to remove sulfur compounds from fuel. Cu-BDC demonstrated high adsorption capacity towards thiophene at practically room temperatures. The adsorption capacity order of four used MOFs follow Cu-BTC > Cr-BDC > Cr-BTC > Cu-BDC. Q_{max} for Cu-BTC, Cr-BDC, and Cr-BTC was 56.1, 41.0, and 30.7 g kg⁻¹, separately. Comparative adsorption capacities of thiophene and benzothiophene were accomplished with Cu-BTC. Notwithstanding, exceptionally high adsorption of S mixes (210.4 - 273.5 mg g⁻¹) was an endless supply of high porosity Cu-BTC. Contrasted with MOFs, MOFs containing composites mg g⁻¹ indicated higher greatest elimination capacities with regards to sulfur compounds. The elimination of benzothiophene was expanded from 117.6 g kg⁻¹ for Cu-BTC to 149.2 mg g⁻¹ for phosphotungstic acid (PWA)/Cu-BTC complex, as PWA stacking brought about a 26% expansion in Q_{max}. Because of the improved porosity, the graphite oxide doped copper-based MOFs (GO@Cu-BTC) upgraded the elimination of thiophene from 38 mg g⁻¹ to 61 mg g⁻¹. Direct presentation of PWA inside MIL-101 (Cr) expanded the elimination of di-benzo-thiophene (136.5) by a factor of 4.2 times rather than MIL-101 (Cr).

A compound of MIL-53-NH₂ as MOF with cotton and wool were fabricated utilizing infrared helped strategies through direct development of MOF within the sight of fabrics. The shaped MIL-53-NH₂/fabrics mixes demonstrated higher thiophene evacuation productivity and the greatest adsorption capacities were 469.4 - 516.5 mg g⁻¹. The adsorption capacity was decreased by just 28.4- 43.6 mg g⁻¹, after reuse for four cycles [58]. The adsorption of thiophene onto the composite is related to three mechanisms, i) hydrogen bonding between the sulfur atom of thiophene and the hydrogen atom of cellulose, ii) the porosity of MOFs play important role in the capture of thiophene from fuel, iii) the aromaticity of both thiophene and the backbone of the framework make π - π stacking (Figure 6).

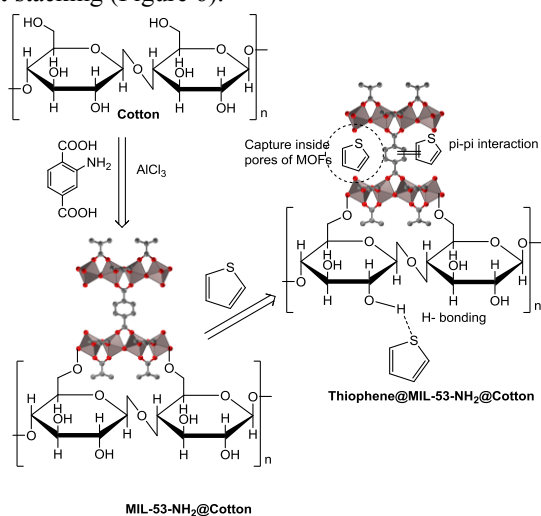


Fig.6. Mechanism of adsorption of thiophene by MIL-53-NH₂@cotton composites

4.2. Removal of nitrogenated compounds

Nitrogen-containing contaminants (NCCs) which are found in the fluid stage can be ordered into two principle group; 1) Basic nitrogenous mixes have 6-membered rings, for instance, quinoline, pyridine, acridine, and tetrahydroquinoline, and 2) non-essential nitrogen mixes with 5-atom rings, for instance, indole, pyrrole, and carbazole, alongside their derivatives. NCC must be taken out first before continuing to work with fuel. A few adsorbents have been utilized in eliminating nitrogen from fluid fuel, for example, activated carbon, zeolite, silicates, and polymers. By and by, MOFs have demonstrated critical points of interest as per their high adsorption capacity. The utilization of UiO-66 (Zr) was accomplished great indole adsorption from fluid fuel

