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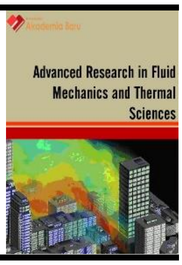

The Application of Ferric-Metal-Organic Framework for Dye Removal: A Mini Review

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ABSTRACT

Dye effluent released from the industries is one of the most severe environmental concerns due to their potential adverse effects on human health. There are many obstacles encountered in degrading dye materials as they are not only very stable to light and heat but also resistant to biodegradation and oxidation reactions. Currently, porous metal-organic frameworks (MOFs), an important class of advanced functional materials due to its novel coordination structures and diverse topologies, have shown potential applications in various fields, including dye removal. Among the highly water stable MOFs, Ferric-based MOFs like iron (III) trimesate, which is also known as MIL-100(Fe), is favorably ascribed by its simple synthesizing method as well as its wide availability. Herein, this paper summarized the recent progress achieved by MIL-100(Fe) in removing different types of dye, together with its sustainable preparation method.

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1. Introduction

Synthetic dyes are valuable in numerous industries, including paper printing, leather, textile, cosmetics, food, and pharmaceutical. However, effluents released from the industries becoming ubiquitous sources of environmental pollution, and their existence has severely affected the aquatic organisms and life cycle. According to statistics, there are currently more than 10,000 types of dyes for commercial purposes, and the yearly output of dyes exceeds 700,000 tons, of which about 10-15% is released into the environment [1]. With growing concerns regarding a clean environment and human health, technologies with high efficiency and low cost to reduce the pollutant contents of wastewater are urgently needed. To date, various methods have been developed to remove dyes

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from aqueous solutions, including biodegradation, photodegradation, and adsorption. The adsorption method is attractive for the removal of dyes because dyes are not only moderately stable to light and heat, but also resistant to oxidation and biodegradation. Besides, the adsorption technique works effectively without the need for additional pretreatment before its application. Though low-cost sorbent material like carbon has been used widely for the adsorption and removal of dyes, the adsorption capacity is quite limited [2]. Thus, it is still a great significance to discover new materials for efficient adsorption for the removal of dyes.

On the other hand, metal-organic-frameworks (MOFs) are a fascinating class of porous crystalline materials self-assembled from metal ions and polyfunctional organic ligands. They have attracted significant research interest in recent years because of their unique characters such as diverse structure topology, tunable pore size, permanent nanoscale porosity, high surface area, good thermostability, and uniform structured cavities [3]. There are growing potential applications of MOFs in recent years, including MOFs intriguing in catalysis [4], gas purification [5,6], selective adsorption [7,8], gas storage [9], and drug delivery [10]. Among known MOFs, ferric-based MOFs like MIL-100(Fe) (MIL stands for Material of Institute Lavoisier) has high-temperature stability, remarkable chemical resistance, unsaturated metal centers with Lewis acid and redox properties, a simple synthesizing method as well as its wide availability of linker and metal sources [9,10], made it the best candidate to be used for wastewater treatment.

Generally, MIL-100(Fe) is generated by coordination self-assembly of Fe (III) octahedral trimmers and trimesic acids (BTC) into hybrid super-tetrahedra (ST), which assemble, giving rise to a rigid micro-mesoporous zeotypic-like structure. It possesses two types of mesoporous cages were ~25Å and 29Å in polyhedral shape, in which small cages (SC) accessible through pentagonal windows of 5.5Å and large cages (LC) also delimited by the bigger hexagonal opening of 8.6Å, as described in Figure 1(a). MIL-100(Fe) has a polyhedron shape (Figure 1(b)), and an average crystal size less than 1µm with BET specific surface areas and pore volumes ranged from 2500 to 4500 m^2/g and from 1.2 to 2.0 cm^3/g, respectively [9,11-12].

