

Preparation of Ionic Liquid Supported Metal Frame Py/MOF-199 and Its Adsorption Desulfurization Performance

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Abstract: The metal framework MOF-199 (Cu-BTC) was prepared and the [Hnmp][H₂PO₄] ionic liquid was loaded onto MOF-199 to synthesize the ionic liquid supported metal framework Py/MOF-199. The adsorbent was characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy and specific surface area. The effects of pretreatment conditions of MOF-199, ionic liquid loading mode, loading, load temperature and loading time on the adsorption and removal performance of thiophene were investigated. The preparation conditions and adsorption desulfurization conditions of the adsorbent were optimized by orthogonal experiment. The results show that Py/MOF-199 obtained by ionic liquid modification maintains the regular octahedral structure of MOF-199. The suitable preparation conditions for Py/MOF-199 are as follows: pretreatment of MOF-199 by vacuum Soxhlet extraction and vacuum drying, followed by solvothermal loading [Hnmp][H₂PO₄], load temperature of 50 °C, load The time is 8h and the load is 7%. The order of influence of various factors on the desulfurization performance of the adsorbent is: load temperature>loading time>ionic liquid loading. Suitable Py/MOF-199 adsorption desulfurization conditions are: simulated oil is 10mL, adsorbent dosage is 0.2g, adsorption temperature is 70 °C, adsorption time is 1h. Under these conditions, the thiophene removal rate can reach 96.7%.

Keywords: Adsorption desulfurization; Ionic liquids; Py/MOF-199; Thiophene (TP)

The SO₂ produced after the combustion of the fuel is the main cause of air pollution, acid rain and exhaust gas after-treatment device damage ^[1], therefore, the total sulfur content of the fuel is increasingly required ^[2]. The Environmental Protection Agency (EPA) stipulates that the total sulfur content in federal gasoline must not exceed 10 mg/kg ^[3], and the EU's environmental regulations also limit the total sulfur content to less than 10 mg/kg ^[4, 5]. In order to meet the total sulfur content standards, protect the environment and reduce economic losses, deep desulfurization has attracted the attention of researchers all over the world.

Adsorption desulfurization (ADS) technology has attracted more and more people to invest in desulfurization technology with the advantages of desulfurization effect to ultra-low level, mild adsorption conditions and good regeneration performance. Metal-organic frameworks (MOFs) have attracted much attention in adsorption desulfurization due to their advantages of adjustable pore size, high porosity, large specific surface area and open active sites ^[6-8]. Among them, MOF-199 (Cu-BTC-MOF) has a suitable pore size ^[9-11], and has a good metal open position due to the simultaneous presence of Cu⁺ and Cu²⁺, which can provide a π complex center for thiophene compounds ^[12]. Wu et al. ^[13] found that MOF-199 has abundant adsorption sites and exhibits high adsorption capacity for thiophene compounds. It is suggested that the adsorption of thiophene compounds by MOF-199 is mainly affected by the conjugated π system (π -M). And the interaction of the lone pair of sulfur atoms in the thiophene with the unsaturated metal sites in MOF-199 (σ -M). Therefore, MOFs having higher strength and higher density of unsaturated metal sites are suitable adsorptive desulfurization materials. Ionic liquid (ILs) material is an organic salt with a low melting point and very low vapor pressure, good chemical stability and good thermal stability ^[14], which can be alkaline by acid-base interaction. Sulfur compounds provide acidic sites ^[15]. Khan et al. ^[16] prepared an acidic imidazole ionic liquid supported organometallic framework MIL-101, and found that the BT selectivity and sulfur capacity of the adsorbent obtained by loading the ionic liquid into the metal framework were improved. Therefore, the adsorbent prepared by loading the ionic liquid on the MOFs is expected to achieve the superior

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desulfurization effect by the synergistic effect between the two, so that the obtained research results are more excellent, but related reports are less [16].

In this experimental study, Py/MOF-199 was prepared by loading pyridine dihydrogen phosphate or [Hnmp][H₂PO₄] ionic liquid onto MOF-199. The pretreatment conditions, ionic liquid loading mode, ionic liquid loading content and load were investigated. The effects of temperature and loading time on the adsorption performance of thiophene were optimized. The preparation conditions of Py/MOF-199 were optimized by orthogonal experiment.

1. Experimental Section

1.1 Drugs and Simulated Oil

N-methylpyrrolidone (analytical grade, Aladdin Reagent Co., Ltd., Shanghai); phosphoric acid (85%) (analytical grade, Aladdin Reagent Co., Ltd., Shanghai); absolute ethanol (analytical grade, Liaoning Quanrui Reagent Co., Ltd.); copper nitrate (analytical grade, Tianjin Fuchen Chemical Reagent Factory); 1,3,5-benzenetricarboxylic acid (analytical grade, Aladdin Reagent Co., Ltd., Shanghai); N, N-dimethylformamide (analytical grade, Tianjin Fuchen Chemical Reagent Factory); dichloromethane (analytical grade, Liaoning Quanrui Reagent Co., Ltd.); thiophene (TP) (analytically pure, Lyon reagent, USA).

In the experiment, thiophene was used as a model sulfide, and n-octane was used as a solvent to prepare a simulated oil with a sulfur content of 100 mg/L.

1.2 Preparation of Adsorbent

1.2.1 Synthesis and Pretreatment of Metal Organic Frameworks

2.146g of Cu(NO₃)₂·3H₂O was dissolved in 17mL of deionized water and fully dissolved to obtain solution A; 1g of 1,3,5-benzenetricarboxylic acid (H₃BTC) was dissolved in 17mL of ethanol and 17N, N-dimethyl formamide. In the middle, the solution B is sufficiently dissolved. Mix the A and B solutions until the solution is a clear blue solution. Then, in a 100 mL solvothermal reactor with a Teflon-lined, thermostat at 85 ° C for 12 h, continue to increase the temperature to 100 ° C for 12 h. To room temperature. The obtained reaction product was suction filtered, washed with water and ethanol, and then immersed in ethanol for 24 hours, and then suction-filtered to obtain a blue solid.

After washing the blue solid with CH₂Cl₂ suction filtration, it was pretreated in four ways. Solvent exchange method: The sample was placed in a dichloromethane solvent, soaked for 3 days, and the solvent was changed once a day. Vacuum pretreatment: vacuum treatment was carried out at 140 °C. High temperature nitrogen pretreatment: temperature is 140 ° C, nitrogen flow rate is 20 mL / m³. Soxhlet extraction + vacuum drying: after 12 hours of methylene chloride extraction, vacuum drying at 140 ° C for 12 h. That is, a pure blue solid MOF-199 (Cu-BTC) is obtained. When not specified in the experiment, MOF-199 refers to the preparation of the Soti + vacuum drying pretreatment method.