with an adsorption capacity of 199 - 213 g kg⁻¹. Though, practical UiO-66(Zr) (including amino or sulfate groups) indicated fundamentally higher take-up than unfunctional UiO-66(Zr) because of the extra function affected on the adsorption process. UiO-66 (Zr)-NH₂, and UiO-66 (Zr)-SO₃H eliminated indole from fuel in a measure of 265, and 239 mg g⁻¹, separately. UiO-66 (Zr)-COOH indicated a higher elimination of indole (130 mg g⁻¹) and pyrrole (142 mg g⁻¹) contrasted with UiO-66-(Zr). Furthermore, the adsorption of different nitrogenous mixes including indole, quinoline, pyrrole, pyridine, and methylpyrrol on UiO-66 (Zr) was examined utilizing free carboxylic acid. The adsorption capacity reached 170 mg g⁻¹ because hydrogen bonding improved the elimination process. Then again, the use of a functional group in the framework (UiO-66(Zr)-SO₃H) prompted a further increment in the elimination ability of indole to 2.2 times rather than the utilization of UiO-66(Zr).

Phosphotungstic acid (PWA)/MIL-101 (Cr) was blended and utilized for engrossing nitrogenous mixes from fluid fuel. PWA (1%)/MIL-101 (Cr) affirmed a 20% expansion in quinolone take-up limit (274 mg g⁻¹) contrasted with MIL-101 (Cr) (229 mg g⁻¹). While indole uptake diminished marginally from 152 mg g⁻¹ to 162 mg g⁻¹ with PWA impregnation inside MOF. As of late, the actuation of MIL-101-NH₂ with oxalyl chloride (OC-ED-A-M101) was switched in expanding the adsorption capacity of indole and quinoline by 11.7 and 9.3 times rather than activated carbon. In examination with different MOFs, OC-ED-A-M101 indicated the most elevated elimination limit of 714 mg g⁻¹ versus indole. MIL-101 (Cr) was integrated within graphite (GO) oxide creating GO/MIL-101 (Cr) composite to be acted in the adsorption of NCCs. Contrasted with MIL-101, the surface area of the GO compound (0.25%)/MIL-101 was expanded by 22%. Thus, the elimination of indole and quinoline was fundamentally expanded from 244 and 481 mg g⁻¹ for MIL-101 to 319 and 549 mg g⁻¹ for the GO/MIL-101 composite, respectively. Utilizing graphene oxide@MIL-101 exacerbates an essentially higher elimination limit of indole (542-593 mg g⁻¹) and lower quinoline removal (484-498 g g⁻¹) was recorded by examination with GO/MIL-101 compound. Because of hydrogen bond development abilities, initiation of MIL-101(Cr) by amino groups altogether expanded indole take-up limit by a factor of 1.7 and 2.3 times rather than nonfunctional MIL-101(Cr). Adenine joining on MIL-101(Cr) was related to improved quinoline and indole adsorption by a factor of 1.3 and 1.4 times, individually, contrasted with MIL-101(Cr). The higher adsorption capacity was recorded on account of P-Ade@MIL-

101 (Cr), inferable from the arrangement of a hydrogen bonding among MOF and NCC with the complementarity of cation- responses. After alteration of MIL-125(Ti) by NH₂ and resulting protons, the freedom of NCCs was expanded by 1.9-2.2 times for indole and 4.5- 5.3 times for quinoline. MIL-125 (Ti)-NH₂ and P-MIL-125(Ti)-NH₂ indicated adsorption of NCCs in amounts of 460-502 and 546-583 mg g⁻¹, separately.

Both CuCl and AlCl₃ were separately joined into MIL-100 (Cr) and MIL-100 (Fe), individually to apply adsorption to NCCs. MIL-100(Cr), CuCl@MIL-100(Cr) indicated an expansion in indole and quinoline adsorption by 15% and 9%, separately. While joining of AlCl₃ with MIL-100(Fe) improved the capacity by 17% for take-up of quinoline from the fuel. The measure of quinoline consumed by MIL-100 (Cr), MIL-100 (Fe), CuCl@MIL-100 (Cr), and AlCl₃@MIL-100(Fe) were 420, 357, 457, and 417 mg g⁻¹, separately.

