

Study on the adsorptive denitrification performance of MIL-101(Cr) and its theoretical calculation

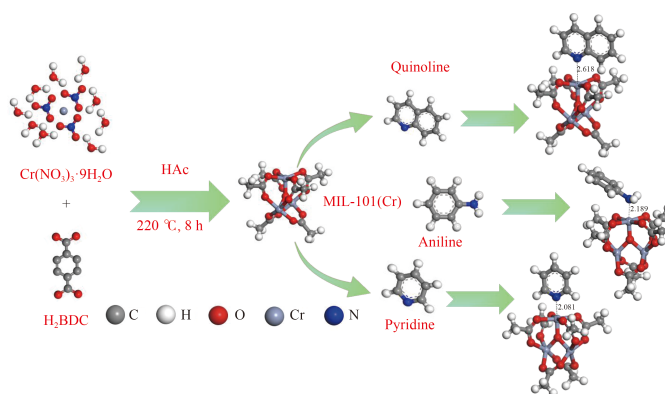
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Abstract: The adsorptive denitrification performance of MIL-101(Cr)-0.5 toward pyridine, aniline or quinoline in simulated fuels with basic nitrogen content of 1732 $\mu\text{g/g}$ was evaluated separately. Furthermore, the effects of adsorption temperature, adsorption time and adsorbent dosage on their adsorptive denitrification performance were systematically investigated. The experimental results demonstrated that under a fixed adsorbent dosage of 0.05 g and a simulated fuel volume of 10 mL, the optimal removal efficiency for aniline was achieved at 30 °C within 30 min, whereas

higher temperatures and longer times (40 °C and 40 min) were required for effective removal of pyridine and quinoline. Density Functional Theory (DFT) calculations were conducted via Materials Studio (MS) software to study the adsorptive denitrification mechanism of MIL-101(Cr) toward these three basic nitrogen-containing compounds. The simulation calculation results revealed that the interaction between pyridine and MIL-101(Cr) primarily involved coordination adsorption. In contrast, the interaction between aniline or quinoline and MIL-101(Cr) proceeded mainly through coordination, with additional contributions from π -complexation and hydrogen bonding. The overall adsorption strength order is pyridine > aniline > quinoline. During the adsorption process, pyridine and quinoline transfer electrons to the MIL-101(Cr) surface through the $\text{H} \rightarrow \text{C} \rightarrow \text{N} \rightarrow \text{Cr}^{3+}$ pathway, while aniline transfers electrons to the MIL-101(Cr) surface through various pathways, including $\text{N} \rightarrow \text{Cr}^{3+}$, $\text{N} \rightarrow \text{C} \rightarrow \text{Cr}^{3+}$ and $\text{N} \rightarrow \text{H} \rightarrow \text{O}$. Furthermore, adsorption kinetics studies indicated that the adsorption processes for all three basic nitrogen-containing compounds followed the quasi second order kinetic models. The experimental results on the effect of benzene on the adsorptive denitrification performance of MIL-101(Cr)-0.5 demonstrated that benzene exerted a more significant impact on the adsorption of aniline and quinoline. Finally, the adsorbent was regenerated using ethanol washing. It was found that MIL-101(Cr)-0.5 retained stable denitrification performance after two regeneration cycles.

Key words: MIL-101(Cr); adsorptive denitrification; competitive adsorption; regeneration performance; simulation calculation



Basic nitrogen-containing compounds in oils, such as pyridine, aniline and quinoline, not only adversely affect the physicochemical properties of oil products but also pose significant environmental hazards through the formation of nitrogen oxides (NO_x) during combustion^[1-2]. Therefore, oil denitrogenation technologies have attracted considerable research interest. Current technologies for clean diesel

production primarily include hydrodenitrogenation (HDN) and non-hydrodenitrogenation (NHDN). However, HDN suffers from high hydrogen consumption and high aromatic loss rates^[3]. In contrast, NHDN techniques, such as solvent extraction denitrogenation^[4], oxidative denitrogenation^[5] and adsorptive denitrogenation (ADN)^[6], are promising alternatives due to their high denitrogenation efficiency