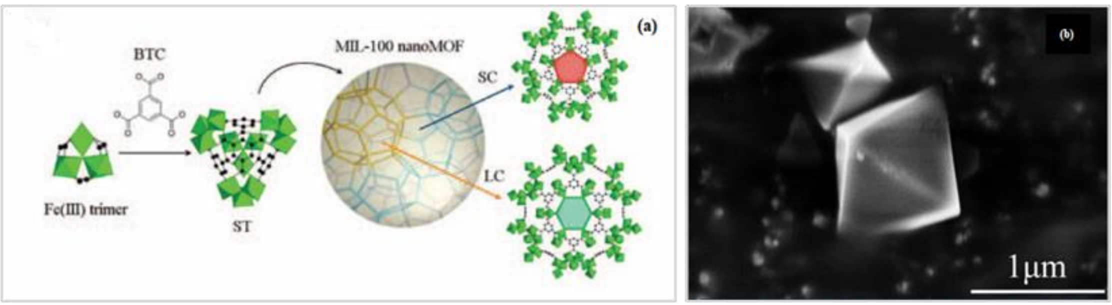

Fig. 1. (a) Illustration of self-assembly coordination and (b) SEM image of MIL-100(Fe) [15]

As MIL-100(Fe) is iron-based metal, it is more suitable for industrial use in comparison with copper, cobalt, or chromium-based materials regarding the toxicity of the metal towards water and microorganism has made it become a quite attractive MOFs material for dye wastewater treatment [14]. Moreover, increasing scientific research of MIL-100(Fe)-based material over the past few years, in which mainly discussing several topics including its unique physicochemical properties, preparation methods, and promising material to be used in the wastewater treatment process, as shown in Figure 2.

A couple of papers have reviewed the MIL-series for different applications in general [14,15]. However, there is still no paper mainly reviewed on MIL-100(Fe) for dye removal application. Herein, this mini-review summarized the recent progress achieved by MIL-100(Fe) in removing dyes from aqueous solution, and briefly reviewed the preparation of MIL-100(Fe) on improving its sustainability from the conventional process. This paper may provide insights and ideas for researchers who are looking for new hybrid materials, especially in MIL-100(Fe)-based nanostructured, to address the emerging environmental challenge.

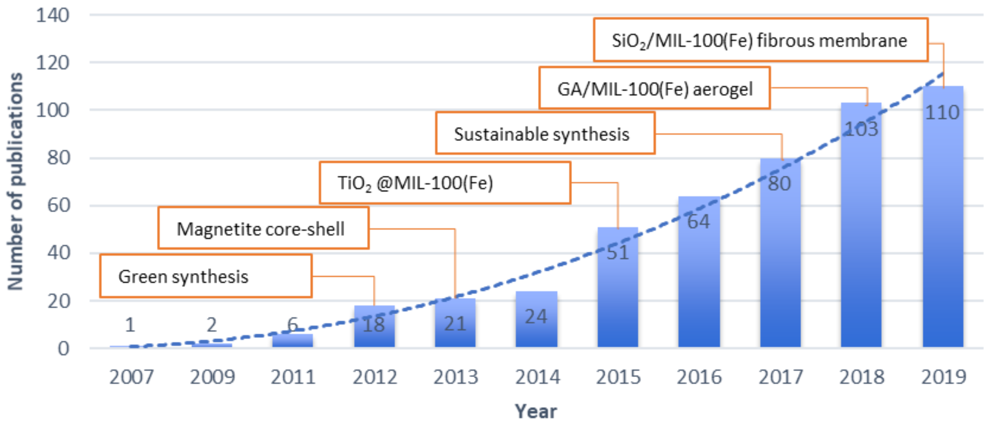

Fig. 2. Growth of research activity of MIL-100(Fe) over the years [Data extracted from the Web of Science database up to December 2019]

2. Development of Sustainable Preparation of MIL-100(Fe)

The versatility of MOFs does not only become extraordinarily broad in its physicochemical properties such as porosity, structures, and composition but also a variety of methodologies are available to prepare the material. As such, from fundamental understanding and practical application perspectives, the development of a simple method for MOF synthesis is still a challengeable topic over the past few years.

Horcajada *et al.,* [11] reported the first MIL-100(Fe) preparation method taken from the MIL-100(Cr) synthesizing method via hydrothermal treatment with the presence of environmentally harmful and corrosive acids like hydrofluoric acid (HF) and nitric acid (HNO_3). This method resulting in a very acidic (pH less than 1) mixture throughout the synthesis, and therefore the recovered solid product required tedious washing steps. Moreover, this hydrothermal method possesses other limitations, such as high synthesis temperature, long synthesis duration, and low product yield in combination with the synthesis conducted at autogenously high pressure.