The polysulfone@Cu-BTC composite films with various Cu-BTC substances were utilized in eliminating indole and quinoline from the fluid fuel. The joining of Cu-BTC was ascribed to the huge improvement in the uptake of indole and quinoline from 220 and 188 mg g⁻¹ to 676 and 619 mg g⁻¹, separately (Figure 7) [59].

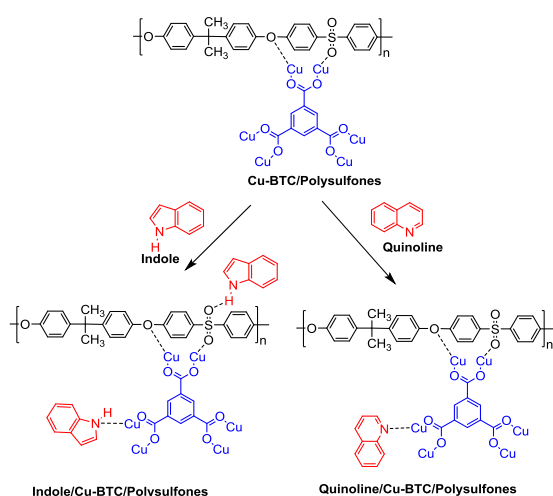


Fig.7.Mechanism of adsorption of quinoline and indole by Cu-BTC@polysulfones composites

MIL-53-NH₂ was developed inside over characteristic textures (cotton and wool) and acquired mixes used to eliminate NCCs. The adsorption abilities to eliminate indole and quinoline were 149 and 204 mg g⁻¹. After recovery for 4 cycles, the adsorption limit of MIL-53-NH₂/fabric mixes was

diminished by 19.2 - 40.9% (Figure 8)[60].

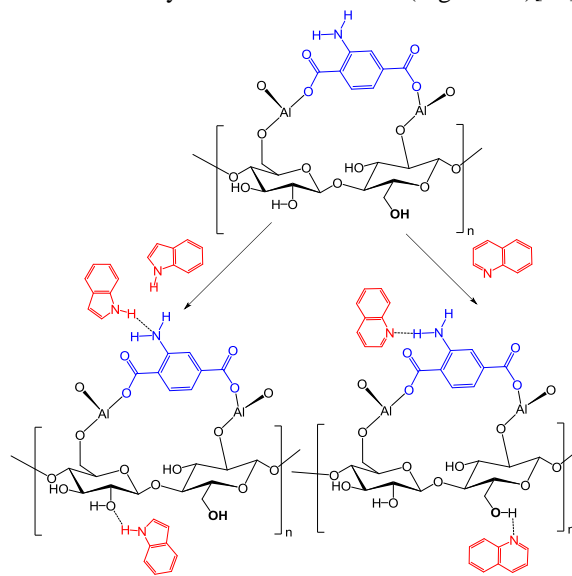


Fig.8.Mechanism of adsorption of quinoline by MIL-53-NH₂@cotton composites

4.3. Removal of oxygenated compounds

Oxygen-containing contaminations (OCCs) are the most undesirable oil toxins and a lot of them can be moved to diesel during the refining cycle, which prompts a few issues, for example, compartment consumption. The most oxygenated group of mixes in fuel are phenols, which are exceptionally harmful to creatures. During burning, phenols structure tars in inside motors and square channels. Subsequently, eliminating phenol from unrefined petroleum is monetarily significant for oil refining. Fluid and fluid extraction, sedimentation, and fingernail skin are among the most conventional strategies used to eliminate phenol from energizes. They indicated critical issues with high substance utilizes, draining of phenolic mixes in wastewater, including unsafe natural solvents, and various treatment steps. A large portion of the disservices featured is not shown if adsorption innovation is utilized to eliminate phenol making it all the more broadly relevant. The examinations detailed with the expulsion of phenols from model fuel have been restricted. MIL-101(Cr) indicated a great phenol adsorption capacity of 2.7 times higher than that of activated carbon (AC). More hydroxyl bunches were brought into MIL-101(Cr) by joining ethanolamine (EA) to deliver EA-MIL-101 (Cr) [HO-MIL-101(Cr)]. Also, in the wake of acquainting the OH bunch with MIL-101(Cr), the adsorption capacity expanded (up to 3.7 times than