1.2.2 Synthesis of Ionic Liquids

60mL N-methylpyrrolidone was placed in a three-necked flask, and 35 mL of concentrated phosphoric acid with a concentration of 85% was slowly added under magnetic stirring. After the completion of the dropwise addition, the temperature was raised to 80 ° C for 2 hours, then cooled to room temperature, and the remaining reactants and water were distilled off. And washing with ethanol several times, vacuum drying at 40 ° C for 24 h to obtain a colorless transparent ionic liquid pyridine phosphate dihydrogen [Hnmp] [H₂PO₄].

1.2.3 Synthesis of Metal Frames Supported by Ionic Liquids

The MOF-199 metal frame loaded ionic liquid obtained by pretreatment with Soti + vacuum drying was used. Using ethanol as a dispersing solvent, 0.01 g of ionic liquid pyridine dihydrogen phosphate ([Hnmp][H₂PO₄]) was dissolved in 1 mL of ethanol. After the ionic liquid was completely dissolved, an appropriate amount of MOF-199 was added, and after stirring for 10 minutes, the following were respectively used. Four ways to deal with:

Dipping method: immersion at 50 ° C for 12 h. The resulting mixture was dried at 100 ° C to remove the solvent to prepare an ionic liquid supported metal framework adsorbent, designated Py/MOF-199-impregnated.

Solvothermal: The ionic liquid was loaded under reflux at 50 ° C for 0.5 h, and the adsorbent obtained by removing

the solvent ethanol by a rotary evaporator was designated as Py/MOF-199-solvent heat.

Microwave method: The mixed solution was placed in a microwave synthesizer, and the microwave power was set to 400 W. At 50 °C, after microwave irradiation for 20 min, the adsorbent obtained by removing the solvent ethanol by a rotary evaporator was recorded as Py/MOF-199-microwave.

Ultrasound-assisted method: The mixed solution was placed in an ultrasonic oscillator with a power of 400 W and ultrasonic vibration for 30 min. The adsorbent obtained by removing the solvent ethanol by a rotary evaporator was recorded as Py/MOF-199-ultrasound.

When not specified in the experiment, Py/MOF-199 refers to the theoretical loading of ionic liquid is 7%, and the loading method is solvothermal method. Thermogravimetric analysis was performed on MOF-199 and Py/MOF-199 (the theoretical loading of ionic liquid was 7%), and the actual loading of the ionic liquid calculated by the difference in weight loss was 6.7%.

1.3 Characterization Method

X-ray diffraction (XRD) analysis was performed using a D/max-2200PC X-ray diffractometer from Japan Science, using a Cu target, $K\alpha$ ray radiation, operating voltage 40 kV, operating current 30 mA, scanning rate 10 (°) / min, 5 °-50 ° scan. The catalyst specific surface area (BET) was measured by a NOVA2000e type specific surface area pore size analyzer, the adsorbate was liquid nitrogen, and the adsorption temperature was -196 °C. Infrared analysis of the adsorbent samples was carried out using a German Bruker Tensor27 Fourier infrared spectrometer, scanning 400-4000 cm^{-1} . The morphology of the experimental samples was analyzed using a high-resolution field emission scanning electron microscope from ZEISS SIGMA, Germany.

1.4 Adsorption Desulfurization Experiment

At 50 °C, weigh 10 mL of sulphur content of 100 mg / L of simulated oil into a conical flask, add 0.2g of adsorbent, adsorbed for 1h, and then use the belt produced by American Platinum Elmer Instrument (Shanghai) Co., Ltd. Sulfur content analysis was performed on a PE gas chromatograph with a flame photometric detector (FPD).

2. Results and Discussions

2.1 Characterization of Adsorbents

2.1.1 X-ray powder diffraction (XRD)

Figure 1 shows the XRD spectra of the adsorbents MOF-199, Py/MOF-199, and MOF-199 (BASF) to verify the effect of the loading of the ionic liquid on the original crystal structure of the metal organic framework. It can be seen from Fig. 1 that the MOF-199 synthesized in this experiment completely coincides with the diffraction peak position of MOF-199 sold by BASF, which proves that MOF-199 was successfully obtained. Compared with MOF-199, the diffraction peak of Py/MOF-199 showed no significant change, indicating that the supported ionic liquid did not destroy the skeleton of the metal organic framework and maintained the original lattice structure. After the ionic liquid is loaded, the characteristic peak intensity of the adsorbent decreases, because the organic group of the ionic liquid is supported in the skeleton, so that the electron density between the skeleton and the pore is differentiated, and the unit cell parameters are changed.

2.1.2 Scanning Electron Microscope (SEM)

Fig. 2 is a SEM photograph corresponding to the MOF-199, Py/MOF-199 adsorbent. It can be seen from Fig. 2 that the morphology of the metal organic framework supported by the ionic liquid (Fig. 2(b)) is similar to that of the unsupported metal organic framework (Fig. 2(a)), both of which are regular octahedral structures, and an evenly dispersed ionic liquid can be observed from the surface of the frame. This indicates that the loaded ionic liquid was successfully loaded onto the MOF-199 and did not change the original physical structure of the metal organic framework, which was consistent with the XRD characterization results.

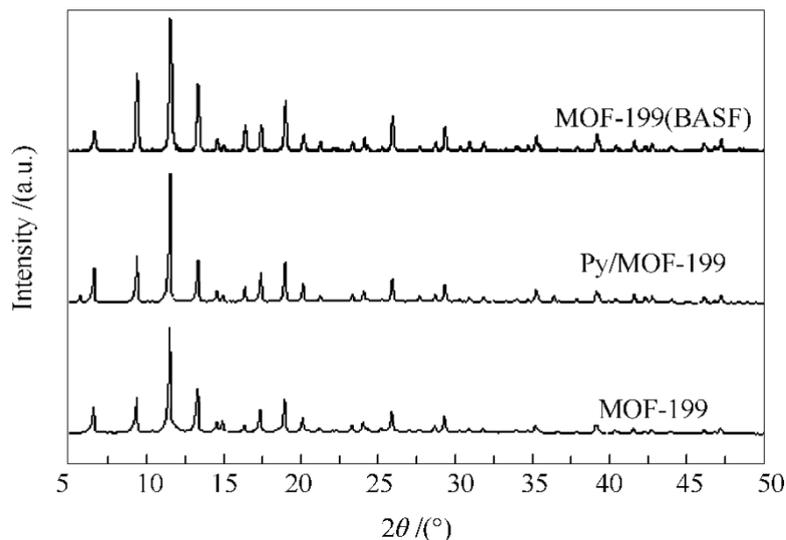


Figure 1 XRD spectra of MOF-199, Py/MOF-199, and MOF-199 (BASF)