After that, some research has already shown the efforts to find a green synthesis path with great efficiency by at least avoiding the use of corrosive acids [16-19]. Márquez *et al.,* [18] prepared MIL-100(Fe) via a microwave-assisted solvothermal route with green solvents. Despite the effort, it is an unattractive approach due to a low yield of the obtained product makes it difficult for practical use. Besides that, Zhang *et al.,* [20] reported mesoporous MIL-100(Fe) could be synthesized by a simple unappreciated low-temperature (<100°C) route via the reaction of ferric nitrate and trimesic acid under HF-free conditions. Apart from preparation conditions at room temperature, Sanchez *et al.,* [21] reported semi-amorphous Fe-BTC could be synthesized in the absence of HF, water as the solvent, and a base NaOH as the deprotonating agent of the linker. However, this method gives the resultant suspension in the acidic range (pH 2.1), which still required post-treatment to balance the pH. Then, Duan *et al.,* [19] synthesized amorphous MIL-100(Fe) in the absence of HNO_3 or HF at 140°C for 12 hours and reported a higher yield of MIL-100(Fe) than the conventional methods. Despite the efforts for green synthesis, these methods still use high operating temperatures or need aggressive post-synthesis washing treatment, thus unfavorable for practical application.

Recently, Guesh *et al.,* [22] reported a novel synthesis method that modifies from Sanchez *et al.,* [21] and claimed to be the most sustainable and straightforward method for the preparation of high-quality MIL-100(Fe) nanoparticles. Although both ways conduct under similar parameters, the only distinction causing the different crystallinity formation was the use of Fe(II) salts instead of Fe(III) as iron sources. As a result, this method gives a mixture of pH around 5, which is less acidic, thus does not require any aggressive post-synthesis washing treatment at high temperatures—moreover, this simple approach resulting in 76% of the final product, which is considered practicable.

As a summary for this subtopic, the ideal sustainable preparation of MOFs would include the absence of harmful solvents and corrosive reactants, the use of inexpensive solvents, conducted at room temperature, short synthesis times, non-generation of any harmful by-products, or avoiding long and aggressive post-synthesis washing to purify the product. Further research still needs to be done in synthesizing high-quality MIL-100(Fe) with a sustainable method that gives a higher yield of the product. In short, the development of a cheap, simple, and environmentally friendly approach to synthesis MIL-100(Fe)-based material on a large scale for practical applications is the goal towards worldwide sustainability.

3. Recent Progress of MIL-100(Fe) on Dyes Removal Application

Owing to two sets of mesoporous cages that are accessible through microporous windows and corresponding large Langmuir surface area, MIL-100(Fe) has received significant attention concerning its dye adsorption. However, a single adsorption process with MIL-100(Fe) often brings some problems that the contaminants may not be removed entirely because of the adsorption equilibrium [23], and difficult regeneration of MIL-100(Fe) due to their fragile framework [24]. Several modification techniques have used to enhance the properties of MOFs material in water adsorption; (1) modifying the organic ligands with functionalized groups can improve the adsorption behavior of MOFs material towards specified contaminants, (2) altering the pore size and structures of MOFs can attain selective adsorption performance by using different organic linkers or preparation techniques, (3) another modification method is to compound MOFs with other materials to create MOF-based composites that not only limit the drawbacks of MOFs but also achieve synergistic properties. Herein, this paper reviewed the recent progress of MIL-100(Fe) incorporated with other materials, like titanium dioxide (TiO_2), magnetite (Fe_3O_4), graphene aerogel, or silica membrane, to form nanocomposites for different applications in achieving a deep removal of dyes in aqueous solution.