AC) because of the hydrogen bonding. An H-bond could be shaped between the O atom of HO-MIL-101(Cr) and the H atom of phenol-OH (Figure 9), which was affirmed by a near adsorption investigation of phenol on HO-MIL-101 (Cr) and MIL-101 (Cr). The uptake of phenol on AC, MIL-101 (Cr), and HO-MIL-101 (Cr) were 91 mg g⁻¹, 250 mg g⁻¹, and 330 mg g⁻¹, individually.

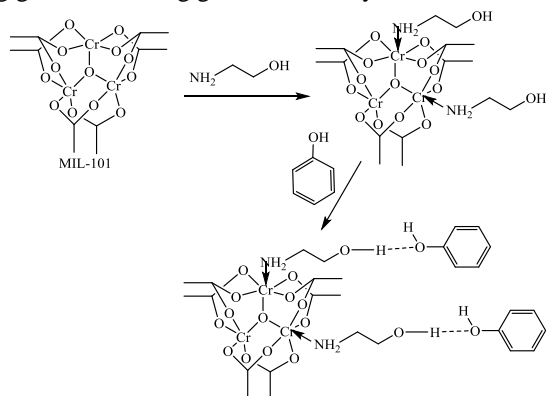


Fig. 9. Post-synthetic modification of MIL-101(Cr) with ethanolamine and the mechanism of adsorption of phenol by composites

Viscose and wool textures were incorporated by Cu-BTC through off-situ and in-situ methods, and showed phenol uptake capacity 303 and 333 mg g⁻¹ for Cu-BTC@viscose and Cu-BTC@wool, separately. Phenolate adsorption is performed through physical hypothesis in the pores, hydrogen bonding between cellulose group, and phenol chelation with copper (II) by coordination (Figure 10) [52].

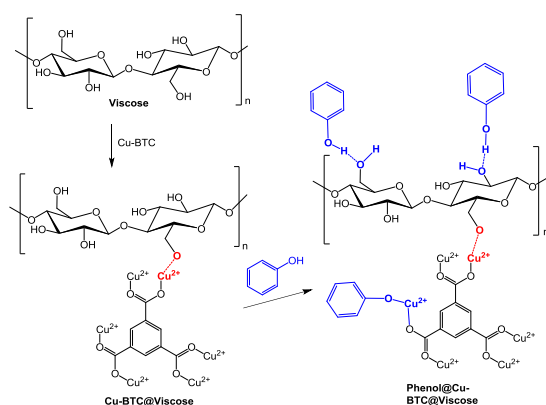


Fig. 10. Mechanism of Cu-BTC@Viscose composites formation and adsorption of phenol

5. Conclusions

As a class of versatile porous materials, MOFs have shown enormous potential for adsorption for environmental remediation and fuel purification. To efficiently remove harmful gases, it is not sufficient to use MOFs of the appropriate size/shape of the pores, and other more specific interactions between harmful adsorbents and the host are desirable. Most of the harmful gases are highly reactive. The adsorption of these gases often degrades the porous structures of MOFs. However, much progress has been made in the last few years to develop very persistent organic frameworks. Certainly more and more fundamental studies will appear in this direction, which should enhance the practical application of this type of new porous material for air purification and related fields in the future. In general, MOFs suffering from relatively poor water stability and reuse potential except for some types of MOFs such as MIL, UiO and ZIF are relatively stable in water. The big challenge is converting unstable MOFs in water to stable MOFs; this will lead to high recovery and extend its application. The author problem of MOFs is the production with Kg; therefore more studies are suggested to find the method of production on large scale. Meanwhile, studies should be done on more complex wastewater streams to simulate a real wastewater environment, which usually includes other toxic components like heavy metal ions, organic matter, aquatic biological pollutants, etc. MOFs contain multiple functional groups, conjugate bonds, and metal ions that can increase the adsorption efficiency. The adsorption capacity can be improved by incorporating the following conditions: 1) The volume-dependent reaction, in which the molecular dimension of the pollutants and the pore size of the MOFs are similar; 2) Electrostatic reaction, which can be adjusted by adjusting the surface charge of the MOFs to suit the pollutants charge; 3) The hydrogen bonding reaction, which may be enhanced by introducing oxygen-containing functional groups into the MOFs for pollutants binding (such as dyes). To understand the interactions between MOFs and pollutants is required to develop effective MOF sorbents