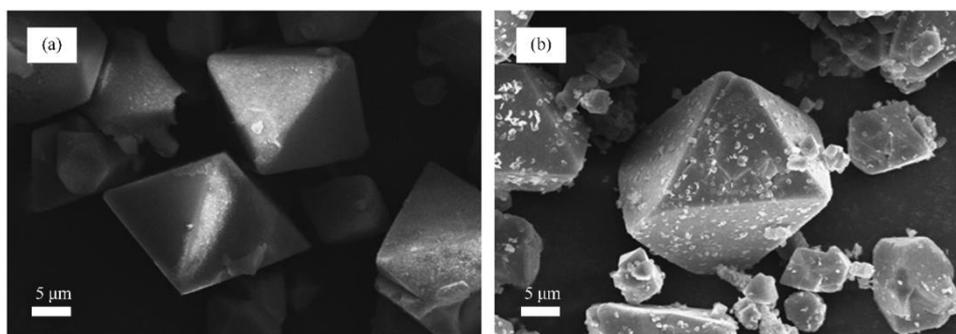


Figure 2 SEM photograph of MOF-199 and Py/MOF-199

2.1.3 Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 3 shows the FT-IR spectrum of MOF-199 and different loadings of Py/MOF-199 to study the mechanism of action of ionic liquids on MOF-199. It can be seen from Fig. 3(a) that the off-plane vibration of BTC3- on the skeleton can be seen from the infrared spectrum of 600-1300 cm^{-1} ; the peak at 1106 cm^{-1} represents the stretching peak of the C-H bond on the benzene ring in the ligand. The peak at 1447 cm^{-1} is the combined peak of the stretching vibration and deformation vibration of the benzene ring skeleton in the ligand; the pair of medium strong peaks at 1646 and 1372 cm^{-1} are respectively attributed to the antisymmetry of C-O2 in the carboxyl group of the ligand. And symmetric stretching vibration peak; the peak at 490 cm^{-1} is related to Cu-O stretching vibration; the two absorption peaks at 728 and 761 cm^{-1} indicate that the group on the benzene ring is replaced by Cu; the two appear at 1106 and 940 cm^{-1} . A weak absorption peak is assigned to the stretching vibration absorption peak of C-O-Cu. According to Borfecchia et al. [17], a number of Cu-related peaks were observed at 600-50 cm^{-1} . The symmetry and antisymmetric contraction vibration peaks of C-O2 in the carboxyl group of the trimellitic acid ligand are located at 1372 and 1646 cm^{-1} , respectively, which are moderately strong peaks. The carboxylic acid anti-vibration absorption peak of the ionic liquid [Hnmp][H₂PO₄] is usually located at a lower frequency, and thus the peak at 1646 cm^{-1} is red-shifted after the ionic liquid is loaded, and the characteristic peak intensity at 1589 cm^{-1} becomes large (Figure 3 (c)). It can be seen from Fig. 3(b) that with the introduction of the ionic liquid [Hnmp][H₂PO₄], a new signal intensity enhancement occurs at 1044 cm^{-1} , indicating that the ionic liquid [Hnmp][H₂PO₄] is loaded to the metal organic framework MOF- 199.

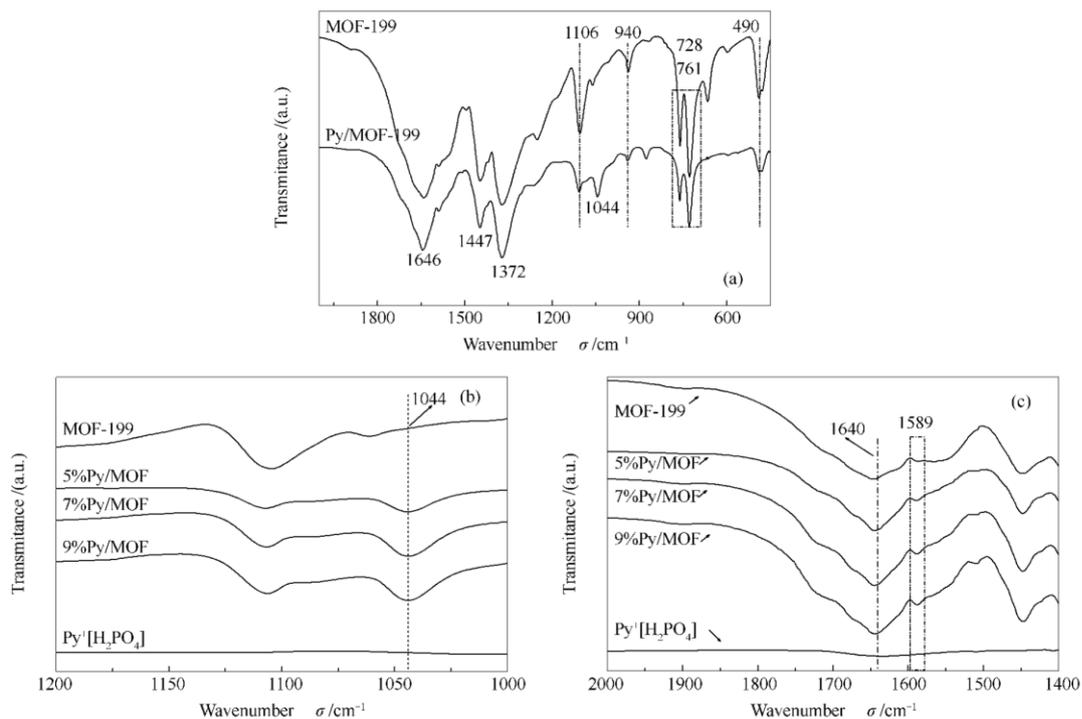


Figure 3 FT-IR spectrum of MOF-199 and Py/MOF-199

2.1.4 Specific Surface Area Determination (BET)

Table 1 shows the BET specific surface area, pore volume and pore diameter of the adsorbent, and Fig. 4 shows the BJH adsorption pore size distribution of MOF-199 and Py/MOF-199 (7%). As can be seen from Table 1, the specific surface area and pore volume of MOF-199 were 1362 m²/g and 0.71 cm³/g, respectively, and the specific surface area and pore volume decreased after loading the ionic liquid, but the average pore diameter increased compared with MOF-199. As can be seen from Fig. 4, MOF-199 is mainly a pore having a pore diameter of 2.1 nm and a small number of pores having a pore diameter of 3.6 nm.

After the ionic liquid was loaded, the pore distribution changed greatly. The pores with a pore size of 3.8 nm increased significantly, and a small number of pores with a pore diameter of 11.3 nm appeared, indicating that the ionic liquid not only existed on the surface and pores of the carrier, but also partially. The ionic liquid is bridged to the frame by ion bonds to form mesopores of larger pore size resulting in an increase in the average pore diameter.

