Efficient Adsorption of Dyes Using Polyethyleneimine-Modified NH$_2$-MIL-101(Al) and its Sustainable Application as a Flame Retardant for an Epoxy Resin

Jia Wang, Yansong Liu, Xiuyan Guo, Hongqiang Qu, Ran Chang,*, and Jing Ma*

ABSTRACT: Metal–organic frameworks (MOFs) exhibit highly designable properties and have been used in wide applications. To further improve their performance, the modification of MOFs is an effective method. However, the modification process is usually complicated. Besides, the sustainable use of MOFs is difficult to achieve due to the complicated recycling treatment. Herein, we designed a polyethyleneimine (PEI)-modified NH$_2$-MIL-101(Al) composite (PEI@NH$_2$-MIL-101(Al)). This composite showed excellent dye removal performance of methyl orange (MO, 89.4%) and Direct Red 80 (DR80, 99.8%). Remarkably, the dye removal application of PEI@NH$_2$-MIL-101(Al) also acted as a modification process toward flame retardant application. Thus, the dye-adsorbed PEI@NH$_2$-MIL-101(Al) composite (MO-PEI@NH$_2$-MIL-101(Al) and DR80-PEI@NH$_2$-MIL-101(Al)) was sustainably used as an effective flame retardant for an epoxy resin (EP) at low additions (4.0 wt %). The limiting oxygen values of EP/MO-PEI@NH$_2$-MIL-101(Al) and EP/DR80-PEI@NH$_2$-MIL-101(Al) increased to 26.5 and 26.7%, respectively. The heat release and the smoke production of dyes-PEI@NH$_2$-MIL-101(Al)/EP were greatly reduced compared with those of EP. This strategy provides a simple and effective modification method for MOFs. Meanwhile, the modified MOF composite can achieve sustainable application, giving full play to the advantages of MOFs.

1. INTRODUCTION

An epoxy resin (EP) exhibits special properties such as easy processing, good corrosion resistance, and electrical insulation. It is widely used as building materials, coating, adhesive, etc. However, EP shows high flammability. Once a fire accident occurs, the generated smoke and heat of EP will seriously harm human health and the environment, which seriously limits its applications under high-temperature conditions. To improve the fire safety of EP, a design efficient flame retardant is an effective method. Among the various flame retardants, nanomaterials exhibit great advantages in improving the flame retardant properties for EP due to the unique nanoparticle effect.

Metal–organic frameworks (MOFs), a typical nanoporous material, have many desirable characteristics such as large surface area and highly designable chemical properties. As a result of their advantage, MOFs are one of the most promising materials for the flame retardant application. For example, Hou et al. synthesized Fe-MOF and Co-MOF. The thermostability and flame retardancy of polystyrene have been improved by the addition of Fe-MOF and Co-MOF. Shi et al. used ZIF-8 as an additive in poly(lactic acid) (PLA). The results showed that the limiting oxygen value of PLA/ZIF-8 increased to 26%, while the flame retardant effect of a pure MOF is relatively limited, and the MOF modification is a common method to further improve the effect of MOF.
example, Hou et al.14 successfully synthesized a DOPOModified Co-based MOF (DOPO@Co-MOF) and found that the presence of DOPO@Co-MOF had a positive effect on the flame retardancy of PLA due to the heat insulation and smoke suppression effect. Li et al.15 designed a ZIF@NH2-MIL-101(Al) composite. The ZIF@NH2-MIL-101(Al) effectively promoted catalytic carbon formation during EP combustion. Our group designed an ionic-liquid-functionalized MOF composite. The designed MOF-based materials are usually used once in one application field. Especially in the field of flame retardant, they cannot be used sustainably.16 For some other applications like dye adsorption, recycling processes are needed. However, the recycling processes will increase the cost and reduce the performance.19 If the dye-adsorbed material can be applied directly, the problem of recycling will be solved.

To achieve the above purpose, we designed a simple and effective method to synthesize a modified MOF composite and investigate the dye adsorption performance. Then, the dye-adsorbed MOF composite can be used as a flame retardant. In this way, application of MOF in dye adsorption also works as the modification process of MOF toward flame retardant application, which can extend the application value of MOF. Herein, we choose polyethylenimine (PEI) to modify NH2-MIL-101(Al). NH2-MIL-101(Al) is a typical mesoporous crystal material with two kinds of pores, that is, 2.9 and 3.4 nm. The mesoporous structure is helpful for the high adsorption capacity of dyes. The exposed —NH2 groups of NH2-MIL-101(Al) can act as Lewis bases due to the presence of lone pair electrons. Based on these, NH2-MIL-101(Al) may effectively adsorb dye molecules. In addition, PEI exhibits good adsorption performance toward dyes due to its rich amino groups. Combining PEI with NH2-MIL-101(Al) can combine the advantages of the two components. For the flame retardant application, the amino groups in the composite can promote the cross-linking effect with EP. Meanwhile, the rich nitrogen and carbon of PEI@NH2-MIL-101(Al) are beneficial for flame retardants. With this strategy, the application of the MOF in one field used as a modification process for another field achieved sustainable application.