6. References

- [1] Q.-L. Zhu, Q. Xu, Metal-organic framework composites, *Chemical Society Reviews* 43(16) (2014) 5468-5512.
- [2] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Metal-organic framework materials as catalysts, *Chemical Society Reviews* 38(5) (2009) 1450-1459.
- [3] L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, Metal-organic framework materials as chemical sensors, *Chemical reviews* 112(2) (2012) 1105-1125.
- [4] N. Stock, S. Biswas, Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites, *Chemical reviews* 112(2) (2012) 933-969.
- [5] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keeffe, O.M. Yaghi, Hydrogen storage in microporous metal-organic frameworks, *Science* 300(5622) (2003) 1127-1129.
- [6] A. Pichon, A. Lazuen-Garay, S.L. James, Solvent-free synthesis of a microporous metal-organic framework, *CrystEngComm* 8(3) (2006) 211-214.
- [7] L.-G. Qiu, Z.-Q. Li, Y. Wu, W. Wang, T. Xu, X. Jiang, Facile synthesis of nanocrystals of a microporous metal-organic framework by an ultrasonic method and selective sensing of organoamines, *Chemical communications* (31) (2008) 3642-3644.
- [8] S.-H. Jung, J.-H. Lee, J.-S. Chang, Microwave synthesis of a nanoporous hybrid material, chromium trimesate, *Bulletin of the Korean Chemical Society* 26(6) (2005) 880-881.
- [9] R. Ameloot, L. Stappers, J. Fransaer, L. Alaerts, B.F. Sels, D.E. De Vos, Patterned growth of metal-organic framework coatings by electrochemical synthesis, *Chemistry of Materials* 21(13) (2009) 2580-2582.
- [10] A.J. Rieth, Y. Tulchinsky, M. Dincă, High and reversible ammonia uptake in mesoporous azolate metal-organic frameworks with open Mn, Co, and Ni sites, *Journal of the American Chemical Society* 138(30) (2016) 9401-9404.
- [11] Y. Chen, C. Yang, X. Wang, J. Yang, K. Ouyang, J. Li, Kinetically controlled ammonia vapor diffusion synthesis of a Zn (ii) MOF and its H₂O/NH₃ adsorption properties, *Journal of Materials Chemistry A* 4(26) (2016) 10345-10351.
- [12] J.N. Joshi, E.Y. Garcia-Gutierrez, C.M. Moran, J.I. Deneff, K.S. Walton, Engineering copper carboxylate functionalities on water stable metal-organic frameworks for enhancement of ammonia removal capacities, *The Journal of Physical Chemistry C* 121(6) (2017) 3310-3319.
- [13] Z. Zhao, S. Wang, Y. Yang, X. Li, J. Li, Z. Li, Competitive adsorption and selectivity of benzene and water vapor on the microporous metal organic frameworks (HKUST-1), *Chemical engineering journal* 259 (2015) 79-89.
- [14] D. Ma, Y. Li, Z. Li, Tuning the moisture stability of metal-organic frameworks by incorporating hydrophobic functional groups at different positions of ligands, *Chemical communications* 47(26) (2011) 7377-7379.
- [15] W.W. He, G.S. Yang, Y.J. Tang, S.L. Li, S.R. Zhang, Z.M. Su, Y.Q. Lan, Phenyl groups result in the highest benzene storage and most efficient desulfurization in a series of isostructural metal-organic frameworks, *Chemistry-A European Journal* 21(27) (2015) 9784-9789.
- [16] G.W. Peterson, J.J. Mahle, J.B. DeCoste, W.O. Gordon, J.A. Rossin, Extraordinary NO₂ Removal by the Metal-Organic Framework UiO-66-NH₂, *Angewandte Chemie* 128(21) (2016) 6343-6346.
- [17] A.M. Ebrahim, T.J. Bandoz, Effect of amine modification on the properties of zirconium-carboxylic acid based materials and their applications as NO₂ adsorbents at ambient conditions, *Microporous and mesoporous materials* 188 (2014) 149-162.