2.2 Py/MOF-199 Optimization of Preparation Conditions

2.2.1 Effect of Pretreatment Conditions on Desulfurization Performance MOF-199 Pure Frame

MOF-199 has a secondary structural unit formed by four BTC units connected by six dimeric copper units. The secondary structural unit is in the form of an octahedron, and the Cu center is in a state of coordination and unsaturation, and thus is generated with the adsorbate molecules. Interaction provides an active site for adsorption desulfurization. However, during the preparation process, MOF-199 adsorbs certain solvent molecules and small molecular substances in the air, occupying the active sites of the framework, causing the pores to clog and the specific surface area to decrease, resulting in a decrease in adsorption capacity. Therefore, its activation is an indispensable step before the adsorption experiments of metal organic framework compounds. At present, activation means such as solvent soaking, nitrogen purging, and vacuum drying are widely used.

Table 1 BET surface area pore volume and pore size of the adsorbents

Adsorbent	BET area $A /$ ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume $v /$ ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore size d / nm
MOF-199	1362	0.71	2.13
7%Py/ MOF-199	1074	0.62	2.35

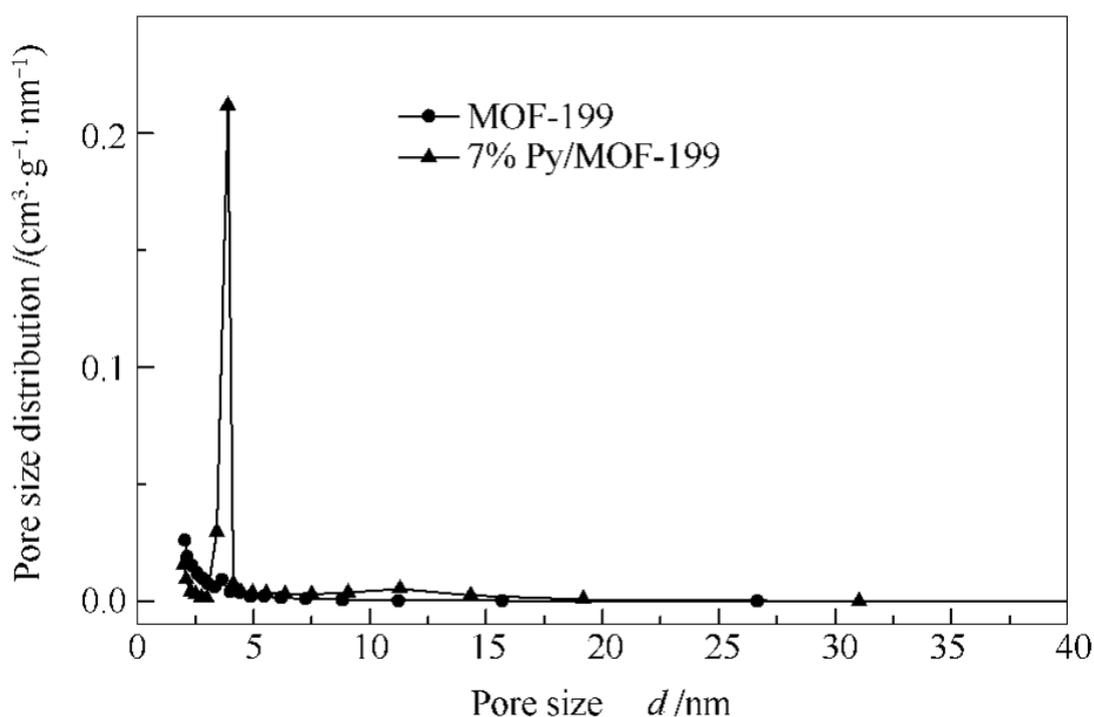


Figure 4: Pore size distribution of MOF-199 and 7% Py/MOF-199

In order to determine the optimal pretreatment method, the activity of MOF-199 adsorbent prepared by different pretreatment conditions was evaluated. The results are shown in Fig. 5. The adsorption desulfurization condition is 10mL simulated oil, 0.1g adsorbent MOF-199, the adsorption temperature is 50 °C, and the adsorption time is 0.5h. When there is no special explanation, the preparation conditions optimize the adsorption desulfurization experimental conditions. It can be seen from Fig. 5 that the sample obtained by direct vacuum drying has the worst adsorption performance, and the sample subjected to Soxhlet extraction and vacuum drying has the best desulfurization effect. It is inferred that the solvent molecules adsorbed by MOF-199 cannot be completely removed due to a single vacuum drying, and the solvent exchange method cannot completely release small molecules in the air. Therefore, the experiment used a pretreatment method of first-distillation of dichloromethane and vacuum drying.

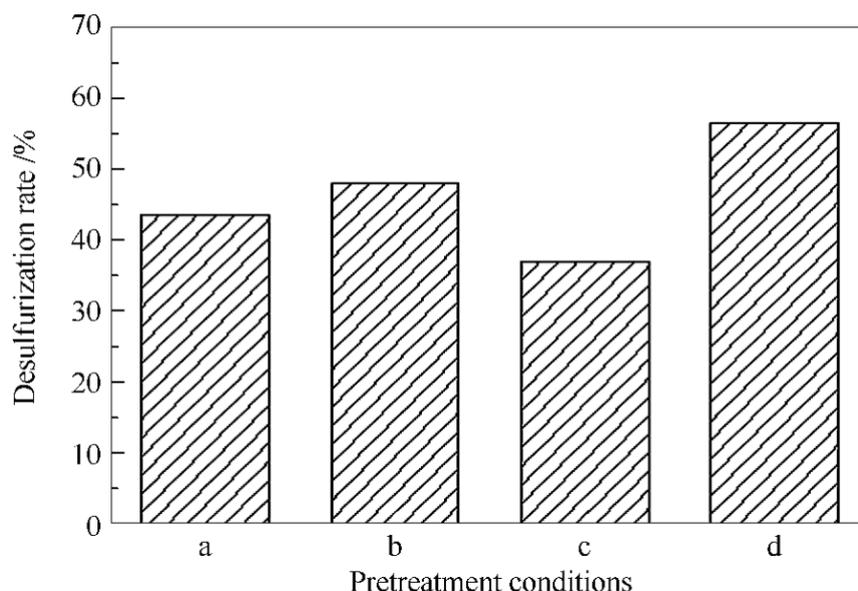


Fig. 5 The effect of pretreatment conditions on the adsorption and desulfurization activity of MOF-199

2.2.2 Effect of Ionic Liquid Loading Mode on Adsorption Performance of Py/MOF-199 Adsorbent

Fig. 6 shows the Py/MOF- prepared by the four load modes (impregnation, solvothermal synthesis, microwave assisted and ultrasonic assisted) with the load temperature of 50 °C, the load time of 6 h and the load of 11%. Desulfurization results of 199.