2. EXPERIMENTAL SECTION

2.1. Materials. 2-Aminoterephthalic acid (99%) was supplied by J&K Scientific Co., Ltd. PEI (MW 600, 99%) and m-phenylenediamine (99%) were obtained from Aladdin Industrial Corporation. Aluminum chloride hexahydrate (AlCl3·6H2O, 99%) was supplied by Guangfu Fine Chemical Research Institute. N,N-dimethylformamide (DMF), ethanol, and methanol were obtained from Comiaio Chemical Reagent Co., Ltd. MO (C14H14N3SO3Na, 98%) was provided by Tianjin Guangfu Technology Development Co., Ltd. DR80 (C45H28N10NaO21S6, 98%) was supplied by Shanghai Maclean Biochemical Technology Co., Ltd. EP was supplied by Jiangfeng Chemical Industry Co., Ltd.

2.2. Synthesis of MOF. The MOF was prepared by the solvent hydrothermal method.22 AlCl3·6H2O (1.02 g), 2-aminoterephthalic acid (1.12 g), and DMF (60 mL) were fully mixed by stirring. Afterward, the mixture was transferred to an autoclave. The reactant was heated at 130 °C for 72 h when cooled to room temperature; the product was obtained by centrifugation. Then, the yellow NH2-MIL-101(Al) was washed with ethanol thoroughly. Finally, the NH2-MIL-101(Al) was dried at 80 °C.

2.3. Synthesis of PEI-Modified NH2-MIL-101(Al). First, the PEI solution was prepared by mixing PEI (4 mL) and methanol (10 mL). Then, NH2-MIL-101(Al) (0.2 g) was poured into the obtained PEI and stirred for 12 h. Then, the powder was collected and washed thoroughly with methanol. Finally, the powder was dried at 60 °C in a vacuum oven overnight. The obtained material was named PEI@NH2-MIL-101(Al).

2.4. Adsorption Experiments. PEI@NH2-MIL-101(Al) was used as an absorbent to remove the dyes (MO and DR80). MO and DR are widely used common dyes in waste water. To test the comprehensive adsorption performance of PEI@NH2-MIL-101(Al), the concentrations of the dye solution are selected as 100, 500, and 1000 mg/L to represent the low, medium, and high concentrations of the dye solution respectively. The adsorptive volume of the dye solution was 5 mL, and the pH of the dye solution was adjusted to 7. The amount of PEI@NH2-MIL-101(Al) was 5 mg. The absorbent and the dye solution were placed in flasks. During the experiment, the flasks were agitated using a water bath shaker. The adsorption capacity is measured every 10 min. The adsorbed materials were collected by centrifugation. Then, the dye concentrates were tested using UV–visible spectrophotometer. The dye-adsorbed PEI@NH2-MIL-101(Al) materials (dye-PEI@NH2-MIL-101(Al)) are named as MO-PEI@NH2-MIL-101 (Al) or DR80-PEI@NH2-MIL-101(Al). The adsorption capacity (qt, mg/g) is calculated by

\[ q_t = \frac{(C_0 - C_f) \times V}{m} \]

where qt (mg/g) is the adsorption weight of the dyes, C0 (mg/L) is the concentration of the dyes before adsorption, Cf (mg/L) is the concentration of the solution when the adsorption reaches equilibrium, V (L) is the volume of the dye solution, and m (g) is the mass of PEI@NH2-MIL-101(Al).

The removal efficiency (R %) of the dyes is calculated by

\[ R (%) = \frac{(C_0 - C_f) \times 100}{C_0} \]

where C0 (mg/L) is the concentration of the solution obtained at different time intervals.

2.5. Synthesis of EP Composites. First, EP (80 g) was heated in a water bath and stirred for 20 min at 60 °C under vacuum of 0.3 MPa to remove the bubbles completely. Then, dye-PEI@NH2-MIL-101(Al) (3.2 g) and m-phenylenediamine (8.8 g) are slowly added to EP and stirred for 20 min. Then, the solution was transferred into a prepared mold. To remove the bubbles that may be generated during the pouring process, the reactants were placed in an oven at 60 °C for 20 min under vacuum. In the curing process, the mold was dried at 80 °C for
120 min and then heated at 150 °C for 180 min in an oven. The pure EP sample was also obtained by the above procedure without adding other materials. EP composites are named MO-PEI@MOF/EP and DR80-PEI@MOF/EP.

2.6. Characterizations. To analyze the lattice structures of MOF and MOF composites, powder X-ray diffraction analysis (XRD) analysis was used using D8ADVANCE equipment. The scanning angle ranged from 5 to 60° at a scan speed of 5°/min. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using Tensor-27. The morphology of the samples was measured by field emission scanning electron microscopy (SEM) using JSM-7500 F (Japan) equipment. Thermogravimetric analysis (TGA) was employed using STA449CQMS403C (NETZSCH, Germany). The test condition was 35–800 °C at a heating rate of 10 °C/min under different atmospheres (N₂ and air). A UV–vis spectrophotometer was used to detect the concentration of the dye solutions. The limited oxygen index (LOI) of the materials was tested using an HC-3 oxygen index meter. The dimension of the samples was 130 mm × 6 mm × 3 mm. Combustion performances of the materials were tested using an FTT CONE (FTT, U.K.) device. The size of the samples was 100 mm × 100 mm × 3 mm. The heat flux was 50 kW/m².

