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Preparation of Metal-Organic Framework Materials and Their Adsorption Performance for Methylene Blue in Wastewater Treatment

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Abstract. The rapid development of industry in China has improved economic levels but also led to severe environmental pollution. Water contamination ranks among the planet's three most critical environmental crises and has remained a persistent priority for scientists, regulators, and the public alike. Colored organic dyes discharged from industries such as textiles and printing are toxic and difficult to degrade, posing risks to human health and causing serious damage to the ecosystem. This work systematically synthesizes the MIL-68(In) family and maps how pendant functional groups perturb the framework, quantifying changes in BET area, micropore volume, and overall crystallinity. The adsorption performance of both unmodified and modified MIL-68(In) materials for methylene blue (MB) in industrial wastewater was examined. Core work was carried out in four stages. (1) Crystalline MIL-68(In) and its amino derivative were prepared under solvothermal conditions. (2) The products were analysed by powder XRD, nitrogen physisorption, SEM/TEM imaging and FT-IR to establish phase purity, porosity, particle shape and surface chemistry; the effect of reaction temperature, time and precursor ratio on framework formation was also mapped. (3) Three sorbents—pristine MOF, NH_2-tagged MOF and thiol–carboxyl-enriched MOF (MIL-68(In)-SC)—were screened for the removal of the cationic dye methylene blue. (4) Equilibrium tests revealed that the engineered thiol–carboxyl variant outperformed the parent solids, giving 96.6 % uptake within 2 h and a Langmuir capacity of 204 mg g^{-1}, roughly double that of the unmodified material. The findings demonstrate that MIL-68(In)-SC has practical application value for adsorbing MB from wastewater.

Keywords: *Metal-organic frameworks; wastewater; adsorption; methylene blue*

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1 Introduction

Colorants are extensively utilized across textile, paper, leather, and printing sectors. With increasing demands for product variety and high added-value, new types of dyes and auxiliaries have been introduced, leading to the discharge of large amounts of wastewater. Dye wastewater primarily originates from production and dyeing processes. During production, wastewater containing sulfonation, nitration, acylation, and diazotization components is generated. Dyeing processes, including washing, fixing, and dehydration, also produce significant amounts of wastewater [1]. Effluents from dyeing operations contain intricate chemical mixtures and intense color, making their remediation unusually demanding.China produces over 1,000 types of dyes [2], with annual production ranking among the highest globally. More than 10–15% of dyes are released into the environment during production and use [3–4], causing severe pollution.

Methylene blue (MB) is a common toxic aromatic dye used in printing and textiles. Its discharge into water bodies can cause discoloration, hinder aquatic life, disrupt ecological balance, and lead to symptoms such as dizziness, vomiting, shock, and tissue necrosis. It may also damage the nervous system, liver, and kidneys, with potential carcinogenic risks [5–6]. Therefore, effective reduction of MB in wastewater is urgent.

Various methods have been explored for MB treatment, including physical, chemical, and biological approaches. Physical methods, such as adsorption, membrane separation, and extraction, are often used for preliminary treatment [7]. Adsorption relies on the interaction between adsorbents and dye molecules, utilizing surface pores and internal voids to capture dyes. Chemical methods involve reactions to degrade pollutants [8], including oxidation, coagulation, and electrochemical techniques [9]. Biological methods use microbial enzymes to decompose dyes, employing aerobic, anaerobic, or combined processes [10].

MOFs are crystalline, high-porosity networks generated through the spontaneous coordination of metal nodes with multitopic organic linkers.Common metal ions include alkali, transition, and rare-earth metals [11–13], such as Al^{3+}, Cr^{3+}, Zr^{4+}, Fe^{3+}, Zn^{2+}, and In^{3+}. Organic ligands typically contain N or O, such as aromatic acids or polycarboxylic acids. A broad palette of metallic centers and linker scaffolds grants synthetic freedom, so frameworks can be blueprinted with predetermined metrics and functions.

The first MOF was synthesized by Yaghi et al. in 1995 [34], but early structures were unstable. A milestone was achieved in 1999 with MOF-5 [35], sparking interest in nano-microstructures. Since then, thousands of MOFs have been developed, offering high surface area, porosity, and tunability [17–18], with applications in gas storage, catalysis, and adsorption.

Indium-based MOFs (MIFs), pioneered by Férey's group, use trivalent metals (e.g., Al, Fe, Cr) and ligands like terephthalic acid or trimesic acid. They exhibit high surface area, stability, and well-defined pores. This study prepares MIL-68(In) and NH_2-MIL-68(In) via solvothermal synthesis, modifies MIL-68(In) with sodium citrate, and evaluates their adsorption performance for MB.