3.1 Photocatalyst

The organic linkers and transition metal centers in MOFs result in the different ligand-to-metal charge transfer transitions, which make it an efficient photocatalyst [24–27]. Also, MIL-100(Fe) has proved to be a promising compound for photocatalytic performance because Fe^{3+} and O^{2-} clusters can be quickly excited by visible irradiation [29]. Unfortunately, low efficient excitons generation and charge separation of MIL-100(Fe) lead to low quantum efficiency in photocatalytic reactions [30]. However, MOFs are commonly known for their highly tunable bandgap due to its huge compositional and structural versatility [21, 30-31]. Thus, it could be a plausible strategy to improve the quantum efficiency of MIL-100(Fe) employing the incorporation of MIL-100(Fe) with other materials like semiconductor TiO_2, magnetite Fe_3O_4, and graphitic carbon nitride (g-C_3N_4). Unmodified MIL-100(Fe) photocatalyst is usually able to degrade around 60% of 50mg/L dyes in aqueous solution at pH 5 under visible light irradiation within 180 min [33]. In comparison, incorporation with other materials improved the removal efficiency up to 100% in the same conditions within 100 min, as shown in Table 1. Notably, a synergistic effect between MIL-100(Fe) and other nanomaterials enhanced photocatalytic performance, mainly attributed to the high separation efficiency of photo-induced electrons from the lowest unoccupied molecular orbital (LUMO) of other materials injected into the MOF cages of MIL-100(Fe) matrix [34].

Table 1
Recent modification of MIL-100(Fe) as photocatalyst

Material	Synthesis method	Operating condition	Band gap (eV)	Dye	% Removal	Ref.
Nanosheet TiO_2/ MIL-100(Fe)	Step-by-step self-assembly method.	Vis light, 150 min	2.52	MB	100	[35]
N-doped TiO_2 @MIL-100(Fe)	Self-assembly chemical precipitation.	Vis light, 80 min	2.50	MB, Rh B	99.1, 93.5	[36]
MIL-100(Fe)/ Titania Nanofiber	Sustainable, Chemical precipitation	Vis light, 150 min	2.53	MB	99.4	[37]
MIL-100(Fe) @Bi_2S_3	Hydrothermal	Vis light, 60 min	2.00	Rh B	94	[38]
Protonated g-C_3N_4 coated MIL-100(Fe)	*In situ* protonation and coating	Vis light, 100 min	2.64	MB, Rh B	100, 100	[39]
Amberlite IRA200 @FeBTC	Chemical precipitation	Vis light, 60 min	2.31	Rh B	88.8	[25]
CNNS/MIL-100(Fe)	Two-step calcination-exfoliation, solvothermal	Presence of H_2O_2, Vis light, 4h	2.88	Rh B	100	[34]
Fe_3O_4@MIL-100(Fe)	Solvothermal	Vis light, 200 min	-	MB	99.77	[40]

Note: MB is methylene blue; Rh B is Rhodamine B

Taking an example of photocatalysis by nanosheet-TiO_2@MIL-100(Fe) nanocomposite, the basic mechanism during the photodegradation of dyes over hybrid photocatalyst proposed by Liu and coworkers is illustrated in Figure 3 [35]. The photo-excited electrons (e^-) transfer from the valence band to the conduction band on MIL-100(Fe), and holes (h^+) are produced in MIL-100(Fe)'s valence band. In addition, photo-excited electrons (e^-) transfer from the conduction band of MIL-100(Fe) to that of nanosheet-TiO_2 through the interaction between nanosheet-TiO_2 and MIL-100(Fe), which suppresses the recombination of photogenerated electron-hole pairs and improves the efficiency of photocatalytic activity. The photo-excited holes (h^+) in the valence band of MIL-100(Fe) reacts directly with H_2O/OH^- to generate hydrogen peroxide (•OH). As such, both the photogenerated holes (h^+) and the formed •OH can directly oxidize the adsorbed organic molecules.

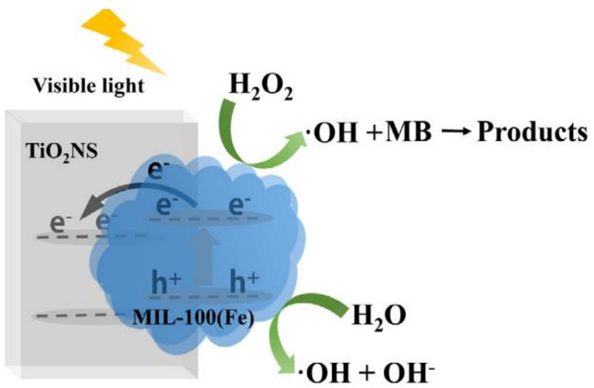

Fig. 3. Photodegradation mechanism of MB by nanosheet-TiO_2@MIL-100(Fe) nanocomposite [35]