3. RESULTS AND DISCUSSION

3.1. Characterization of the Materials. The XRD results of NH₂-MIL-101(Al) and modified NH₂-MIL-101(Al) composites are shown in Figure 1. The resulted XRD curve of NH₂-MIL-101(Al) is consistent with the reported curves, indicating that NH₂-MIL-101(Al) was successfully prepared.22 There is no difference between the patterns of PEI@NH₂-MIL-101(Al) composites and NH₂-MIL-101(Al). The main lattice planes at 2θ of 9, 10, 14, and 18° in the dye-adsorbed PEI@NH₂-MIL-101(Al) composites are consistent with that of NH₂-MIL-101(Al), indicating the integrity of the crystal structure of NH₂-MIL-101(Al) after the dye adsorption process. It exhibits that the lattice structure of NH₂-MIL-101(Al) is undamaged after the surface modification process.

Figure 2 illustrates the FTIR results of NH₂-MIL-101(Al) and PEI@NH₂-MIL-101(Al). As we can see, the stretching vibrations at 3495 and 3385 cm⁻¹ of NH₂-MIL-101(Al) represent the symmetric and asymmetric stretching of –NH₂ in an organic ligand. The peaks at 1686, 1600, and 1336 cm⁻¹ are attributed to the N–H vibration due to the C–N stretching of the aromatic amines. The above results indicate the successful synthesis of NH₂-MIL-101(Al).22 For the patterns of PEI@NH₂-MIL-101(Al), the wavenumber at 1651 cm⁻¹ is attributed to the N–H vibration of PEI.24 The stretching vibration of C–N at 1336 cm⁻¹ is stronger than that of NH₂-MIL-101(Al), which was caused by the interaction between the –NH₂ of PEI and the –COOH groups of NH₂-MIL-101(Al). The above results illustrate the successful synthesis of PEI@NH₂-MIL-101(Al).

Figure 3 demonstrates the morphology of NH₂-MIL-101(Al) and PEI@NH₂-MIL-101(Al) particles. As shown in Figure 3, NH₂-MIL-101(Al) particles have a size of 150 nm. Meanwhile, PEI@NH₂-MIL-101(Al) and NH₂-MIL-101(Al) displayed the same morphology.

The TG analysis can explore the thermal stability of the materials. The results are presented in Figure 4. Table 1 shows the detailed values. From Figure 4b, we can see that the DTG results of PEI@NH₂-MIL-101(Al) contain two steps. At the first stage ranging from 200 to 450 °C, the initial decomposition temperature Tds of PEI@NH₂-MIL-101(Al) is 269.9 °C, which is higher than the temperature of NH₂-MIL-101(Al), manifesting that the introduction of PEI significantly improves the thermal stability of MOF. The Tds values of MO-PEI@NH₂-MIL-101(Al) and DR80-PEI@NH₂-MIL-101(Al) were further increased to 282.3 and 253.5 °C, respectively. R means the weight of the residue materials. The weight loss rate of MO-PEI@NH₂-MIL-101(Al) was slower than that of PEI@NH₂-MIL-101(Al). The stability of dye-PEI@NH₂-MIL-101(Al) was further enhanced. At the second stage ranging from 450 to 650 °C, the maximum weight loss was mainly because of the collapse of the MOF.22 The slower weight loss rate of MO-PEI@NH₂-MIL-101(Al) indicates the enhanced stability of PEI@NH₂-MIL-101(Al) after adsorption of MO. However, the decomposition rate of DR80-PEI@NH₂-MIL-101(Al) has increased, which means that the addition of DR80 can promote the decomposition of PEI@NH₂-MIL-101(Al). The residual carbon content of PEI@NH₂-MIL-101(Al) at 750 °C is 46.54%. After adsorption, the residual carbon amount of
MO-PEI@NH₃-2-MIL-101(Al) and DR80-PEI@NH₂-MIL-101(Al), respectively, increased to 59.84 and 55.46%, which is due to the synergy effect by dyes and PEI@NH₂-MIL-101(Al). For the elemental components of dye-PEI@NH₂-MIL-101(Al) composites, the weight ratio of MO in the MO-PEI@NH₂-MIL-101(Al) composite is 86.7%. The weight ratio of DR80 in the DR80-PEI@NH₂-MIL-101(Al) composite is 82.7%.

3.2. Adsorption Performance of PEI@NH₂-MIL-101(Al).

Figure 5 shows the adsorption behavior of PEI@NH₂-MIL-101(Al) for the dye solutions. The dye-adsorbed PEI@NH₂-MIL-101(Al) composite was analyzed by XRD, FTIR, and SEM, and the results showed that the crystal structure, chemical group, and particle morphology of PEI@NH₂-MIL-101(Al) were not changed, demonstrating that the PEI does not dissolve in the dye solution. Meanwhile, PEI@NH₂-MIL-101(Al) has good stability in the dye solution. As shown in Figure 5, the dye removal rate was 86% (MO) and 100% (DR) at a dye concentration of 100 mg/L. In this case, the dye molecules are distributed in a relatively dispersed condition, PEI@NH₂-MIL-101(Al) can quickly adsorb the dye molecules. At a dye concentration of 500 mg/L, the removal of DR80 in the DR80-PEI@NH₂-MIL-101(Al) composite is 82.7%.