2 Materials and methods

2.1 Synthesis of MIFs

Indium nitrate hydrate and terephthalic acid were dissolved in DMF, transferred to a Teflon-lined vessel, and kept at 100 °C for two days. The resulting solid was recovered by centrifugation, rinsed sequentially with DMF and ethanol, solvent-exchanged in ethanol for 72 h, and finally dried under vacuum at 60 °C overnight to yield a white microcrystalline product.

Amino-functionalized MIL-68(In) was obtained by a parallel route in which 2-aminoterephthalic acid replaced the pristine linker. The reaction proceeded at 125 °C for 5 h, and subsequent washing and drying delivered a light-yellow microcrystalline solid.

The thiol-carboxyl variant, MIL-68(In)-SC, was produced by introducing sodium citrate into the standard solvothermal mixture. After 30 min at 100 °C, the solid was isolated, rinsed, and dried to give a white powder.

2.2 Material Characterization

Surface area, pore volume and diameter were quantified with an Autosorb-IQ instrument following pretreatment under vacuum at 100 °C. SEM (S-4800-1) and TEM (JEOL4000) were used to observe morphology and pore structure.

2.3 Adsorption Experiments

Adsorption runs were carried out in 20 mL of methylene-blue solutions (10–300 mg L^{-1}) charged with 5 mg of sorbent and agitated at 150 rpm. Variables—contact window (0–12 h), pH (2–11), starting dye level and sorbent mass (1–11 mg)—were screened. After equilibration, aliquots were membrane-filtered and the residual MB concentration was read at λmax by UV-Vis.

3 Results and discussion

By modifying MOF materials, their structural properties can be improved. There are two types of modification methods: 1. Changing the raw materials used in synthesis or directly adding regulators during the synthesis process. Replace the matrix material with derivatives with functional groups or add regulatory substances during the synthesis process to directly synthesize the initial product of the target material. 2. After the synthesis of the matrix material, the modified initial product is prepared by introducing substances containing amino, carboxyl, sulfur, hydroxyl and other functional groups or loading metals and their oxides, and then using impregnation and other methods.

This chapter adopts the solvothermal synthesis method to prepare MIL-68 (In), explores the influence of raw material molar ratio on material synthesis, and determines the more suitable preparation conditions; Replace the organic ligand terephthalic acid with amino terephthalic acid and prepare NH2-MIL-68 (In) modified material according to the synthesis conditions of MIL-68 (In); Based on the preparation method of MIL-68 (In), sodium citrate was used as a modifier to modify the synthesized MIL-68 (In) to obtain indium based material MIL-68 (In) - SC. The optimal modifier level and loading were pinpointed by tracking changes in BET area and pore texture. A full suite of XRD, nitrogen physisorption, SEM, TEM and FT-IR measurements was then deployed to map crystal phase, porosity, morphology and surface chemistry of the parent MIL-68(In) and its amine- and citrate-engineered derivatives.

3.1 Effect of Reactant Ratio on MIL-68(In) Structure

Under the conditions of a reaction temperature of 100 ℃, a reaction time of 48h, and a certain rotational speed (1200rpm), the influence of the molar ratio of In (NO3) 2 · XH2O: H2BDC: DMF=1: (0.85~1.45): (100~200) on the synthesis structure of MIL-68 (In) was investigated. The experimental results are shown in Table 1.

Table 1 Structural Parameters of MIL-68 (In)

In(NO3)2·XH2O (mmol)	H2BDC (mmol)	DMF (mmol)	SSA (m2/g)	Pore diameter (nm)
1	1	200	700	2.15
1	1	200	754	2.18
1	1.2	200	701	2.22
1	1.5	200	664	1.96
1	1.8	200	487	2.01
1	1	200	603	2.16
1	1	200	706	1.97
1	1	200	487	2.02

According to Table 1, when the amount of DMF remains constant and the molar ratio of In (NO3) 2 · XH2O to H2BDC is adjusted between 0.85 and 1.45, the specific surface area of the synthesized material first increases and then decreases with the increase of molar ratio. The suitable molar ratio is In (NO3) 2 · XH2O: H2BDC=1:1; When the molar ratio of In (NO3) 2 · XH2O: H2BCC is maintained at 1:1 and the molar amount of DMF is between 100-200mmol, the specific surface area of the synthesized material first increases and then decreases with the increase of molar ratio. A suitable synthesis condition is when the amount of DMF is 150mmol, that is, In (NO3) 2 · XH2O: H2BCC: DMF=1:150. The MIL-68 (In) material prepared has a larger specific surface area of 743.72m2/g.