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without requiring a hydrogen source. Among these, ADN is recognized as an economical and operationally simple method due to its straightforward operation, low cost^[7] and facile separation of the denitrogenated oil from the spent adsorbent. Material of Institute Lavoisier-101 (Chromium) (MIL-101(Cr)), a prominent member of the MIL series, shows great potential for oil adsorptive denitrogenation because of its high specific surface area and large pore size. In our previous work^[8], we successfully synthesized MIL-101(Cr)-x (molecular formula: $\text{Cr}_3\text{O}(\text{OH})(\text{H}_2\text{O})_2(\text{BDC})_3$) via a hydrothermal method with acetic acid as a modulator and conducted detailed characterization. The adsorptive denitrogenation performance of the synthesized material for pyridine or quinoline from model fuels was subsequently evaluated. The results demonstrated that MIL-101(Cr)-0.5, leveraging its unique crystal structure and large specific surface area, exhibited excellent ADN performance for both pyridine and quinoline within 40 min at 40 °C. Furthermore, preliminary simulations were conducted using Materials Studio (MS) software to calculate the adsorption energy and adsorption distance of pyridine or quinoline molecules on the metal cluster ligand structure of MIL-101(Cr). The simulation results indicated a stronger adsorption affinity of MIL-101(Cr) for pyridine than for quinoline, implying that acid-base interactions between MIL-101(Cr) and basic nitrogen-containing compounds play a critical role in the adsorption process. Building upon this foundation, the present study provides a more in-depth investigation of the ADN performance of MIL-101(Cr)-0.5 for pyridine, aniline and quinoline. However, whereas prior research focused primarily on single-component basic nitrogen-containing compounds adsorption, real oils contain aromatic compounds (e.g., benzene, toluene)^[9] which may compete with basic nitrogen-containing compounds for adsorption sites during the process^[10], thereby potentially reducing the selectivity of MIL-101(Cr) towards basic nitrogen-containing compounds. Therefore, benzene was introduced into the model fuel to simulate real oil conditions, enabling a systematic investigation of its impact on the ADN performance of MIL-101(Cr). Additionally, the regeneration performance of MIL-101(Cr) was evaluated. The adsorption energies and distances of pyridine, aniline or quinoline on three distinct adsorption sites of the MIL-101(Cr) surface were simulated and calculated via MS software. The Mulliken charge of three basic nitrogen-containing compounds before and after adsorption at the Cr^{3+} sites of MIL-101(Cr) were analyzed. The charge density and charge difference density diagrams after adsorption were also examined. Collectively, these analyses provide microscopic-level insights into the adsorptive denitrogenation mechanism of MIL-101(Cr).

1 Experimental section

1.1 Materials

Chromium(III) nitrate nonahydrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$],

terephthalic acid (H_2BDC), pyridine, aniline, quinoline, ethanol, glacial acetic acid (HAc), acetic anhydride, perchloric acid and benzene were purchased from Tianjin Guangfu Technology Development Co., Ltd. *n*-dodecane was sourced from Shanghai Puzhen Biotechnology Co., Ltd.. All chemicals were of analytical grade and used without further purification. The synthesis method for MIL-101(Cr), as well as the characterization methods including XRD, SEM, FT-IR and N_2 adsorption-desorption, has been described in detail in our previous work^[8].

1.2 Adsorptive denitrogenation experiments

Model fuels were prepared by dissolving pyridine, aniline or quinoline in *n*-dodecane with the concentration of each basic nitrogen content set at 1732 $\mu\text{g/g}$. In each adsorption experiment, 0.05 g of MIL-101(Cr)-x was added to a conical flask containing 10 mL of the model fuel. The adsorptive denitrogenation experiments were conducted at 30 °C for 30 min. Subsequently, the mixture was centrifuged for separation. The supernatant was then collected, and its basic nitrogen content was determined according to the SH/T 0162—1992 standard method.

1.3 Recycling and regeneration experiments

After the completion of adsorption, the spent MIL-101(Cr)-x was separated from the model fuel and collected. Subsequently, the adsorbent was first dried, then washed with ethanol under reflux for 4 h, recovered by centrifugation, and finally dried again.