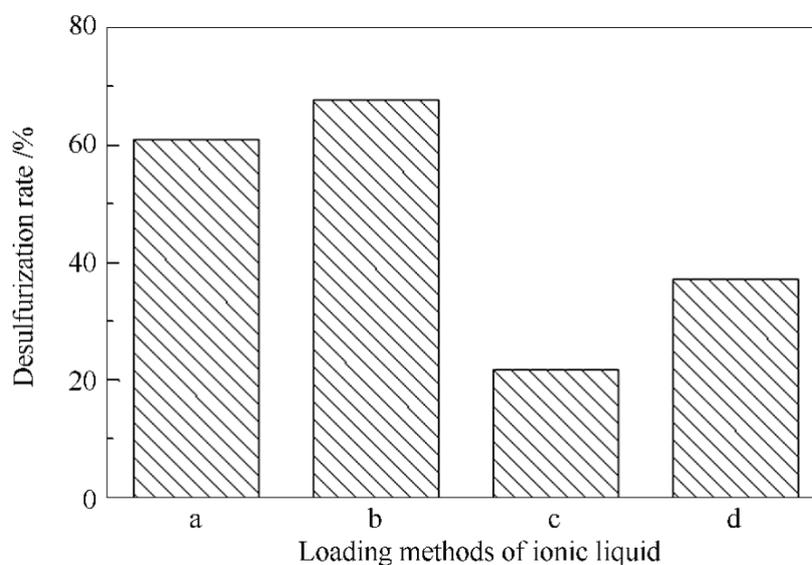


Figure 6. Desulfurization rate of Py/MOF-199 under different ionic liquid loading modes

As can be seen from Fig. 6, the order of desulfurization activity is: solvothermal method > impregnation method > ultrasonic method > microwave method. The desulfurization effect of the adsorbent obtained by microwave method and ultrasonic method is not good. It is speculated that the process of ionic liquid and framework bridging to the aromatic ring substitution position through carboxylic acid bond is interfered by microwave or ultrasonic. The adsorbent prepared by the impregnation method is lighter in color than other methods, indicating that a large part of the ionic liquid adheres to the surface of the MOF-199, and the dispersion on the surface of the inner pore is weakened, thereby limiting the desulfurization property. The solvothermal method is carried out under magnetic stirring, so that the ionic liquid is

uniformly dispersed in the solvent, and a suitable temperature contributes to an accelerated diffusion rate, so that the ionic liquid easily enters the inside of the carrier pores to ensure uniform loading on the surface of the carrier, and therefore, the solvent Py/MOF-199 obtained by the thermal method has the best adsorption desulfurization effect.

2.2.3 Effect of Ionic Liquid Loading on Desulfurization Performance of Adsorbents

The ionic liquid loadings were prepared by solvothermal method at 1%, 3%, 5%, 7%, 9%, 11%, and 13%, respectively, while maintaining a load temperature of 50 °C and a load time of 6 h. The Py/MOF-199 adsorbent was measured for desulfurization rate, and the results are shown in Fig. 7. It can be seen from Fig. 7 that the desulfurization rate of the adsorbent increases first and then decreases with the increase of the loading of the ionic liquid. The adsorption desulfurization effect of Py/MOF-199 with the loading of 7% is the best, and the subsequent loading is 7% adsorbent.

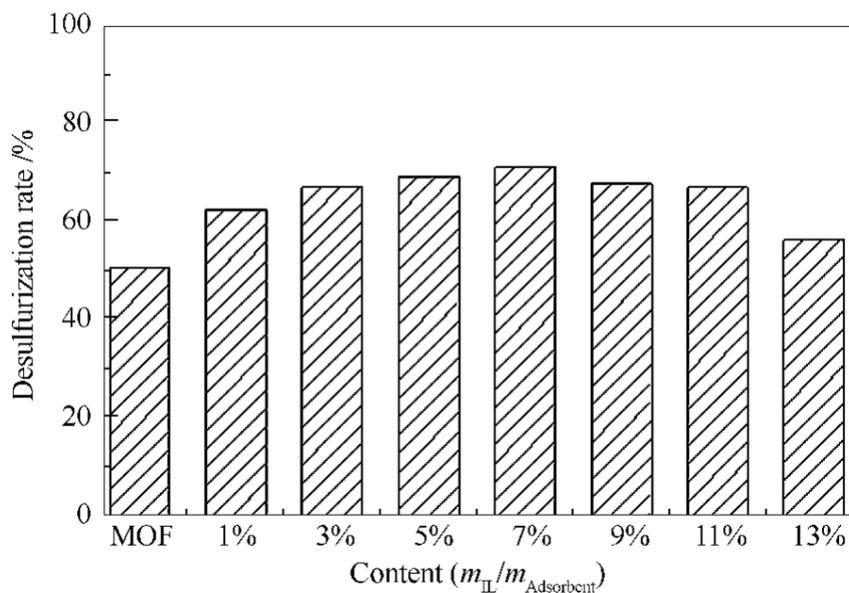


Figure 7. Desulfurization rate of Py/MOF-199 under different ionic liquid loadings

2.2.4 Effect of Loading Temperature of Ionic Liquids on Desulfurization Performance of Adsorbents

To investigate the effect of different loading temperatures on the desulfurization performance of Py/MOF-199, ethanol was used as the solvent (0.01g-1(IL)·mL(C₂H₅OH)), and the loading of ionic liquid [Hnmp][H₂PO₄] was 7%. Under the premise of the load time being 6h, the load temperature (30, 40, 50 and 60 °C) was changed, and the desulfurization rate was measured. The results are shown in Fig. 8. It can be seen from Fig. 8 that the adsorption desulfurization performance of Py/MOF-199 increases with the increase of the loading temperature of the ionic liquid, and the increase rate slightly decreases after the load temperature exceeds 50 °C. Increasing the temperature helps to enhance the dispersibility of the ionic liquid, which is beneficial to the uniform loading of the ionic liquid. When the ionic liquid is completely liquid, its dispersibility is less affected by temperature, and too high temperature will cause some of the ionic liquid to be loaded. Ionic liquids fall off, which is not conducive to desulfurization. Therefore, the ionic liquid loading temperature is suitably 50 °C.