MIL-68 (In) uses hydrated indium nitrate and terephthalic acid ligands to form a material framework, while DMF acts as a solvent and template. When the amount of metal salt is constant, an increase in the amount of organic ligand will affect the length of the chain, to some extent, it will increase the pore diameter and pore volume of the synthesized material, thereby affecting the comparative surface area; During the material synthesis process, DMF molecules will fill the pores to support the material structure. Raising the solvent ratio initially widens pore channels, yet any excess that remains trapped in the framework can later clog these same voids, eroding surface area. Consequently, the reactant–solvent stoichiometry is a decisive lever for steering the final architecture.

3.2 Effect of Amino Modification on MIL-68(In) Structure

To tailor pore metrics—diameter, volume, surface area, or overall architecture—for targeted uptake tasks, well-defined MOF scaffolds are deliberately postsynthetically functionalized. Functionalization includes "pre functionalization modification" and "post synthesis modification" [21-22]. Pre functionalization modification "refers to the direct modification of organic ligands with functional groups or the modification of materials by adding templates, regulators, and other substances before material synthesis, selecting appropriate preparation conditions, and synthesizing the desired target structure. Post synthetic modification "is the process of modifying MOF materials by adding different organic compounds to the original MOF material as a matrix and conducting in-situ organic reactions to introduce the desired functional groups.

By using the method of "pre functionalization modification", the organic ligand terephthalic acid in the raw material for synthesizing MIL-68 (In) was changed to amino terephthalic acid with amino functional groups, that is, amino functional groups were introduced to obtain the modified NH2-MIL-68 (In). According to the research results in section 3.1, the molar ratio of the raw materials, namely In (NO3) 2 · XH2O: NH2-H2BDC: DMF=1:1:150, was determined under the conditions of reaction temperature of 125 ℃, reaction time of 0.5 h, and stirring speed (1200rpm). Textural data for NH_2-MIL-68(In) and the parent MIL-68(In)—BET area, pore size and pore volume—are collated for comparison in Table 2.

Table 2 Comparison of structural parameters between NH2-MIL-68 (In) and MIL-68 (In)

	SSA	V	Pore diameter (nm)
MIL-68(In)	743.72	0.42	1.96
NH2-MIL-68(In)	726.12	0.38	2.04

Table 2 reveals that grafting amino groups trims both surface area and pore volume marginally, yet produces a slight upshift in average pore diameter. This indicates that replacing the raw organic ligand directly with an organic ligand with an amino functional group does not result in significant structural changes in the synthesized material [23].

3.3 Effect of Sodium Citrate Modification on the Structure of MIL-68 (In)

The research results indicate that the NH2-MIL-68 (In) material synthesized from amino terephthalic acid containing amino functional groups has little change in specific surface area. For wastewater cleanup, a MOF needs maximal surface area and ample void space—both metrics directly amplify uptake capacity.

During the solvothermal assembly of MIL-68(In), sodium citrate was dosed as a structure-directing additive; the resulting MIL-68(In)-SC framework combined enlarged porosity with a markedly elevated BET area, allowing us to probe how subtle changes in modification protocol dictate final texture.

3.3.1 Effect of Sodium Citrate Dosage on Material Structure

Add sodium citrate solution during the synthesis process, maintain the solution concentration constant, and investigate the effect of different addition amounts on the structure of the material. The changes in structural parameters such as specific surface area, pore volume, and pore size of MIL-68 (In) - SC (1-8) materials synthesized under the conditions of sodium citrate solution concentration of 1mol/L and addition amounts of 0.1, 0.2, 0.3, 0.5, 0.7, 1, 3, and 5mL are shown in Table 3.

According to Table 3, when the concentration of sodium citrate solution is 1mol/L and the amount of modifier added ranges from 0.1 to 5 mL, the specific surface area of the synthesized material increases first and then decreases with the amount of sodium citrate, reaching a maximum of 994.42m2/g; The pore volume of synthetic materials increases first and then decreases with the amount of sodium citrate solution used; The pore size first decreases and then increases with the increase of sodium citrate solution dosage. Based on comprehensive comparative analysis, the appropriate conditions for the synthesis process are the addition of 0.2mL 1mol/L sodium citrate solution. The as-synthesized solid delivers a BET area of 994 $m^2 g^{-1}$ and a pore volume of 0.52 $cm^3 g^{-1}$—both metrics exceeding those of the parent framework.