1.4 Computational details

Structural optimization was performed, followed by calculations and analyses of the electrostatic potential and Mulliken charge by using the Dmol3 module in the MS simulation software. Furthermore, the adsorption energy, adsorption distance, electron density and charge density difference were computed for the adsorption of pyridine, aniline or quinoline on MIL-101(Cr). The generalized gradient approximation (GGA) with the PW91 functional was employed. The calculation precision was set to “Fine”. The convergence criterion for displacement was set to 5.0×10^{-3} Å. The core treatment was selected as DFT Semi-core Pseudopotentials and the basis set was DNP 3.5. The smearing value was set to 0.005 Ha.

2 Results and discussion

2.1 Influence of temperature on the adsorptive denitrogenation over MIL-101(Cr)-0.5

Figure 1 illustrates the effect of adsorption temperature on the denitrogenation performance of MIL-101(Cr)-0.5. As

shown in Figure 1, adsorption temperature had a minor effect on pyridine and quinoline adsorption. The adsorption capacity and removal rate for both pyridine and quinoline reached their maximum values at 40 °C, then they slightly decreased with increasing temperature. In contrast, the adsorption of aniline was highly temperature-sensitive. Its adsorption capacity and removal rate reached their maximum at 30 °C, followed by a sharp decline upon further heating. This distinct temperature dependence can be attributed to coexistence of chemisorption and physisorption in the adsorption process. Cr^{3+} , being a transition metal, possesses vacant orbitals in its outer valence electron configuration. The nitrogen atoms in pyridine, aniline and quinoline molecules all contain a lone pair of electrons. According to coordination bond theory, nitrogen readily forms coordination bonds with Cr^{3+} sites in MIL-101(Cr)-0.5. Concurrently, π -complexation interactions occur between these three basic nitrogen-containing compounds and the Cr^{3+} sites. Given that coordination forces is strong, whereas the π -complexation and physisorption forces are weaker, the overall adsorption capacity and removal rate for these three basic nitrogen-containing compounds decreased with rising temperature. However, this decline was markedly more pronounced for aniline. This enhanced sensitivity is due to the additional presence of hydrogen bonding between the $-\text{NH}_2$ group in aniline and the framework of MIL-101(Cr)-0.5. The π -complexation, hydrogen bonding and physisorption forces are all relatively weak and temperature-sensitive interactions. Hence, aniline's adsorption capacity and removal rate decreased markedly with temperature increasing.

Furthermore, Figure 1 also reveals that the denitrogenation performance of MIL-101(Cr)-0.5 followed the order: pyridine > aniline > quinoline. This trend is attributed to the higher alkalinity of pyridine^[11].

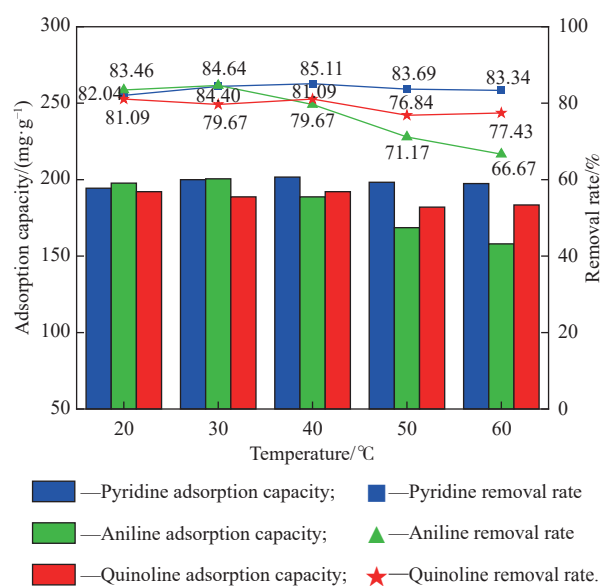


Fig. 1 Effect of adsorption temperature on the adsorption of pyridine, aniline or quinoline by MIL-101(Cr)-0.5