Table 1. TGA Parameters of NH₂-MIL-101(Al) and NH₂-MIL-101(Al) Composites

| samples                | temperature (°C) | weight loss (wt %) |
|------------------------|------------------|--------------------|
| NH₂-MIL-101(Al)        | 230.4            | 48.90              |
| PEI@NH₂-MIL-101(Al)    | 269.9            | 46.54              |
| MO-PEI@NH₂-MIL-101(Al) | 282.3            | 59.84              |
| DR80-PEI@NH₂-MIL-101(Al)| 253.5         | 55.46              |

MO-PEI@NH₂-MIL-101(Al) and DR80-PEI@NH₂-MIL-101(Al), respectively, increased to 59.84 and 55.46%, which is due to the synergy effect by dyes and PEI@NH₂-MIL-101(Al). For the elemental components of dye-PEI@NH₂-MIL-101(Al) composites, the weight ratio of MO in the MO-PEI@NH₂-MIL-101(Al) composite is 86.7%. The weight ratio of DR80 in the DR80-PEI@NH₂-MIL-101(Al) composite is 82.7%.

Figure 5. Different concentration adsorption curves of NH₂-MIL-101(Al) and PEI@NH₂-MIL-101(Al) for MO (a, c, e) and DR80 (b, d, f).
rate reached 89.4% (MO) and 99.8% (DR), respectively. Meanwhile, the equilibrium adsorption amount individually reached 894 mg/g (MO) and 998 mg/g (DR), while the removal rates diminished to 86.7% (MO) and 82.0% (DR) at a dye concentration of 1000 mg/L. In this process, the increased dye molecules will increase the molecular motion resistance, thus reducing the adsorption rate. Besides, the adsorption amount of PEI@NH$_2$-MIL-101(Al) will reach saturation. For different concentrations of dyes, the adsorption amount of PEI@NH$_2$-MIL-101(Al) all higher than that of pure MOF. The enhanced adsorption performance may be due to the electrostatic interaction between the positive PEI@NH$_2$-MIL-101(Al) and negative dyes. At this point, the introduced PEI of PEI@NH$_2$-MIL-101(Al) can strengthen the interactions of the hydrogen and electrostatic bonds toward dyes, which increase the adsorption capacity of dyes.

The adsorption properties of other materials to dyes are shown in Table 2. PEI@NH$_2$-MIL-101(Al) exhibits excellent adsorption capacity of MO and DR80. More importantly, the dye-adsorbed MOF composites can be used as flame retardants. To our best knowledge, this is the first research in which the MOF composite achieved sustainable application in dye removal and flame retardant applications.

### 3.3. Thermal Stability Performance

Thermal stability is an important aspect that affects the flame retardant property of the materials. Figure 6 shows the results in different atmospheres (N$_2$ and air). The detailed values are listed in Table 3. Usually, $T_{5\%}$ represents the temperature at which the mass loss is 5%. $T_{\text{max}}$ represents the temperature at which the mass loss is the greatest, and $C_Y$ is the char yield at 800 °C.

In a N$_2$ atmosphere, the decomposition process contains one degradation stage for all the samples. As shown in Table 3, the $T_{5\%}$ and $T_{\text{max}}$ values of the pure EP under a N$_2$ atmosphere are 363.2 and 377.8 °C, respectively. The $T_{5\%}$ and $T_{\text{max}}$ values of EP composites were slightly reduced because of the presence of dye-PEI@NH$_2$-MIL-101(Al) (350.2 and 376.5 °C, respectively). The reduced decomposition temperature indicates that the decomposition processes are accelerated because of the presence of dye-PEI@NH$_2$-MIL-101(Al). The organic–inorganic structure of NH$_2$-MIL-101(Al) can promote the char formation process, which can further prevent the release of heat and smoke. Meanwhile, the metal oxides from NH$_2$-MIL-101(Al) exhibit the catalytic effect on the promotion of char formation and reduction of the heat release rate. Moreover, the $C_Y$ value of the pure EP is 11.17% at 800 °C. In comparison, the $C_Y$ values of 4% MO-PEI@MOF/EP and 4% DR80-PEI@MOF/EP are increased to 14.57 and 15.06%, respectively. The increased char residue manifests that the presence of flame retardants can accelerate the char formation, owing to the combined effect of the rigid structure of the aromatic ring and metal oxides. Meanwhile, the increased char can act as an effective protective barrier between air and EP, reducing the rate of heat release.

In an air atmosphere, the decomposition process contains two degradation stages for the samples. The first stage represents the degradation process of EP. The second stage represents the degradation process of the char residue and...
After the addition of dye-PEI@NH<sub>2</sub>-MIL-101(Al), T<sub>5%</sub>, T<sub>max1</sub>, and T<sub>max2</sub> were reduced slightly in comparison with those of EP but were higher than those of PEI@NH<sub>2</sub>-MIL-101(Al), demonstrating the promoted degradation process of EP by the addition of PEI@NH<sub>2</sub>-MIL-101(Al). In addition, the dye-PEI@NH<sub>2</sub>-MIL-101(Al)/EP composite shows increased char residue, which is helpful for the flame retardant effect.