Table 3 Structural parameters of synthesized MIL-68 (In) - SC

	Modifier V/mL	S_{BET}/(m^2/g)	V/ (cm^3/g)	D/nm
MIL-68(In)-SC-1	0.1	905.73	0.47	2.01
MIL-68(In)-SC-2	0.2	994.42	0.52	1.66
MIL-68(In)-SC-3	0.3	953.33	0.51	1.68
MIL-68(In)-SC-4	0.5	368.68	0.49	1.73
MIL-68(In)-SC-5	0.7	289.77	0.45	2.77
MIL-68(In)-SC-6	1	154.92	0.39	3.12
MIL-68(In)-SC-7	3	106.22	0.32	3.52
MIL-68(In)-SC-8	5	24.8	0.11	3.57

3.3.2 Effect of Sodium Citrate Concentration on Material Structure

When the amount of sodium citrate added is 0.2mL and the solution concentrations are 0.1, 0.3, 0.5, 1.0, 1.5, and 1.7 mol/L, the structural parameters of MIL-68 (In) - SC (9-14) synthesized are affected as shown in Table 4:

Table 4 Structural parameters of synthesized MIL-68 (In) - SC (9-14)

materials	C/(mol/L)	S_{BET}/(m^2/g)	V/(cm^3/g)	D/nm
MIL-68(In)-SC-9	0.1	964.42	0.51	1.68
MIL-68(In)-SC-10	0.3	1102.34	0.54	1.63
MIL-68(In)-SC-11	0.5	1164.91	0.56	1.63
MIL-68(In)-SC-12	1	994.42	0.52	1.66
MIL-68(In)-SC-13	1.5	948.87	0.47	1.94

Table 4 shows that, at a fixed citrate volume of 0.2 mL, raising its molarity from 0.1 to 1.7 mol L^{-1} produces a bell-shaped trend: both surface area and pore volume climb to a maximum and then retreat, whereas mean pore diameter remains essentially flat. Comprehensive analysis shows that the suitable concentration of sodium citrate solution is 0.5mol/L. Under this condition, the synthesized MIL-68 (In) - SC-11 has a specific surface area of 1164.91m2/g, a pore volume of 0.56cm3/g, and a pore size of 1.63nm. The experimental results show that the synthesized material has good adsorption and application structural conditions.

3.3.3 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Analysis

SEM and TEM inspections of the three frameworks are compiled in Figure 1. Panel b confirms that pristine MIL-68(In) grows as smooth, rod-like crystallites ~4 µm in length; Figure 1 (a) shows the SEM image of NH2-MIL-68

(In), which presents a mixed structure of rough block and needle shaped crystal stacks with a small overall size and a crystal length of about 1 μ m. Figure 1 (d) shows the SEM image of MIL-68 (In) - SC-11, which presents a surface layered and memory pore like structure with a grain like structure and a crystal length of about 2 μ m. TEM micrographs of MIL-68(In), NH_2-MIL-68(In) and MIL-68(In)-SC are displayed in Figures 1c, 1f and 1e, respectively. All three synthetic materials exhibit irregular and disordered pore structures. Figure 1 shows finer lattice stripes [24].

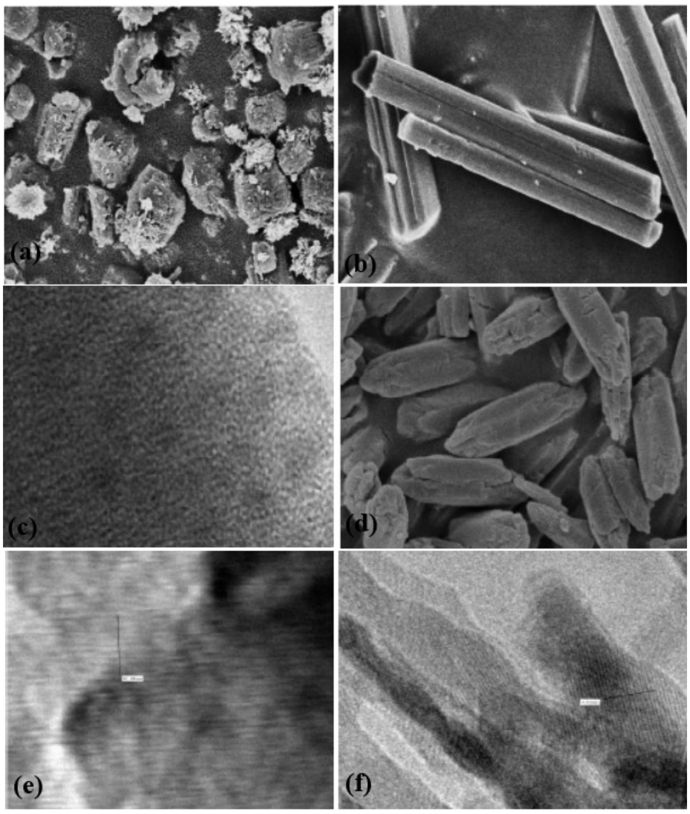

Figure 1 TEM and SEM images of synthetic materials

3.4 Study on MB Adsorption by MIL-68 (In) and Modified Materials

3.4.1 Effect of adsorption time on adsorption performance

The impact of contact duration on MB sequestration by MIL-68(In), NH_2-MIL-68(In) and MIL-68(In)-SC-11 was probed in batch mode: 5 mg sorbent, 50 mg L^{-1} dye, pH 6.5, 25 °C, sampling at 15, 30, 60, 90, 120, 150 and 180 min; outcomes are plotted in Figure 2.