MIL-101(Cr)-0.5, containing Lewis acidic sites (Cr^{3+}), exhibits enhanced adsorption capacity for the more basic pyridine molecule^[12]. Moreover, MIL-101(Cr)-0.5 showed superior adsorption performance for aniline compared to quinoline. This is because aniline has a structure consisting of a benzene ring connected to an $-\text{NH}_2$ group^[13], whereas quinoline is a planar structure formed by the fusion of a benzene ring with a pyridine ring^[14], resulting in greater steric hindrance. Additionally, the presence of hydrogen bonding interactions between aniline and MIL-101(Cr)-0.5 contributes to its more effective adsorption compared to quinoline.

2.2 Simulation calculation of MIL-101(Cr) adsorbing pyridine, aniline or quinoline

To further study the adsorption mechanism of MIL-101(Cr) toward pyridine, aniline and quinoline, the adsorption configurations of pyridine, aniline and quinoline on the surface of MIL-101(Cr) at three adsorption sites (active site $\text{Cr}^{3+}(\text{Cr})$, the oxygen atom adjacent to Cr^{3+} and the phthalic acid ligand (π)) were constructed using the Dmol3 module in the MS software. Owing to the strong electronegativity of the oxygen atom adjacent to Cr^{3+} , it readily forms hydrogen bonds with the hydrogen atoms in these three basic nitrogen-containing compounds. To identify the specific hydrogen atoms participating in adsorption, the Mulliken charge for these three basic nitrogen-containing compounds were calculated (Figure 2). The results revealed that H_{10} atom in pyridine, H_{13} atom in aniline and H_{17} atom in quinoline carry relatively higher positive charges, thus forming stronger hydrogen bonding interactions with the oxygen atom adjacent to Cr^{3+} . Subsequently, the structures were optimized using the Dmol3 module, and the adsorption distances were calculated. The adsorption energy was calculated according to the formula $\Delta E_{\text{ads}} = E_{\text{adsorbent-adsorbate}} - E_{\text{adsorbate}} - E_{\text{adsorbent}}$ ^[15]. The optimized adsorption configurations are shown in Figure 3, and the corresponding adsorption energies are summarized in Table 1. The adsorption distance reflects the strength of the adsorption interaction^[16], while a larger absolute value of the adsorption energy indicates a more stable adsorption configuration^[17].

Structural optimization was performed on the adsorption configuration of these three basic nitrogen-containing compounds that are perpendicular and directly facing the Cr^{3+} . The resulting optimized structures are shown in Figure 3 (a). As shown in Figure 3(a), the molecular planes of pyridine and quinoline are perpendicular to the MIL-101(Cr) surface, whereas aniline is adsorbed in a tilted configuration on the MIL-101(Cr) surface^[18]. This difference originates from the nitrogen atoms in pyridine and quinoline are sp^2 -hybridized. The sp^2 hybrid orbitals are in a planar triangular configuration.

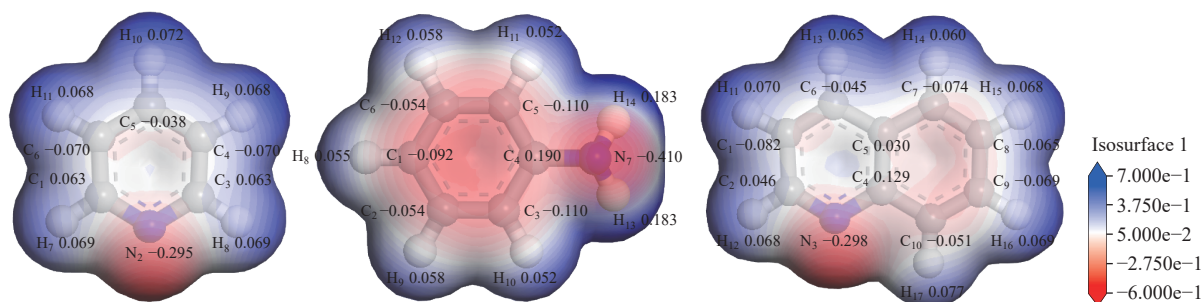


Fig. 2 Electrostatic potential and Mulliken charge of pyridine, aniline and quinoline before adsorption