3.2 Adsorbent

Standalone MIL-100(Fe) adsorbent required tedious and laborious centrifugation both in preparation and applications limits its practical applications. To solve this problem, considerable efforts have been made in the past few years to incorporate Fe_3O_4 nanoparticles with MOFs for dye removal due to its properties, including high saturation magnetization, biocompatibility, and low toxicity to microorganisms [40,41]. Several published research synthesized Fe_3O_4@MIL-100(Fe) core-shell adsorbent to remove dye from aqueous solution and proved that the hybrid adsorbent could be easily collected and recycled by a magnetic field due to its super-magnetic characteristic, as shown in Figure 4. These adsorbents achieved maximum adsorption towards dyes around 221 mg/g up to 625 mg/g and retained 96% of removal efficiency after six cycles, in comparison to pristine MIL-100(Fe) adsorbent [22,42–44]. Liu *et al.,* [46] studied the adsorption behavior of Fe_3O_4@MIL-100(Fe) in terms of adsorption isotherm, kinetics, and thermodynamics. They highlighted that it followed Freundlich isotherm and pseudo-second-order and has a spontaneous endothermic reaction.

Fig. 4. Schematic diagram of dye removal by Fe_3O_4@MIL-100(Fe) core-shell

Additional to that, Fan *et al.,* [47] reported hybrid nanocomposite by immobilization of Fe_3O_4@MIL-100(Fe) core-shell on *P. putida* bacteria cells via a carbon-diimide cross-linking method, as illustrated in Figure 5. This hybrid adsorbent degrades dyes completely by following a pseudo-second-order model within 5h at an initial dye concentration of 25mg/L, which is attributed to the synergistic process of adsorption coupled with biodegradation. Apart from it can be easily separated from the solution; this bio-adsorbent may have excellent potential to be applied in real industrial wastewater treatment.

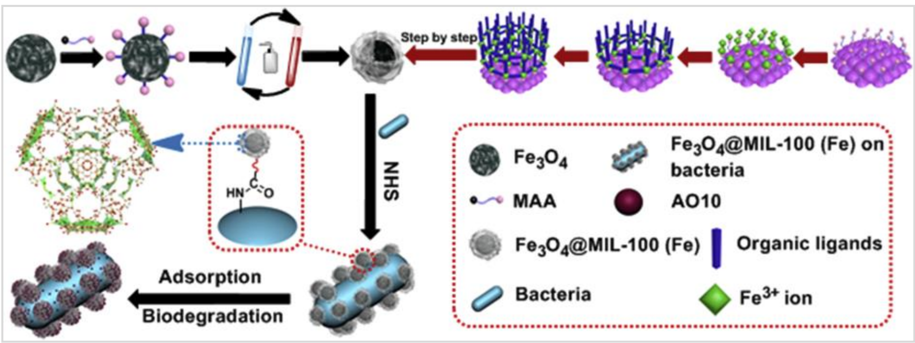

Fig. 5. Schematic diagram of preparation hybrid bio-adsorbent [47]

3.3 Aerogel

Even though MIL-100(Fe)-based photocatalyst or adsorbent could be a promising nanocomposite to degrade dyes by significant researches over the years, however, the powdered crystalline state limits the industrial applicability of MOFs due to the technical challenges of powders such as poor handling and mass transfer limitations [47,48]. On the other hand, graphene aerogel inherits the properties of graphene, especially having the structure of a macro-material body, high accessible surface areas, and tunable macropores, and thus have attracted significant attention in adsorption. Thus, hybrid aerogel MIL-100(Fe)/GA seems to be a great potential to solve the issue.

Wan *et al.,* [49] reported an *in-situ* decoration procedure to load MIL-100(Fe) on the graphene aerogel to form nanocomposite, a three-dimensional hybrid aerogel, where the synergetic effect of catalysis by MIL-100(Fe) and adsorption by graphene aerogel took place, as shown in Figure 6. Initially, MIL-100(Fe)/GA aerogel adsorbed MB from aqueous solution, then catalyzed the degradation of MB by the activation of H_2O_2. It has achieved maximum adsorption capacity up to 3333.33 mg/g, in comparison with MIL-100(Fe)-based adsorbent, via a pseudo-second-order adsorption process and pseudo-first-order catalytic degradation kinetics. They highlighted that it has the capability to remove highly concentrated pollutants without leaving secondary pollution and retained 93.4% of its removal efficiency after five consecutive cycles. The excellent regeneration of this macro-material body with a sponge-like shape promotes the stability of hybrid aerogel and contributes to the development of reusable water treatment materials.