From Figure 2, it can be seen that the adsorption rates of MIL-68 (In), NH2-MIL-68 (In), and MIL-68 (In) - SC-11 all increase rapidly with increasing adsorption time, then gradually slow down, and eventually reach equilibrium. Initially, abundant vacant sites on the sorbent surface bind MB molecules instantly, yielding a steep uptake surge; as these sites fill, the rate slackens and finally plateaus when saturation is reached.

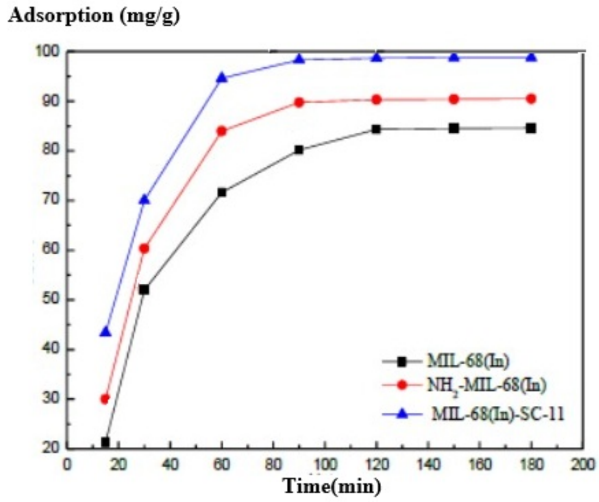

Figure 2 The Effect of Different Adsorption Times on MB Adsorption Performance

The adsorption equilibrium times of MIL-68 (In), NH2-MIL-68 (In), and MIL-68 (In) - SC-11 are 120, 90, and 90 minutes, respectively. The adsorption rates and amounts of MB are ranked from high to low as follows: MIL-68 (In) - SC-11>NH2-MIL-68 (In)>MIL-68 (In). MIL-68 (In) - SC-11 has better adsorption performance, with adsorption rates and amounts of 96.63% and 204.16mg/g, respectively. The specific surface area of MIL-68 (In) - SC-11 (1164.9m2/g) is higher than NH2-MIL-68 (In) (726.12m2/g) and MIL-68 (In) (743.72m2/g), and the introduced carboxylic acid group (sodium citrate) can react with methylene blue [26], so MIL-68 (In) - SC-11 has a higher removal rate of MB.

3.4.2 The Influence of pH Value on Adsorption Performance

Solution pH governs the protonation state of both dye and framework, so it is a key lever for MB uptake. Guided by the kinetic data in Section 4.1, the optimal contact times for MIL-68(In), NH_2-MIL-68(In) and MIL-68(In)-SC-11 were fixed before the pH-dependent runs. All other conditions were the same as section 4.1. The effects of methylene blue solution pH values of 2, 3, 4, 6.5, 7, 8, 9, 10, and 11 on the adsorption properties of the three materials were investigated, and the results are shown in Figure 3.

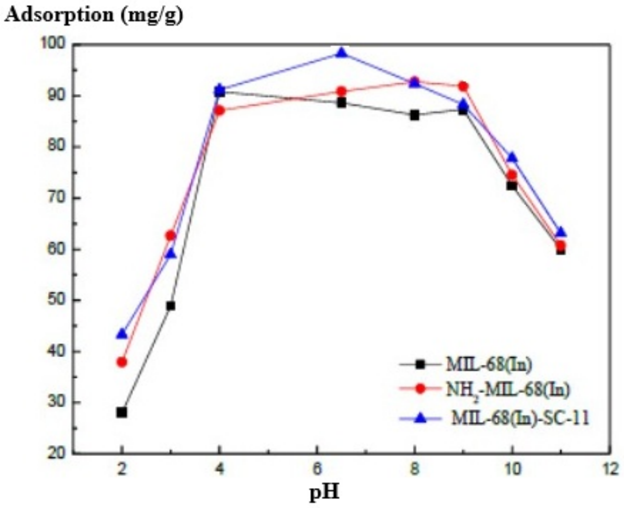

Figure 3 The Effect of Different pH Values on the Adsorption Performance of Synthetic Materials