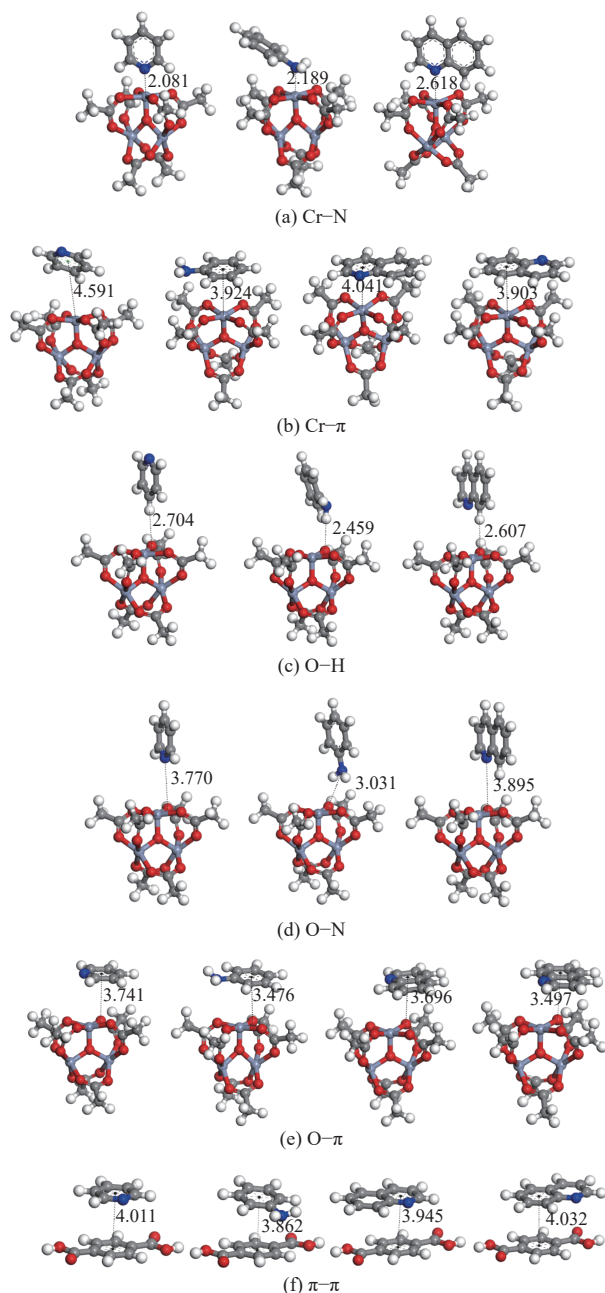


Fig. 3 The adsorption configuration of pyridine, aniline or quinoline molecules on MIL-101(Cr) surface

Consequently, the lone pair electron orbitals of nitrogen atoms are coplanar with the aromatic ring, which is