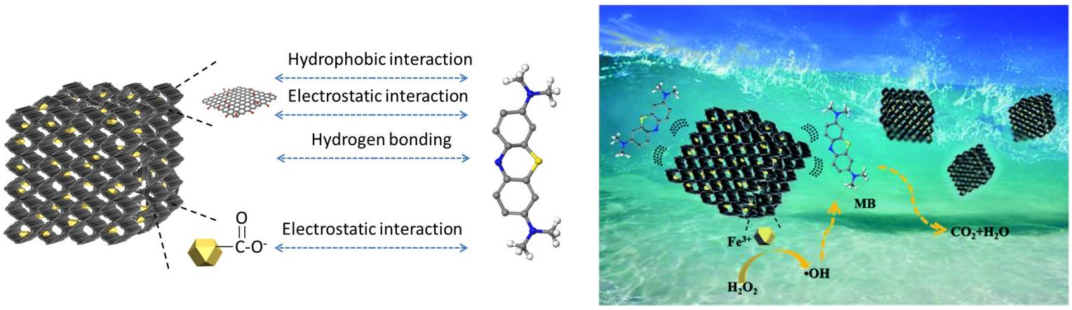

Fig. 6. Illustration of the synergistic adsorption-catalysis coupled process of MB removal by MIL-100(Fe)/GA [49]

3.4 Hybrid Membrane

The powder state of the adsorbent or catalyst is not conducive to recycling due to the submicron or micron size of MOF particles, which usually led to a time-consuming and high-cost recycling process. In order to develop more effective MIL-100(Fe)-based materials for dye removal, the construction of MIL-100(Fe) supported fibrous membrane is one of the optional methods. Besides, this hybrid membrane offers not only separation but also adsorption coupled with photocatalytic properties simultaneously, making it the most suitable approach to be applied for treating industrial dye effluent. Chang *et al.,* [50] fabricated a flexible-structured SiO_2/MIL-100(Fe) fibrous membrane via immobilization of MIL-100(Fe) on the SiO_2 fiber surface (Figure 7) for RhB dye degradation under visible light irradiation. This hybrid photocatalytic membrane possesses a 12.6 times larger specific surface area of 79.11 m^2/g than that of other reported fibrous membranes, which enhanced dye degradation up to 95% within 70 min irradiation with a reaction rate constant of 0.05 min^{-1}. They claimed the membrane could be washed with deionized water only after each photocatalysis reaction and ready to be used for the next cycle. Besides, the photocatalytic activity remained above 80% within 90 min illumination after three cycles. These results have proven the reusability and stability of SiO_2/MIL-100(Fe) fibrous membrane than can be potentially applied in larger-scale water treatment.

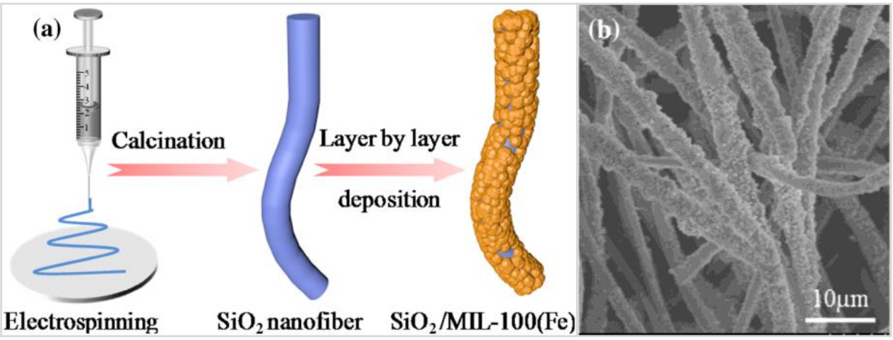

Fig. 7. Fabrication steps (a) and SEM image(b) of SiO_2/MIL-100(Fe) fibrous membrane [50]