- [18] X. Cui, Q. Yang, L. Yang, R. Krishna, Z. Zhang, Z. Bao, H. Wu, Q. Ren, W. Zhou, B. Chen, Ultrahigh and selective SO₂ uptake in inorganic anion-pillared hybrid porous materials, *Advanced Materials* 29(28) (2017) 1606929.
- [19] Y. Belmabkhout, R.S. Pillai, D. Alezi, O. Shekhah, P.M. Bhatt, Z. Chen, K. Adil, S. Vaesen, G. De Weireld, M. Pang, Metal-organic frameworks to satisfy gas upgrading demands: fine-tuning the soc-MOF platform for the operative removal of H₂S, *Journal of Materials Chemistry A* 5(7) (2017) 3293-3303.
- [20] P.M. Bhatt, Y. Belmabkhout, A.H. Assen, L.J. Weseliński, H. Jiang, A. Cadiou, D.-X. Xue, M. Eddaoudi, Isoreticular rare earth fcu-MOFs for the selective removal of H₂S from CO₂ containing gases, *Chemical Engineering Journal* 324 (2017) 392-396.
- [21] A.M. Ebrahim, J. Jagiello, T.J. Bandoz, Enhanced reactive adsorption of H₂S on Cu-BTC/S-and N-doped GO composites, *Journal of Materials Chemistry A* 3(15) (2015) 8194-8204.
- [22] E. Haque, V. Lo, A.I. Minett, A.T. Harris, T.L. Church, Dichotomous adsorption behaviour of dyes on an amino-functionalised metal-organic framework, amino-MIL-101 (Al), *Journal of Materials Chemistry A* 2(1) (2014) 193-203.
- [23] Y. Jia, Q. Jin, Y. Li, Y. Sun, J. Huo, X. Zhao, Investigation of the adsorption behaviour of different types of dyes on MIL-100 (Fe) and their removal from natural water, *Analytical Methods* 7(4) (2015) 1463-1470.
- [24] X. Zhang, Y. Gao, H. Liu, Z. Liu, Fabrication of porous metal-organic frameworks via a mixed-ligand strategy for highly selective and efficient dye adsorption in aqueous solution, *CrystEngComm* 17(31) (2015) 6037-6043.
- [25] H.E. Emam, H.B. Ahmed, E. Gomaa, M.H. Helal, R.M. Abdelhameed, Recyclable photocatalyst composites based on Ag₃VO₄ and Ag₂WO₄@ MOF@ cotton for effective discoloration of dye in visible light, *Cellulose* (2020) 1-17.
- [26] R.M. Abdelhameed, M. El-Shahat, Fabrication of ZIF-67@ MIL-125-NH₂ nanocomposite with enhanced visible light photoreduction activity, *Journal of Environmental Chemical Engineering* 7(3) (2019) 103194.
- [27] R.M. Abdelhameed, M. El-Shahat, H.E. Emam, Employable metal (Ag & Pd)@ MIL-125-NH₂@ cellulose acetate film for visible-light driven photocatalysis for reduction of nitroaromatics, *Carbohydrate Polymers* 247 (2020) 116695.
- [28] R.M. Abdelhameed, M. Abu-Elghait, M. El-Shahat, Hybrid three MOFs composites (ZIF-67@ ZIF-8@ MIL-125-NH₂): Enhancement the biological and visible-light photocatalytic activity, *Journal of Environmental Chemical Engineering* (2020) 104107.
- [29] H. Abdel-Gawad, R. Abdelhameed, A. Elmesalamy, B. Hegazi, Distribution and elimination of 14C-ethion insecticide in chamomile flowers and oil, Phosphorus, Sulfur, and Silicon and the Related Elements 186(10) (2011) 2122-2134.
- [30] R. Abdelhameed, F. Mahdy, H. Abdel-Gawad, B. Hegazi, Green process for adsorptive removal of ethion (O, O', O', O'-tetraethyl S, S'-methylene bis (phosphorodithioate) from agricultural wastewater using modified surface of orange peel and apricot kernel, *Egyptian Journal of Chemistry* 63(10) (2020) 2-3.
- [31] R.M. Abdelhameed, M. El-Zawahry, H.E. Emam, Efficient removal of organophosphorus pesticides from wastewater