### 3.4. Flammability of the EP Samples

The materials with a high limiting oxygen index (LOI) value are relatively difficult to burn, whereas a low LOI value indicates that the material is relatively easy to burn. The LOI value of EP is 24.2%. After the addition of the flame retardant, the EP composites have higher LOI values than the pure EP. The LOI values of 4% MO-PEI@MOF/EP and 4% DR80-PEI@MOF/EP are increased to 26.5 and 26.7%, respectively. The results illustrate that the dye-adsorbed MOF composites can increase the flame retardant performance of EP.

A direct and effective method for measuring the flame retardant properties of the materials is the cone calorimeter test. The results are indicated by five parameters, including the peak of the heat release rate (PHRR), heat release rate (HRR), total heat release (THR), smoke production rate (SPR), and total smoke production (TSP). The results are presented in Figure 7 and Table 4. Figure 7a,b shows that the PHRR and THR values of EP are 1201.31 kW/m<sup>2</sup> and 119.05 MJ/m<sup>2</sup>, respectively.

### Table 3. TGA Parameters of EP and EP Composites

| samples                  | nitrogen | air       |
|--------------------------|----------|-----------|
|                          | T<sub>5%</sub> (°C) | T<sub>max1</sub> (°C) | R (wt %) | T<sub>5%</sub> (°C) | T<sub>max1</sub> (°C) | T<sub>max2</sub> (°C) | R (wt %) |
| EP                       | 363.2    | 377.8     | 11.17    | 365.6  | 377.7     | 572                  | 0.61     |
| 4% PEI@MOF/EP            | 350.2    | 376.5     | 16.13    | 345.6  | 368.2     | 579.3                | 0.42     |
| 4% MO-PEI@MOF/EP         | 362.3    | 376.4     | 14.57    | 351.4  | 374.9     | 590.2                | 2.81     |
| 4% DR80-PEI@MOF/EP       | 361.4    | 377.6     | 15.06    | 347.4  | 375.1     | 595.2                | 0.86     |

### Table 4. Cone Calorimeter Data of EP and EP Composites

| samples                  | PHRR (kW/m<sup>2</sup>) | THR (MJ/m<sup>2</sup>) | SPR (m<sup>2</sup>/s) | TSP (m<sup>2</sup>) | COP (g/s) | mass (g) |
|--------------------------|--------------------------|------------------------|-----------------------|-------------------|-----------|----------|
| EP                       | 1201.31                  | 119.05                 | 0.37                  | 37.86             | 0.029     | 5.61     |
| 4% PEI@MOF/EP            | 865.36                   | 118.35                 | 0.28                  | 36.15             | 0.023     | 5.33     |
| 4% MO-PEI@MOF/EP         | 859.85                   | 105.34                 | 0.26                  | 32.69             | 0.022     | 8.09     |
| 4% DR80-PEI@MOF/EP       | 729.40                   | 111.42                 | 0.27                  | 32.05             | 0.020     | 6.08     |
respectively. When 4% MO-PEI@MOF was added, the PHRR and THR values of the EP composite reduced by 28.4 and 11.5%, respectively. The heat release rate of MO-PEI@NH₂-MIL-101 (Al)/EP is slightly lower than that of DR80-PEI@NH₂-MIL-101(Al)/EP. The reason may be due to the higher char-forming capacity of MO-PEI@NH₂-MIL-101(Al)/EP than that of DR80-PEI@NH₂-MIL-101(Al)/EP, which can effectively prevent the release of heat. The above results indicate the positive effect of MO-PEI@MOF and DR80-PEI@MOF on the flame safety of EP. Meanwhile, the increased flame safety was due to the synergistic effect of dye and PEI@MOF.

The released smoke during the combustion processes is another significant factor that assesses the flame risk of the materials. Reducing the released smoke can prolong the escape time of people in actual fires. Figure 7c,d shows the SPR and TSP results. The SPR and TSP values of EP are 0.368 m²/s and 37.864 m², respectively, while the SPR and TSP values of 4% MO-PEI@MOF/EP are reduced by 29.6 and 13.7%, respectively. The SPR and TSP values of 4% DR80-PEI@MOF/EP are decreased by 26.9 and 15.4%, respectively. The reduced SPR and TSP values may be due to the barrier role of MOF and aromatic ring structure in the dye molecule, which can promote the catalytic reaction.

CO is another factor that seriously endangers human life during the combustion processes, which is principally produced by incomplete combustion of polymers. The release curves of CO are exhibited in Figure 7e. The CO release amount of 4% MO-PEI@MOF/EP and 4% DR80-PEI@MOF/EP are decreased by 22.8 and 31.4% than that of EP, respectively. The reduced release of the CO amount can improve human safety in fire accidents.