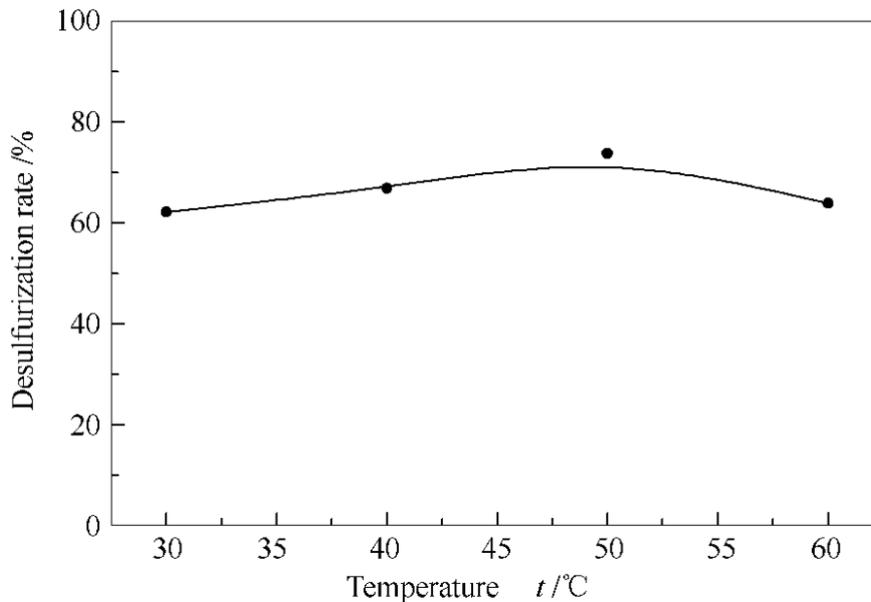


Figure 8 Desulfurization rate of Py/MOF-199 at different load temperatures

2.2.5 Effect of Loading Time of Ionic Liquids on Desulfurization Performance of Adsorbents

The desulfurization rate of the obtained adsorbent under different loading times was measured under the condition that the ionic liquid loading was 7% and the load temperature was 50 ° C. The results are shown in Fig. 9.

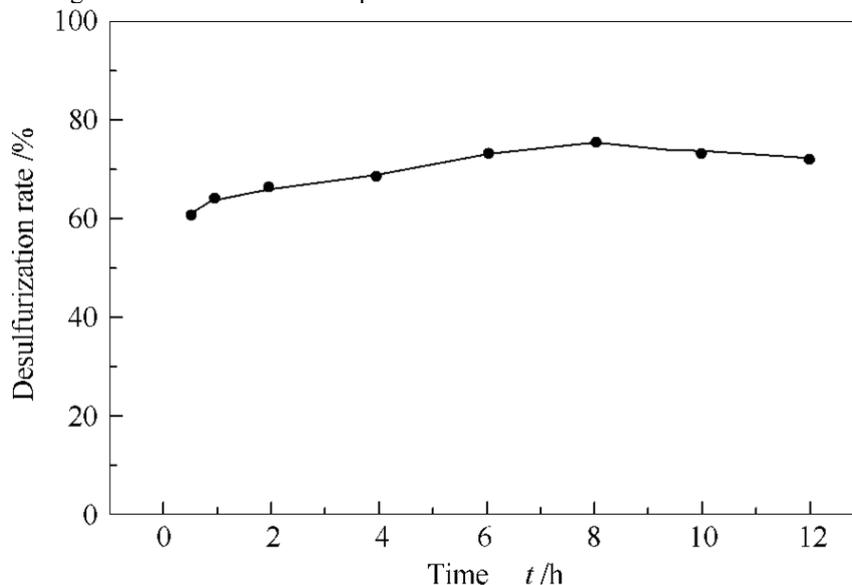


Figure 9. Desulfurization rate of Py/MOF-199 under different ionic liquid loading times

It can be seen from Fig. 9 that with the extension of the loading time of ionic liquid [Hnmp][H₂PO₄], the adsorption capacity of the adsorbent is enhanced. When the loading time is 8h, the desulfurization rate reaches 75.7%, and the load time exceeds 8h, the adsorbent adsorption capacity decreased slightly. The bridging of the ionic liquid [Hnmp][H₂PO₄] on the framework requires reaction time, so the desulfurization performance of the adsorbent increases with time; after more than 8 hours, the load of the ionic liquid reaches saturation, and the load time is extended again. Significantly improved. Therefore, the experimental load time is 8h.

2.2.6 Orthogonal Experiment

In order to explore the comprehensive effects of different loading conditions on the desulfurization performance of Py/MOF-199, a three-factor and three-level orthogonal experiment was designed. Table 2 is a table of orthogonal experimental factors.

Table 3 is a visual analysis table for orthogonal experiments of factors affecting ionic liquid loading conditions.

Table 3 shows that $R_1 > R_2 > R_3$, indicating that the order of influence of various factors on desulfurization performance is: load temperature > loading time > ionic liquid loading. Therefore, the optimum conditions for solvothermal immobilization of ionic liquids on the MOF-199 framework are: 5% ionic liquid loading at 50 °C for 8 h.

Table 2 Level of the factors of orthogonal test

Level	Factor		
	temperature $t/^\circ\text{C}$	time t/h	ionic liquid content $w/\%$
	A	B	C
1	40	6	6
2	50	8	7
3	60	10	8

Table 3 Visual analysis table of orthogonal test for influencing factors of ionic liquid loading condition

Test	Temperature $t/^\circ\text{C}$	Time t/h	Ionic liquid content	Rate of thiophene removal
	A	B	C	
1	40	6	6%	64.6%
2	40	8	7%	67.7%
3	40	10	8%	73.5%
4	50	6	7%	73.8%
5	50	8	8%	69.7%
6	50	10	6%	66.2%
7	60	6	8%	58.7%
8	60	8	6%	69.0%
9	60	10	7%	61.1%
K_1	205.9%	197.2%	199.8%	
K_2	209.8%	206.5%	202.7%	
K_3	188.8%	200.8%	202.0%	
Average k_1	68.6%	65.7%	66.6%	
Average k_2	69.9%	68.8%	67.6%	
Average k_3	62.9%	66.9%	67.3%	
Range R	5.7%	3.1%	0.9%	
Primary order		A>B>C		
Superior level	A ₂	B ₂	C ₂	
Superior combination		A ₂ B ₂ C ₂		

K_n is the comprehensive removal rate of thiophene at different levels of the same influence factor; k_n is the average removal rate of thiophene at different levels of the same influence factor; $R = k_{\max} - k_{\min}$ is the difference between the maximum removal rate and the minimum removal rate of thiophene for the same influence factor

2.3 Optimization of Adsorption Desulfurization Conditions of Py/MOF-199

2.3.1 Effect of Adsorption Temperature on Desulfurization Performance of Py/MOF-199

The desulfurization rate at different adsorption temperatures was measured under the conditions of 10 mL of simulated oil, 0.1 g of adsorbent, and adsorption for 0.5 h. The results are shown in Fig. 10. It can be seen from Fig. 10 that as the temperature increases, the desulfurization rate first increases and then decreases. When the adsorption temperature is 70 °C, the desulfurization activity reaches the highest, which is 87.4%. This may be because when the adsorption temperature is low (<70 °C), the high adsorption temperature is beneficial to increase the surface of the diffusion adsorbent of the sulfide in the simulated oil, so that the adsorption and desorption rate on Py/MOF-199 is accelerated. And as the adsorption temperature increases, the adsorption rate increases more than the desorption rate, thereby improving the ability of Py/MOF-199 to remove sulfides in the simulated oil; but when a certain temperature (70 °C) is reached, The diffusion of sulfide is not a key factor affecting the adsorption process. As the adsorption temperature increases, the

desulfurization rate decreases. Thus a suitable desulfurization temperature is 70 °C.