advantageous for the lone pair electron orbitals of nitrogen atoms to directly point towards the active site Cr^{3+} . In contrast, the nitrogen atom in aniline is sp^3 -hybridized. The sp^3 hybrid orbitals are approximately tetrahedral, and the lone pair electron orbitals of nitrogen atom cannot be coplanar with the benzene ring. Furthermore, the tilted adsorption configuration is stabilized by the π -complexation between the aniline benzene ring and Cr^{3+} , as well as the hydrogen bonding between hydrogen atoms in the amino group ($-\text{NH}_2$) and the adjacent oxygen atoms of Cr^{3+} . The order of Cr-N adsorption distances is quinoline (2.618 Å) > aniline (2.189 Å) > pyridine (2.081 Å), indicating that the coordination interaction between the nitrogen atom of pyridine and Cr^{3+} is stronger. The order of Cr adsorption energy in Table 1 is pyridine (−131.28 kJ/mol) > aniline (−109.07 kJ/mol) > quinoline (−52.51 kJ/mol). This is because the Brønsted basic strength of nitrogen atoms in these three basic nitrogen-containing compounds is different^[19]. Pyridine is the most basic, and the Cr-N coordination bond formed with Cr^{3+} is stronger^[20]. Therefore, MIL-101(Cr) exhibits excellent adsorptive denitrogenation performance for pyridine. Figure 2 shows that the red part in the electrostatic potential represents the negative potential region and the blue part represents the positive potential region. As shown in Figure 2, the electronegativity of the nitrogen atom in pyridine is strong, exhibiting an electron-withdrawing effect. The electron cloud density on the ring decreases, while the electron cloud density of nitrogen atom increases, making pyridine have stronger basicity. In aniline, the lone pair electrons on the amino nitrogen atom engage in p - π conjugation with the benzene ring and the electron cloud of nitrogen atom disperses throughout the benzene ring, increasing the electron cloud density on the ring while decreasing the electron cloud density of nitrogen atom. In quinoline, the π electrons of the pyridine ring and the benzene ring will undergo conjugation, forming a larger conjugation system. Consequently, the electron cloud of nitrogen atom in the pyridine ring partially delocalizes onto the benzene ring, but the delocalization phenomenon of nitrogen atom on the benzene ring in quinoline is weaker^[21], causing a slight increase in the electron cloud density on the benzene ring and a slight decrease in the electron density around nitrogen atom. Therefore, the alkalinity order of these three basic nitrogen-containing compounds is pyridine > quinoline > aniline.

Table 1 Adsorption energy of pyridine, aniline or quinoline molecules on MIL-101(Cr) surface

Type		$\Delta E_{\text{ads}}/(\text{kJ}\cdot\text{mol}^{-1})$	$E_{\text{adsorbent}}/(\text{kJ}\cdot\text{mol}^{-1})$	$E_{\text{adsorbate}}/(\text{kJ}\cdot\text{mol}^{-1})$	$E_{\text{adsorbent-adsorbate}}/(\text{kJ}\cdot\text{mol}^{-1})$
Pyridine	Cr-N	-131.28	-4507012.781	-636944.969	-5144089.032
	Cr- π	-19.04	-4507022.11	-636948.8634	-5143990.009
	O-H	-18.31	-4507022.235	-636948.8378	-5143989.386
	O-N	-11.14	-4507021.745	-636948.8583	-5143981.743
	O- π	-14.29	-4507021.83	-636948.8737	-5143984.996
	π - π	-4.77	-1563565.882	-636948.8993	-2200519.553
Aniline	Cr-N	-109.07	-4507018.505	-737824.521	-5244952.093
	Cr- π	-31.13	-4507021.266	-737827.0044	-5244879.4
	O-H	-34.27	-4507021.833	-737827.0069	-5244883.107
	O-N	-16.77	-4507022.066	-737827.4072	-5244866.246
	O- π	-16.25	-4507022.746	-737827.0429	-5244866.036
	π - π	-6.79	-1563565.836	-737827.4533	-2301400.088
Quinoline	Cr-N	-52.51	-4506602.04	-1031078.729	-5537733.282
	Cr- π (Pyridine ring)	-22.02	-4507021.848	-1031109.395	-5538153.265
	Cr- π (Benzene ring)	-22.35	-4507021.661	-1031109.325	-5538153.332
	O-H	-24.62	-4507022.169	-1031108.917	-5538155.702
	O-N	-17.77	-4507021.576	-1031109.146	-5538148.493
	O- π (Pyridine ring)	-19.50	-4507022.446	-1031109.405	-5538151.351
	O- π (Benzene ring)	-17.90	-4507022.11	-1031109.315	-5538149.324
	π - π (Pyridine ring)	-6.25	-1563566.015	-1031109.392	-2594681.654
	π - π (Benzene ring)	-5.98	-1563565.651	-1031109.408	-2594681.039

Note: $E_{\text{adsorbent-adsorbate}}$ is adsorbed complex energy, $E_{\text{adsorbate}}$ is the energy of the adsorbate, $E_{\text{adsorbent}}$ is the energy of the adsorbent molecule, ΔE_{ads} is adsorption energy.