Figure 3 shows that, for all three frameworks, MB uptake climbs and then declines as the pH is raised. Specifically, MIL-68(In) improves its removal efficiency from 26 % at pH 2 to 89 % at pH 4, after which the curve levels off and finally drops; As the pH value increases, the adsorption rate decreases to 58.33%. Therefore, when the pH value of the solution is 4, MIL-68 (In) has the best adsorption effect on MB, with an adsorption rate of 89.12%. For NH2-MIL-68 (In), as the pH value increases from 2 to 8, the adsorption rate shows a rapid increase followed by a slow increase, with the adsorption rate increasing from 36.38% to 91.07%; When the pH value continued to increase to 11, the adsorption rate continued to decrease to 59.08%, indicating that NH2-MIL-68 (In) had the best adsorption effect on MB at a solution pH of 8, with an adsorption rate of 91.07%. When the pH value is between 2 and 6.5,

The adsorption rate of MB by MIL-68 (In) - SC-11 continued to increase from 41.66% to 96.63%; When the pH value increased from 6.5 to 11, the adsorption rate continued to decrease to 61.47%. That is, at a pH value of 6.5, MIL-68 (In) - SC-11 had the best adsorption effect on MB, with a maximum adsorption rate of 96.63%. By comparing the adsorption rates of three synthetic materials, the addition of amino groups and sodium citrate modification improved the adsorption rate of the synthetic materials.

From Figure 6, it can be seen that MIL-68 (In) - SC-11 has a higher adsorption rate for MB than MIL-68 (In) and NH2-MIL-68 (In), indicating the best adsorption effect. The incorporation of carboxyl functionalities appears to enhance the adsorptive capacity of the material. MIL-68 (In) - SC-11 has a high specific surface area and pore volume, which are important factors conducive to adsorption applications. Methylene blue is a cationic dye with a positive charge. As the acidity of the solution increases, the amount of positive charge on the material surface increases, and H+competes for adsorption sites, resulting in a decrease in adsorption rate; The aromatic acidic groups contained in the material can be adsorbed through electrostatic and π - π bond interactions [27]. Elevated solution alkalinity weakens the binding strength of surface moieties, while the material's framework becomes vulnerable to disintegration under both strongly acidic and basic conditions [28]. Therefore, neutral conditions are favorable for adsorption. The suitable adsorption pH value is 6.5, and the MB removal rate is 96.63%.

3.4.3 The effect of MB concentration on adsorption performance

The optimal pH windows for adsorption were identified for MIL-68(In), NH_2-MIL-68(In) and MIL-68(In)-SC-11, respectively. The effects of MB concentration on the adsorption rate and amount of the three materials were investigated at concentrations of 10, 20, 30, 50, 100, 150, 200, and 300mg/L. The results are shown in Figure 4.

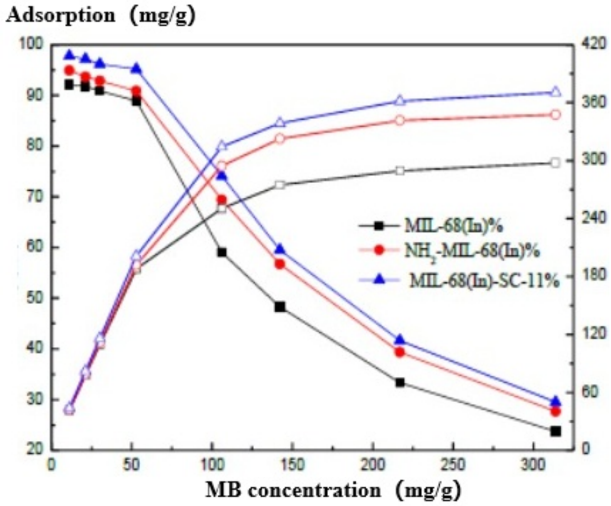

Figure 4 The Effect of MB Concentration on the Adsorption Efficiency of Synthetic Materials

Figure 4 illustrates that the initial MB concentration strongly governs both uptake kinetics and ultimate loading. For every sorbent, the percentage removed drops steadily as the dye level rises, whereas the capacity first surges, then plateaus. MIL-68(In) removal falls from 92 % to 24 % while its loading climbs from 41 mg g^{-1} to ~298 mg g^{-1} before levelling off. NH_2-MIL-68(In) shows a decline from 95 % to 28 %, with capacity stabilising near 348 mg g^{-1}.

The SC-11 derivative exhibits the same trend: removal slides from 98 % to 30 %, and capacity asymptotically approaches 371 mg g^{-1}.