- using polyethylenimine-modified fabrics, *Polymer* 155 (2018) 225-234.
- [32] R.M. Abdelhameed, M. Taha, H. Abdel-Gawad, B. Hegazi, Amino-functionalized Al-MIL-53 for dimethoate pesticide removal from wastewater and their intermolecular interactions, *Journal of Molecular Liquids* (2020) 114852.
- [33] Z. Hasan, S.H. Jung, Removal of hazardous organics from water using metal-organic frameworks (MOFs): plausible mechanisms for selective adsorptions, *Journal of hazardous materials* 283 (2015) 329-339.
- [34] N.A. Khan, Z. Hasan, S.H. Jung, Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs): a review, *Journal of hazardous materials* 244 (2013) 444-456.
- [35] Y.S. Seo, N.A. Khan, S.H. Jung, Adsorptive removal of methylchlorophenoxypropionic acid from water with a metal-organic framework, *Chemical Engineering Journal* 270 (2015) 22-27.
- [36] B.K. Jung, Z. Hasan, S.H. Jung, Adsorptive removal of 2, 4-dichlorophenoxyacetic acid (2, 4-D) from water with a metal-organic framework, *Chemical engineering journal* 234 (2013) 99-105.
- [37] X. Zhu, B. Li, J. Yang, Y. Li, W. Zhao, J. Shi, J. Gu, Effective adsorption and enhanced removal of organophosphorus pesticides from aqueous solution by Zr-based MOFs of UiO-67, *ACS applied materials & interfaces* 7(1) (2015) 223-231.
- [38] C. De Smedt, P. Spanoghe, S. Biswas, K. Leus, P. Van Der Voort, Comparison of different solid adsorbents for the removal of mobile pesticides from aqueous solutions, *Adsorption* 21(3) (2015) 243-254.
- [39] A. Vishnyakov, P.I. Ravikovitch, A.V. Neimark, M. Bülow, Q.M. Wang, Nanopore structure and sorption properties of Cu-BTC metal-organic framework, *Nano Letters* 3(6) (2003) 713-718.
- [40] G.-T. Bae, B. Dellinger, R.W. Hall, Density Functional Calculation of the Structure and Electronic Properties of Cu_nO_n (n= 1– 8) Clusters, *The Journal of Physical Chemistry A* 115(11) (2011) 2087-2095.
- [41] R. Abdelhameed, H. Abdel-Gawad, C. Silva, J. Rocha, B. Hegazi, A. Silva, Kinetic and equilibrium studies on the removal of 14 C-ethion residues from wastewater by copper-based metal-organic framework, *International Journal of Environmental Science and Technology* 15(11) (2018) 2283-2294.
- [42] R.M. Abdelhameed, H. Abdel-Gawad, M. Elshahat, H.E. Emam, Cu-BTC@ cotton composite: design and removal of ethion insecticide from water, *Rsc Advances* 6(48) (2016) 42324-42333.
- [43] R.M. Abdelhameed, M. Taha, H. Abdel-Gawad, F. Mahdy, B. Hegazi, Zeolitic imidazolate frameworks: Experimental and molecular simulation studies for efficient capture of pesticides from wastewater, *Journal of Environmental Chemical Engineering* 7(6) (2019) 103499.
- [44] K.A. Cychosz, A.J. Matzger, Water stability of microporous coordination polymers and the adsorption of pharmaceuticals from water, *Langmuir* 26(22) (2010) 17198-17202.
- [45] B. Wang, X.-L. Lv, D. Feng, L.-H. Xie, J. Zhang, M. Li, Y. Xie, J.-R. Li, H.-C. Zhou, Highly stable Zr (IV)-based metal-organic frameworks for the detection and removal of antibiotics and organic explosives in water, *Journal of the American Chemical Society* 138(19) (2016) 6204-6216.