3.5. Analysis of the Char Residue. The microtopographies of the char residue can be used to analyze the char-forming process. Generally, more char residues generated during the combustion processes can reduce the spreading of fire or generation of smoke. In Figure 8, there are few residues for EP. The char residues are greatly increased for dye-PEI@NH₂-MIL-101(Al)/EP composites. The result is consistent with the above TGA results. The increased char residues indicate that the EP composites have more advantages in flame retardant application than the pure EP. The degree of graphitization of the char residue can be analyzed by Raman spectroscopy. The degree of graphitization can be expressed by the area ratio between the D peak and the G peak (I_D/I_G). A higher ratio of I_D/I_G explains a lower graphitization degree. The higher degree of graphitization represents a better quality of the char layer, corresponding to a stronger protective effect.

3.6. Proposed Mechanism. Through the above analysis, the efficient flame retardant performance of dye-PEI@NH₂-MIL-101(Al)/EP was due to the synergy effect of the dye and PEI@NH₂-MIL-101(Al). In the gas phase, the sulfonyl group in the dye molecules and PEI@NH₂-MIL-101(Al) will generate a noncombustible gas during the combustion process, decreasing the concentration of the flammable gas. Meanwhile, dyes-PEI@NH₂-MIL-101(Al) can catalyze the formation of...
carbon, reducing the release of toxic gases. In the condensed phase, the aromatic ring structure in the dye molecules and the stable organic framework structure in PEI@NH2-MIL-101(Al) can facilitate the formation of a dense carbon layer, which can act as a barrier, inhibiting the release of heat, smoke, and toxic gases. For the two kinds of dye-PEI@NH2-MIL-101(Al) composites, the heat release rate of MO-PEI@NH2-MIL-101(Al)/EP is slightly lower than that of DR80-PEI@NH2-MIL-101(Al)/EP. The reason may be due to the higher charge-forming capacity of MO-PEI@NH2-MIL-101(Al)/EP than that of DR80-PEI@NH2-MIL-101(Al)/EP, which can effectively prevent the release of heat.

4. CONCLUSIONS

In this work, we designed a facile method to prepare a modified MOF composite. The obtained PEI@NH2-MIL-101(Al) shows high adsorption property for MO and DR80. The dye removal rates for MO and DR80 at a concentration of 500 mg/L reached 89.4 and 99.8%, respectively. Remarkably, the dye adsorption application of PEI@NH2-MIL-101(Al) also exhibits effective flame retardation to EP when the additive amount was as low as 4.0 wt %. The LOI value of dye-PEI@NH2-MIL-101(Al) was increased to 26.7%. Besides, the PHHR, THR, SPR, and CO release were decreased. After systematic analysis, we found that the effective flame retardant performance of dye-adsorbed MOF composites was due to the synergy effect of dyes and PEI@NH2-MIL-101(Al) in the gas and condensed phases. The sulfonate groups in dye molecules and PEI@NH2-MIL-101(Al) can catalyze the degradation processes. Meanwhile, the aromatic ring structure in the dye molecules and the stable skeleton structure in PEI@NH2-MIL-101(Al) can facilitate the formation of a dense carbon layer. The generation of nonflammable gases in combustion of dyes-PEI@NH2-MIL-101(Al) also could decrease the concentration of the flammable gas. The feasible modification method and the sustainable application of PEI@NH2-MIL-101(Al) provide a novel strategy for developing an effective flame retardant.

AUTHOR INFORMATION

Corresponding Authors
Ran Chang — Hebei University, Baoding 071002, China; Email: hbdxcr@163.com
Jia Wang — Hebei University, Baoding 071002, China; orcid.org/0000-0002-2416-6844; Email: majing_hbu@126.com

Authors
Jia Wang — Hebei University, Baoding 071002, China
Yansong Liu — Hebei University, Baoding 071002, China
Xiuyan Guo — Hebei University, Baoding 071002, China
Hongqiang Qu — Hebei University, Baoding 071002, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04118

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the Youth Science Foundation of Hebei Province (B2019201420), the Major Project of Water Pollution Control and Treatment (2018XK07110004-04), and the Advanced Talents Incubation Program of Hebei University (050001-52100981137)