As shown in Figure 4, when the concentration of methylene blue solution is less than 50mg/L, the difference in adsorption capacity among the three synthetic materials is minimal; Once the MB concentration surpasses 50 mg L^{-1}, the three sorbents diverge markedly in loading, with MIL-68(In)-SC-11 outperforming the others. At fixed dosage, each framework presents a constant suite of surface area, pore volume and functional sites, so the divergence reflects the intrinsic reactivity of these static attributes rather than any change in their abundance. In the initial stage of adsorption, the material has sufficient adsorption sites to adsorb MB molecules; As the concentration of MB solution increases, the material continues to adsorb, and many adsorption sites are occupied, making it easy to reach adsorption saturation. Therefore, the increase in adsorption capacity is slow, and the adsorption process is limited [29]. The MIL-68 (In) - SC-11 with high specific area and large pore volume has the highest adsorption capacity.

3.4.4 Effect of adsorbent dosage on adsorption performance

Drawing on the foregoing data, the optimal contact time and pH window were fixed for MIL-68(In), NH_2-MIL-68(In) and MIL-68(In)-SC-11. To probe dosage effects, 20 mL of 50 mg L^{-1} MB were challenged with 3, 5, 7, 9, 11, 20 or 30 mg of each sorbent; the resulting uptake efficiencies and capacities are displayed in Figure 5.

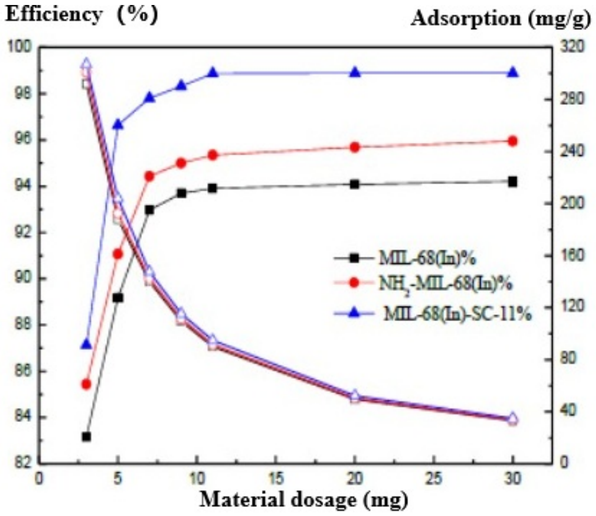

Figure 5 Effect of adsorbent dosage on the adsorption performance of synthetic materials

Figure 5 reveals that, at fixed MB concentration, the removal percentage rises monotonically with increasing sorbent mass until it plateaus, whereas the uptake capacity (mg g^{-1}) declines throughout. Below 7 mg the removal curve climbs steeply; between 7 and 11 mg the slope moderates; beyond 11 mg the increment becomes marginal as the system asymptotically approaches saturation. The adsorption capacity first rapidly decreases and then slowly decreases with the increase of adsorbent dosage.

At fixed MB concentration, raising the sorbent dose enlarges the cumulative pore pool and surface area, so removal efficiency surges initially. Once the residual dye concentration becomes vanishingly low, further solid additions have nothing left to bind; equilibrium is reached and the percentage removed levels off. Because the same dye mass is now distributed over more particles, the loading per gram must decline, giving the observed monotonic drop in capacity.

3.4.5 Adsorption kinetics of MB by MIL-68 (In) and modified materials

The pH value of MB solution is 6.5, and the adsorption doses of MIL-68 (In), NH2-MIL-68 (In), and MIL-68 (In) - SC-11 are 5mg. 20mL of 50mg/L MB solution with a pH value of 6.5 is adsorbed for 15, 30, 60, 90, 120, 150, and

180 minutes. The clarified filtrate is passed through an organic membrane, its absorbance recorded, and the MB uptake computed; the kinetic profile is plotted in Figure 6.

Figure 6 shows that all three engineered sorbents follow a near-identical kinetic signature: an initial surge in capacity, a subsequent gentle rise, and final convergence toward a stable plateau. NH2-MIL-68 (In) and MIL-68 (In) - SC-11 reached adsorption equilibrium earlier than MIL-68 (In). After 90 minutes of adsorption, the adsorption amount remained basically constant and reached adsorption equilibrium; After 120 minutes of adsorption, the adsorption capacity of MIL-68 (In) towards MB solution tends to stabilize and reaches adsorption equilibrium [30].