2.3.2 Effect of Adsorption Time on Desulfurization Performance of Py/MOF-199

Desulfurization experiments were carried out at 70 °C with 10 mL of simulated oil and 0.1 g of adsorbent to study the desulfurization performance at different adsorption times. The results are shown in Fig. 11. It can be seen from Fig. 11 that the desulfurization rate increases rapidly with the extension of time. After 1 h of reaction, the desulfurization rate reaches 89.7%. After adsorption for more than 1 h, the desulfurization rate increases little. At this time, the adsorption capacity of the adsorbent is 8.97 mg/g. This is because the adsorption reaches equilibrium after the adsorption reaches 1 h, and the adsorption time is prolonged, and the desulfurization rate increases slowly.

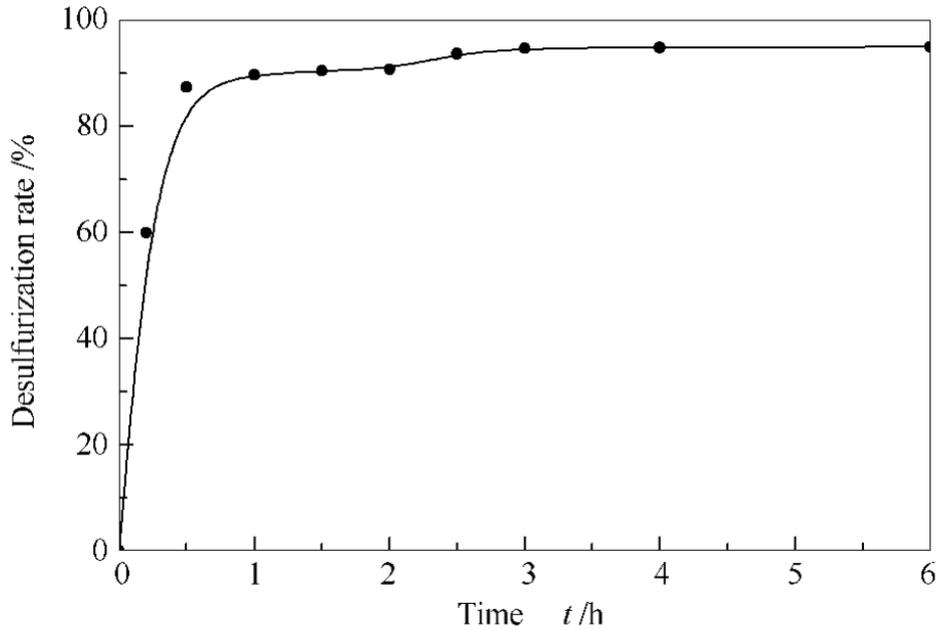


Figure 11 Effect of adsorption time on adsorption desulfurization performance

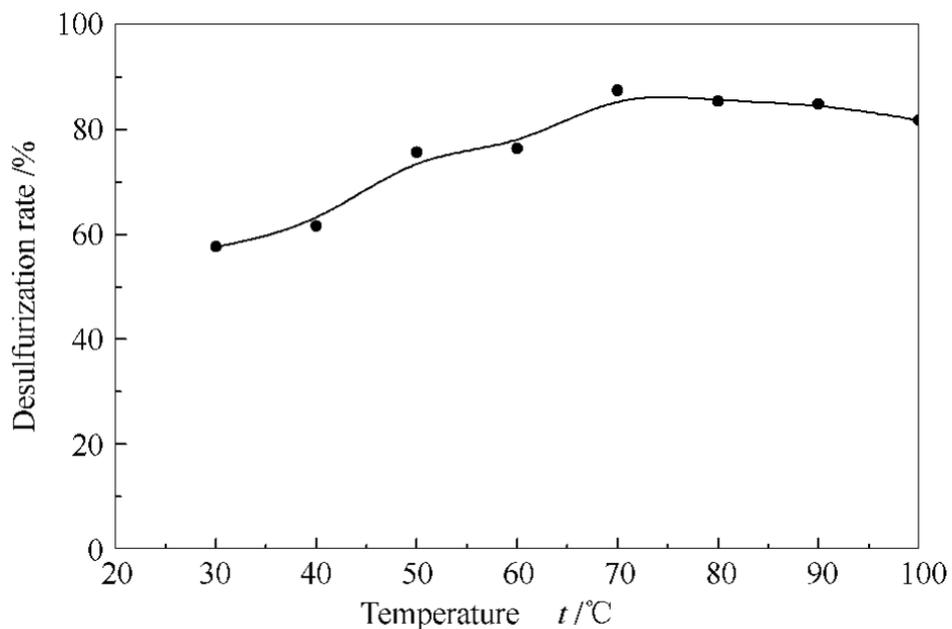


Figure 10 Effect of adsorption temperature on adsorption desulfurization performance

2.3.3 Effect of the Amount of Adsorbent on the Desulfurization Effect of Py/MOF-199

Using 10 mL of simulated oil as raw material and adsorbing at 70 ° C for 1 h, the desulfurization performance under different adsorbent dosages was studied. The results are shown in Fig. 12. It can be seen from Fig. 12 that the desulfurization rate increases with the increase of the amount of adsorbent. When the mass of the adsorbent increases to 0.2 g, the desulfurization rate of the adsorbent reaches 96.7%, and the amount of adsorbent continues to increase, and the desulfurization rate is close to 100%. . This is because after increasing the amount of the adsorbent, the amount of active sites is increased, thereby increasing the desulfurization rate, and when the amount of the adsorbent reaches a certain value (0.3 g), 100% removal of the sulfide can be achieved. This is because the prepared Py/MOF-199 adsorbent collects the unique three-dimensional structure of MOF-199, the acid sites of [Hnmp][H₂PO₄] and the unsaturated copper on MOF-199, so that the adsorbent has high porosity. It can also form an acid-base interaction with sulfide and π complexation, thereby effectively removing sulfides in organic matter.