REFERENCES

(1) Mohan, P. A Critical Review: The Modification, Properties, and Applications of Epoxy Resins. Polym.-Plast. Technol. Eng. 2013, 52, 107–125.
(2) Cong, P.; Chen, S.; Yu, J. Investigation of the properties of epoxy resin-modified asphalt mixtures for application to orthotropic bridge decks. J. Appl. Polym. Sci. 2011, 121, 2310–2316.
(3) Jin, F. L.; Li, X.; Park, S. J. Synthesis and application of epoxy resins: A review. J. Ind. Eng. Chem. 2015, 29, 1–11.
(4) Toldy, A.; Anna, P.; Csontos, I.; Szabó, A.; Marosi, G. Intrinsically flame retardant epoxy resin-Fire performance and background-Part I. Polym. Degrad. Stab. 2007, 92, 2223–2230.
(5) Guo, Y.; Bao, C.; Song, L.; Yuan, B.; Hu, Y. In Situ Polymerization of Graphene, Graphite Oxide, and Functionalized Graphite Oxide into Epoxy Resin and Comparison Study of On-the-Flame Behavior. Ind. Eng. Chem. Res. 2011, 50, 7772–7783.
(6) Sang, B.; Li, Z.; Li, X.; Yu, L.; Zhang, Z. Graphene-based flame retardants: a review. J. Mater. Sci. 2016, 51, 8271–8285.
(7) Liu, Q.; Y.; Wang, D. H.; Li, Z. K.; Li, Z. F.; Peng, X. L.; Liu, C. B.; Zhang, Y.; Zheng, P. L. Recent Developments in the Flame-Retardant System of Epoxy Resin. Materials 2020, 13, 2145.
(8) Qian, L. J.; Qiu, Y.; Sun, N.; Xu, M. L.; Xu, G. Z.; Xin, F.; Chen, Y. J. Pyrolysis route of a novel flame retardant constructed by phosphophenanthrene and triazine-trione groups and its flame-retardant effect on epoxy resin. Polym. Degrad. Stab. 2014, 107, 98–105.
(9) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. Science 2013, 6149, No. 1230444.
(10) Li, B.; Wen, H. M.; Cui, Y.; Zhou, W.; Qian, G.; Chen, B. Emerging Multifunctional Metal-Organic Framework Materials. Adv. Mater. 2016, 28, 8819–8860.
(11) Stock, N.; Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. Chem. Rev. 2012, 112, 933–969.
(12) Hou, Y.; Hu, W.; Gui, Z.; Hu, Y. Preparation of metal-organic frameworks and their application as flame retardants for polystyrene. Ind. Eng. Chem. Res. 2017, 56, 8778–8786.
(13) Shi, X.; Dai, X.; Cao, Y.; Li, J.; Huo, C.; Wang, X. Degradable poly(lactic acid)/metal-organic framework nanocomposites exhibiting good mechanical, flame retardant, and dielectric properties for the fabrication of disposable electronics. Ind. Eng. Chem. Res. 2017, 56, 3887–3894.
(14) Hou, Y.; Liu, L.; Qiu, S.; Zhou, X.; Gui, Z.; Hu, Y. DOP-modified two-dimensional Co-based metal-organic framework: preparation and application for enhancing fire safety of poly(lactic acid). ACS Appl. Mater. Interfaces 2018, 10, 8274–8286.
(15) Li, A.; Xu, W.; Chen, R.; Liu, Y.; Li, W. Fabrication of zeoliticimidazolate frameworks on layered double hydroxide nanosheets to improve the fire safety of epoxy resin. Composites, Part A 2018, 112, 558–571.
(16) Huang, R.; Guo, X.; Ma, S.; Xie, J.; Xu, J.; Ma, J. Novel phosphorus-nitrogen-containing ionic liquid modified metal-organic framework as an effective flame retardant for epoxy resin. Polymers 2020, 12, 108.
(17) Connolly, B. M.; Mehta, J. P.; Moghadam, P. Z.; Wheatley, A. E. H.; Fairen-Jimenez, D. From synthesis to applications: Metal-organic frameworks for an environmentally sustainable future. Curr. Opin. Green Sustainable Chem. 2018, 12, 47–56.
(18) Qi, X. L.; Zhou, D. D.; Zhang, J.; Hu, S.; Haranczyk, M.; Wang, D. Y. Simultaneous Improvement of Mechanical and Fire-Safety Properties of Polymer Composites with Phosphonate-Loaded MOF Additives. ACS Appl. Mater. Interfaces 2019, 11, 20325–20332.
(19) Zhang, Y.; Zhang, Y.; Wang, X.; Yu, J.; Ding, B. Ultrahigh Metal-Organic Framework Loading and Flexible Nanofibrous Membranes for Efficient CO2 Capture with Long-Term, Ultradeformable Recyclability. ACS Appl. Mater. Interfaces 2018, 10, 34802–34810.

(20) Furukawa, H.; Gandara, F.; Zhang, Y.; Jiang, J.; Queen, W.; Hudson, M. R.; Yaghi, O. M. Water Adsorption in Porous Metal-Organic Frameworks and Related Materials. J. Am. Chem. Soc. 2014, 136, 4369–4381.

(21) Tang, Y.; Huang, H.; Xue, W.; Chang, Y.; Li, Y.; Guo, X.; Zhong, C. Rigidifying induced fluorescence enhancement in 2D porous covalent triazine framework nanosheets for the simultaneously luminous detection and adsorption removal of antibiotics. Chem. Eng. J. 2020, 384, 123382.

(22) Serra-Crespo, P.; Ramos-Fernandez, E. V.; Gascon, J.; Kapteijn, F. Synthesis and characterization of a amino functionalized MIL-101(Al): Separation and catalytic properties. Chem. Mater. 2011, 23, 2565–2572.

(23) Yang, Q.; Lu, R.; Ren, S.; Chen, C.; Chen, Z.; Yan, X. Three dimensional reduced graphene oxide/ZIF-67 aerogel: Effective removal cationic and anionic dyes from water. Chem. Eng. J. 2018, 348, 202–211.

(24) Bhorda, N.; Basina, G.; Pokhrel, J.; Reddy, K. S.; Anastasiou, S.; Balasubramanian, V. V.; AlWahedi, Y. F.; Karanikolos, G. N. Functionalization effects on HKUST-1 and HKUST-1/graphene oxide hybrid adsorbents for hydrogen sulfide removal. J. Hazard. Mater. 2020, 394, No. 122565.