MIL-100(Fe) has excellent capability in dyes removal; however, the hydrophobic nature of MIL-100(Fe) limits the development of MIL-100(Fe)-based membrane [51]. Recently, Cho *et al.,* [52] modified MIL-100(Fe) by doping it with chitosan, then employed to PVDF matrix to enhance an antibacterial property, as shown in Figure 8. Apart from improved antibacterial effect, they claimed that the composite of chitosan-MIL-100(Fe) also enhanced hydrophilicity properties of the membrane, thus improving water flux up to 18%, in comparison to pristine PVDF and PVDF/MIL-100(Fe) membranes. This may due to deacetylated chitosan has enriched functional groups including hydroxyl (OH) and amino (NH_2) groups; indirectly, it provides extremely high hydrophilicity to MIL-100(Fe) and facilitates a form of bonding with bacteria cells [53]. The excellent dual properties of PVDF/chitosan-MIL-100(Fe) composite membrane enabled the much higher biofouling resistance (J_W/J_{Wo} = ca. 0.85) compared to PVDF membrane (J_W/J_{Wo} = ca. 0.51) after 24 h operation in the crossflow system with the E. *coli* broth feed solution.

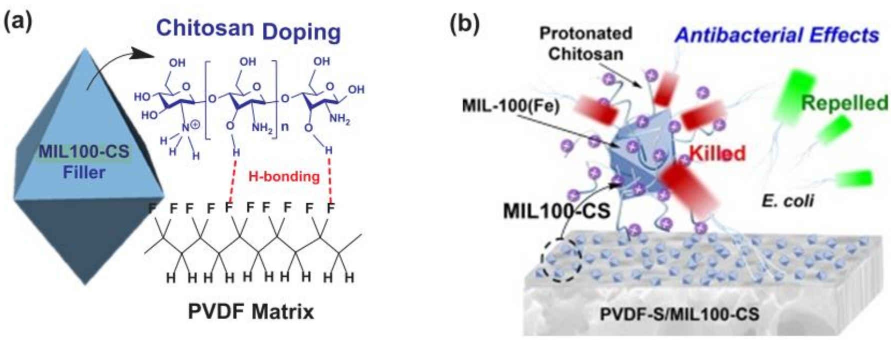

Fig. 8. Schematic diagram of PVDF/MIL-100(Fe)-CS [52]

4. Limitation and Future Perspective

The above-mentioned studies indicate that the unique pore structure of MIL-100(Fe) and its incorporation with other materials contribute to the development of water treatment materials. Hybrid adsorbent, aerogel, and membrane solve the problem of that standalone powdered-MIL-100(Fe) photocatalyst and adsorbent, in terms of reusability and recyclability. Among that, the hybrid membrane is a promising material to be applied for industrial wastewater treatment. However, the use of MIL-100(Fe)-based membrane for efficient water treatment is a new and far-reaching area. In addition, from the reviewed literature, the development of MIL-100(Fe)-based membrane lags behind despite its aforementioned advantages. This may occur due to the hydrophobic nature of MIL-100(Fe) itself. Thus, improving the hydrophilic properties of MIL-100(Fe) could indirectly enhance the compatibility of MIL-100(Fe) and nanocomposite membrane for water treatment applications.

Besides that, MIL-100(Fe) shown a positive outcome in dye removal, however, the fabrication methods and testing are still at the laboratory scale, and their readiness for commercialization is in its infancy. Challenges arise when scaling up the technology from lab-scale to industrial-level processes. This can be overcome by testing in real wastewater from industries and employing more realistic conditions to analyses the practicability of MIL-100(Fe)-based materials in treating dye effluents. With continuous research, it is possible to evaluate the effectiveness of MIL-100(Fe)-based materials on a large scale, including long-term stability of the materials under a practical application.

5. Conclusions

This paper has reviewed the development of a simple and environmentally friendly method conducted at room temperature with the absence of harmful solvents and corrosive reactants, and a simple washing step to synthesis MIL-100(Fe) or known as a sustainable method. Besides that, this paper reviewed the incorporation of MIL-100(Fe) with other materials such as TiO_2, Fe_3O_4, GA, or SiO_2, to form nanocomposites for different applications in achieving a deep removal of dyes in aqueous solution. Despite having intrinsic properties as a standalone material, incorporating MIL-100(Fe)-based material with other materials, forming MOFs nanocomposite materials with superior properties, as well improving the limitations possessed by pristine MIL-100(Fe). In conclusion, MIL-100(Fe)-based material may contribute to the great potential application for water treatment in the future due to its advantages, as mentioned earlier.

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