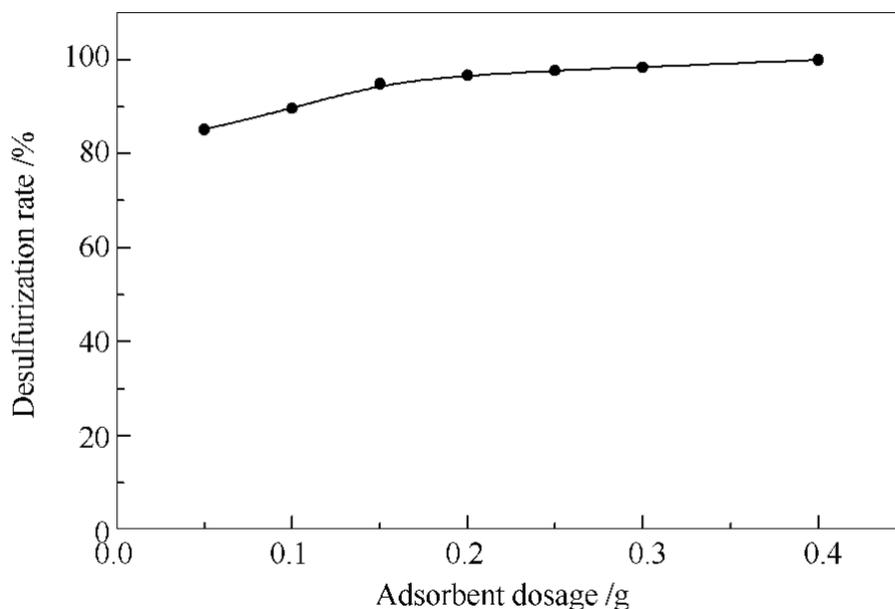


Figure 12 Effect of the amount of adsorbent on the performance of adsorption desulfurization

2.3.4 Regeneration Performance of Adsorbent Py/MOF-199

The regeneration performance of the adsorbent is an important indicator for evaluating the performance of the adsorbent. There are various regeneration methods, including purging, oxidizing charcoal, washing, and the like. In this study, the Py/MOF-199 adsorbent after the simulated oil (experimental conditions: 70 ° C, 1 h, 0.2 g, 10 mL of simulated oil) was adsorbed by Soxhlet extraction to remove the adsorbed sulfide at 140 ° C. It was dried under vacuum for 12 h. The static adsorption desulfurization experiment was carried out with the regenerated adsorbent, and this was repeated five times, and the obtained experimental results are shown in Fig. 13.

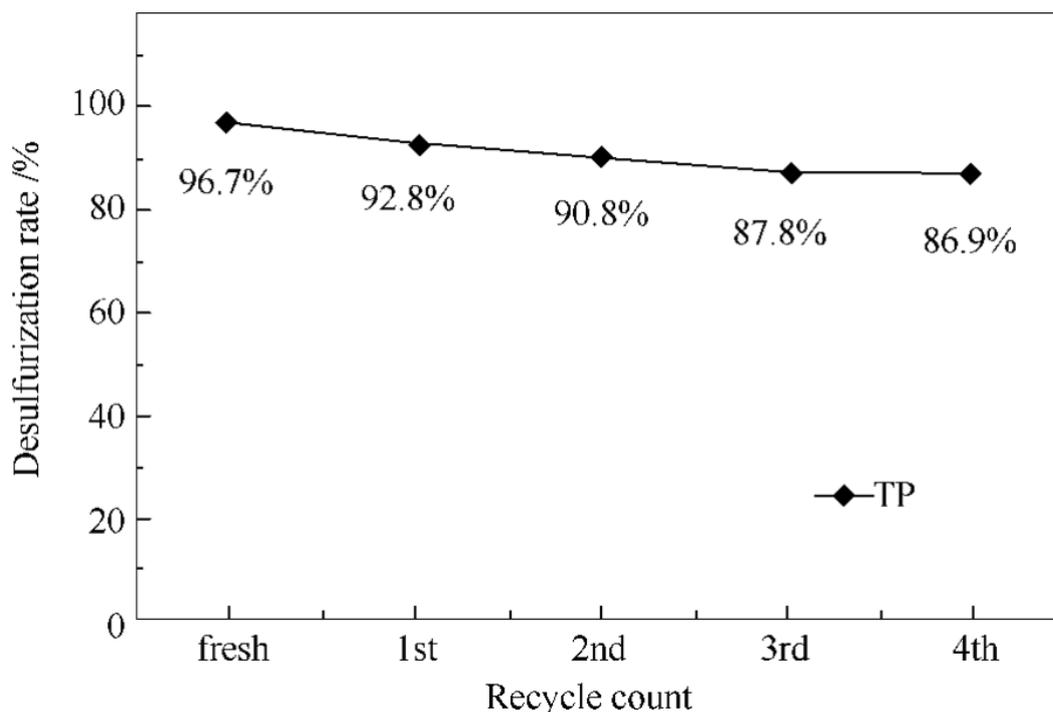


Figure 13. Reuse performance of Py/MOF-199 adsorbent Figure 13 Reusability of Py/MOF-199 adsorbent

It can be seen from Fig. 13 that the Py/MOF-199 adsorbent adsorbs the simulated oil, and the adsorption capacity of the thiophene can be restored to 96.0% of the fresh adsorbent after one regeneration; the adsorption capacity of the adsorbent after four regenerations can be restored to 89.9% of the fresh adsorbent, at which time the removal rate of thiophene was 86.9%.

3. Conclusion

Py/MOF-199 modified by ionic liquid [Hnmp][H₂PO₄] maintains the crystal structure of MOF-199. The ionic liquid is bridged to the substitution position of the aromatic ring through a carboxylic acid bond to fix it to the metal organic Frame MOF-199. After the ionic liquid is loaded, the average pore diameter is increased and mesopores are formed.

Among the Py/MOF-199 adsorbents prepared by different methods, the solvothermally supported Py/MOF-199 has the best adsorption desulfurization effect. The order of desulfurization rate of each adsorbent is: solvothermal method>impregnation method>ultrasonic method> Microwave method.

The suitable conditions for the preparation of Py/MOF-199 are: pretreatment of the metal organic framework MOF-199 by vacuum Soxhlet extraction and vacuum drying, followed by solvothermal loading [Hnmp][H₂PO₄], load temperature 50 °C, the load time is 8h, and the [Hnmp][H₂PO₄] load is 7%. Suitable Py/MOF-199 adsorption desulfurization conditions are: simulated oil is 10mL, adsorbent dosage is 0.2g, adsorption temperature is 70 °C, adsorption time is 1h. Under these conditions, the thiophene removal rate can reach 96.7%. The adsorption capacity of the adsorbent after four regenerations of the adsorbent can be restored to 89.9% of the fresh adsorbent, and the removal rate of the thiophene is 86.9%.

The prepared Py/MOF-199 adsorbent sets the unique three-dimensional structure of MOF-199, the acid position of [Hnmp][H₂PO₄] and the unsaturated copper on MOF-199, so that the adsorbent has high porosity and can Sulfide undergoes acid-base action and π complexation, thereby effectively removing sulfides in organic matter.

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Progress in Energy & Fuels | 13

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