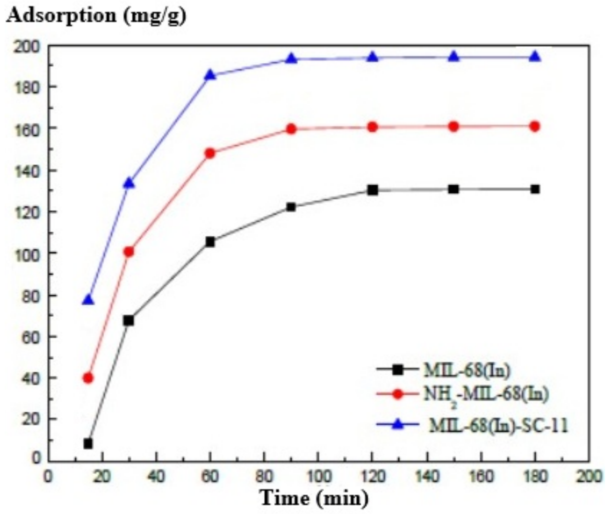

Figure 6 MB adsorption kinetics curves of MIL-68 (In), NH2-MIL-68 (In), and MIL-68 (In) - SC-11

3.4.6 Adsorption MB isotherms of MIL-68 (In) and modified materials

MB concentrations of 10, 20, 30, 50, 100, 150, 200, and 300mg/L were used to investigate the changes in the adsorption capacity of MIL-68 (In), NH2-MIL-68 (In), and MIL-68 (In) - SC-11. The adsorption isotherms were plotted based on the data in Figure 7, with concentration as the horizontal axis and adsorption capacity as the vertical axis. The results are shown in Figure 7.

From Figure 7, it can be seen that when the concentration of MB solution is less than 50mg/L, the adsorption capacity of the three materials shows a similar upward trend at the same rate, with minimal relative incremental changes; After the concentration exceeds 50mg/L, the adsorption capacity first increases rapidly with the increase of concentration, then slowly increases, and finally reaches a constant equilibrium [31]. When the concentration of MIL-68 (In) in MB solution is 150mg/L, the adsorption capacity tends to reach equilibrium; When the concentration of NH2-MIL-68 (In) and MIL-68 (In) - SC-11 in MB solution is around 250mg/L, the adsorption capacity tends to reach equilibrium.

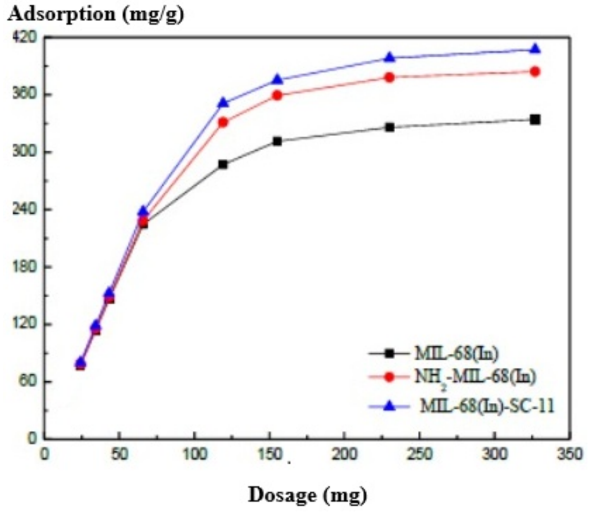

Figure 7 Adsorption isotherms of MB by three materials

4 Conclusion

This chapter systematically studied the adsorption process of three metal organic framework materials, MIL-68 (In), NH2-MIL-68 (In) modified with amino and carboxyl functional groups, and MIL-68 (In) - SC-11, on organic dye MB. The influence of contact time, pH, starting concentration, and sorbent mass on uptake behavior was systematically mapped. The adsorption kinetics and isotherms of three materials were fitted through experimental data; And the regeneration performance of three materials for adsorption applications was investigated, and synthetic materials with excellent adsorption performance were screened. Under the conditions of an adsorbent dose of 5mg and a MB solution concentration of 50mg · L-1, with an adsorption time of 120min and a MB solution pH of 4, MIL-68 (In) is suitable for adsorption. The adsorption rate can reach 89.12%, and the adsorption capacity is 187.78mg/g; When the adsorption time is 90 minutes and the pH value of MB solution is 8, the suitable adsorption conditions for NH2-MIL-68 (In) are achieved, with an adsorption rate of 91.07% and an adsorption capacity of 191.89 mg/g; At 90 min and pH 6.5, MIL-68(In)-SC-11 achieves optimum uptake, delivering 96.6 % removal and a loading of 204 mg g^{-1}. Grafting amino and carboxyl moieties, together with the enlarged surface area and pore volume generated by post-synthetic modification, jointly endow this variant with superior MB affinity.

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