- [46] R.M. Abdelhameed, H.E. Emam, Design of ZIF (Co & Zn)@ wool composite for efficient removal of pharmaceutical intermediate from wastewater, *Journal of colloid and interface science* 552 (2019) 494-505.
- [47] B. Von Oepen, W. Kördel, W. Klein, Sorption of nonpolar and polar compounds to soils: processes, measurements and experience with the applicability of the modified OECD-Guideline 106, *Chemosphere* 22(3-4) (1991) 285-304.
- [48] Y. Ma, N. Gao, W. Chu, C. Li, Removal of phenol by powdered activated carbon adsorption, *Frontiers of Environmental Science & Engineering* 7(2) (2013) 158-165.
- [49] H.E. Emam, F.H. Abdellatif, R.M. Abdelhameed, Cationization of cellulose fibers in respect of liquid fuel purification, *Journal of Cleaner Production* 178 (2018) 457-467.
- [50] X. Yan, X. Hu, T. Chen, S. Zhang, M. Zhou, Adsorptive removal of 1-naphthol from water with Zeolitic imidazolate framework-67, *Journal of Physics and Chemistry of Solids* 107 (2017) 50-54.
- [51] K.-Y.A. Lin, H.-A. Chang, Ultra-high adsorption capacity of zeolitic imidazole framework-67 (ZIF-67) for removal of malachite green from water, *Chemosphere* 139 (2015) 624-631.
- [52] R.M. Abdelhameed, H.E. Emam, J. Rocha, A.M. Silva, Cu-BTC metal-organic framework natural fabric composites for fuel purification, *Fuel Processing Technology* 159 (2017) 306-312.
- [53] R.M. Abdelhameed, M. Rehan, H.E. Emam, Figuration of Zr-based MOF@ cotton fabric composite for potential kidney application, *Carbohydrate polymers* 195 (2018) 460-467.
- [54] J.E. Efome, D. Rana, T. Matsuura, C.Q. Lan, Insight studies on metal-organic framework nanofibrous membrane adsorption and activation for heavy metal ions removal from aqueous solution, *ACS applied materials & interfaces* 10(22) (2018) 18619-18629.
- [55] J.E. Efome, D. Rana, T. Matsuura, C.Q. Lan, Metal-organic frameworks supported on nanofibers to remove heavy metals, *Journal of Materials Chemistry A* 6(10) (2018) 4550-4555.
- [56] J. Li, X. Wang, G. Zhao, C. Chen, Z. Chai, A. Alsaedi, T. Hayat, X. Wang, Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions, *Chemical Society Reviews* 47(7) (2018) 2322-2356.
- [57] M. El-Shahat, A.E. Abdelhamid, R.M. Abdelhameed, Capture of iodide from wastewater by effective adsorptive membrane synthesized from MIL-125-NH₂ and cross-linked chitosan, *Carbohydrate Polymers* 231 (2020) 115742.
- [58] H.E. Emam, H.B. Ahmed, H.R. El-Deib, F.M. El-Dars, R.M. Abdelhameed, Non-invasive route for desulfurization of fuel using infrared-assisted MIL-53 (Al)-NH₂ containing fabric, *Journal of colloid and interface science* 556 (2019) 193-205.
- [59] H.E. Emam, A.E. Abdelhamid, R.M. Abdelhameed, Refining of liquid fuel from N-Containing compounds via using designed Polysulfone@ Metal organic framework composite film, *Journal of cleaner production* 218 (2019) 347-356.
- [60] R.M. Abdelhameed, H.R. el-deib, F.M. El-Dars, H.B. Ahmed, H.E. Emam, Applicable strategy for removing liquid fuel nitrogenated contaminants using MIL-53-NH₂@ natural fabric composites, *Industrial & Engineering Chemistry Research* 57(44) (2018) 15054-15065.