(25) Mahmodi, K.; Hosni, K.; Hamdi, N.; Srasra, E. Kinetics and equilibrium studies on removal of methylene blue and methyl orange by adsorption onto activated carbon prepared from date pits-A comparative study. Korean J. Chem. Eng. 2015, 32, 274–283.

(26) Kang, D.; Yu, X.; Ge, M.; Xiao, F.; Xu, H. Novel Al-doped carbon nanotubes with adsorption and coagulation promotion for organic pollutant removal. J. Environ. Sci. 2017, 54, 1–12.

(27) Chen, B.; Chen, S.; Zhao, H.; Liu, Y.; Long, F.; Pan, X. A versatile β-cyclodextrin and polyethyleneimine bi-functionalized magnetic nanoadsorbent for simultaneous capture of methyl orange and Pb(II) from complex wastewater. Chemosphere 2019, 216, 605–616.

(28) Wong, S.; Tumari, H. H.; Ngadi, N.; Mohamed, N. B.; Hassan, O.; Mat, R.; Amin, N. A. S. Adsorption of Anionic Dyes on Spent Tea Leaves Modified with Polyethyleneimine (PEI-STL). J. Cleaner Prod. 2019, 206, 394–406.

(29) Zhao, Q.; Zhu, X.; Chen, B. Stable Graphene Oxide/ Poly(ethyleneimine) 3D Aerogel with Tunable Surface Charge for High Performance Selective Removal of Ionic Dyes from Water. Chem. Eng. J. 2018, 334, 1119–1127.

(30) Liu, J.; Ma, S.; Zang, L. Preparation and characterization of ammonium-functionalized silica nanoparticles a new adsorbent to remove methyl orange from aqueous solution. Appl. Surf. Sci. 2013, 265, 393–398.

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

(32) Haque, E.; Jun, J. W.; Jhung, S. H. Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235). J. Hazard. Mater. 2011, 185, 507–511.

(33) Haque, E.; Lo, V.; Minett, A. I.; Harris, A. T.; Church, T. L. Dichotomous adsorption behaviour of dyes on an amino-functionalised metal-organic framework, amino-MIL-101(Al). J. Mater. Chem. A 2014, 2, 193.

(34) Cheng, Z.; Zhang, L.; Guo, X.; Jiang, X.; Li, T. Adsorption behavior of direct red 80 and congo red onto activated carbon/ surfactant: Process optimization, kinetics and equilibrium. Spectrochim. Acta, Part A 2015, 137, 1126–1143.

(35) Ardejani, F. D.; Badii, K.; Laimae, N. Y.; Shafaei, S. Z.; Mirhabibi, A. R. Adsorption of Direct Red 80 dye from aqueous solution onto almondsHELL: Effect of pH, initial concentration and shell type. J. Hazard. Mater. 2008, 151, 70–73.

(36) da Silveira Neta, J. J.; Moreira, G. C.; da Silva, C.; Reis, C. Use of polyurethane foams for the removal of the Direct Red 80 and Reactive Blue 21 dyes in aqueous medium. Desalination 2011, 281, 55–60.

(37) Mahmodi, N. M.; Taghizadeh, M.; Taghizadeh, A. Ultra-sound-assisted green synthesis and application of recyclable nanoporous chromium-based metal-organic framework. Korean J. Chem. Eng. 2019, 36, 287–298.

(38) Yang, G.; Wu, W.-H.; Wang, Y.-H.; Jiao, Y.-H.; Lu, L.-Y.; Qu, H.-Q.; Qin, X.-Y. Synthesis of a novel phosphazene-based flame retardant with active amine groups and its application in reducing the fire hazard of Epoxy Resin. J. Hazard. Mater. 2019, 366, 78–87.

(39) Zhang, Y.; Ren, Y.; Liu, X.; Hao, T.; Qin, Y. Preparation of durable flame retardant PAN fabrics based on amidoxidation and phosphorylation. Appl. Surf. Sci. 2018, 428, 395–403.

(40) Tang, H.; Zhu, Z.; Chen, R.; Wang, J.; Zhou, H. Synthesis of DOPO-base pyrazine derivative and its effect on flame retardancy and thermal stability of epoxy resin. Polym. Adv. Technol. 2019, 30, 2331–2339.

(41) Zhang, L.; Chen, S.; Pan, Y.; Zhang, S.; Nie, S.; Wei, P.; Zhang, X.; Wang, R.; Wang, D. Nickel metal-organic framework derived hierarchically mesoporous nickel phosphate toward smoke suppression and mechanical enhancement of intumescent flame retardant wood Fiber/poly(lacticacid) composites. ACS Sustainable Chem. Eng. 2019, 7, 9272–9280.

(42) Liu, Z.; Qiu, Y.; Qian, L.; Chen, Y.; Xu, B. Strengthen flame retardancy of epoxy thermoset by montmorillonite particles adhering phosphorus-containing fragments. J. Appl. Polym. Sci. 2020, 137, No. 47500.

(43) Hou, Y.; Hu, W.; Zhou, X.; Gui, Z.; Hu, Y. Vertically aligned nickel 2-methylimidazole metal-organic framework fabricated from graphene oxides for enhancing fire safety of polystyrene. Ind. Eng. Chem. Res. 2017, 56, 8778–8786.