Structural optimization was subsequently conducted on the adsorption configuration where these three basic nitrogen-containing compounds were oriented parallel to their ring centers directly facing the Cr^{3+} . The optimized results are shown in Figure 3(b). As shown in Figure 3(b), the distances from the centers of the pyridine ring and the quinoline-pyridine ring to Cr^{3+} follow the order: pyridine ring (4.591 Å) > quinoline-pyridine ring (4.041 Å). This is because the electronegativity of the nitrogen atom in pyridine is greater than that of the nitrogen atom in the pyridine ring of quinoline, and the electrostatic repulsion between pyridine nitrogen atom and the adjacent oxygen atom of Cr^{3+} is strong. Consequently, under the influence of electrostatic repulsion, it is farther away from the surface^[22] and the adsorption distance is slightly larger than that of quinoline. The distances from the benzene ring centers of aniline and quinoline to Cr^{3+} are 3.924 and 3.903 Å, respectively. As shown in Figure 2, although the electron cloud density of the benzene ring of aniline is greater than that of the benzene ring of quinoline, the molecular weight of quinoline is larger and the van der Waals force is stronger, thus the adsorption distances of these two are relatively close. Notably, the distances from the ring centers of the benzene ring of aniline and the benzene ring of quinoline to Cr^{3+} are all smaller than those of the pyridine ring and the pyridine ring of quinoline to Cr^{3+} . This indicates that the benzene ring engage in stronger π -complexation with the Cr^{3+} sites in MIL-101(Cr) than the

pyridine ring. This conclusion is corroborated by the Cr- π adsorption energy data in Table 1, which decreases in the order: the benzene ring of aniline (-34.27 kJ/mol) > benzene ring of quinoline (-22.35 kJ/mol) > pyridine ring of quinoline (-22.02 kJ/mol) > pyridine ring (-19.04 kJ/mol). The adsorption energy data further prove that the benzene ring is more likely to undergo π -complexation with the Cr^{3+} sites in MIL-101(Cr) than the pyridine ring.

The adsorption configurations of the H_{10} atom of pyridine, the H_{13} atom of aniline, and the H_{17} atom of quinoline oriented towards an oxygen atom adjacent to Cr^{3+} were geometrically optimized, and the results are presented in Figure 3(c). As shown in Figure 3(c), the measured O-H adsorption distances follow the order: pyridine (2.704 Å) > quinoline (2.607 Å) > aniline (2.4 Å). These results demonstrate that the strength of the N-H...O hydrogen bond in aniline is greater than that of the C-H...O hydrogen bonds in pyridine and quinoline^[23-24], and the C-H...O in quinoline is stronger than that in pyridine. This trend can be attributed to the electronegativity of nitrogen atom is greater than that of carbon atom, which makes the polarity of the N-H bond in aniline stronger and the partial positive charge of the hydrogen atoms higher, making it easier to form a hydrogen bond with the adjacent oxygen of Cr^{3+} . This interpretation is supported by Mulliken charge calculation results for these three basic nitrogen-containing compounds in Figure 2, the charges on H_{10} atom of pyridine, H_{13} atom of aniline, and H_{17} atom of quinoline are 0.072, 0.183 and

0.077, respectively. The partial positive charge of aniline's H_{13} atom is higher, and the hydrogen bond interaction force with the adjacent oxygen of Cr^{3+} is stronger. The positive charge of quinoline's H_{17} atom is greater than the positive charge of pyridine's H_{10} atom, which makes its hydrogen bond interaction with the adjacent oxygen of Cr^{3+} stronger than that of pyridine.

The data in Table 1 demonstrate that the magnitude of the Cr–N adsorption energy is significantly higher than that of other adsorption interactions, which indicates that the coordination adsorption configuration is relatively stable. Therefore, the adsorption process of pyridine, aniline and quinoline on MIL-101(Cr) is dominated by coordination adsorption. The magnitudes of the adsorption energies for π -complexation and hydrogen bonding for these three basic nitrogen-containing compounds are second only to that of coordination adsorption, indicating that the adsorption is supplemented by π -complexation and hydrogen bonding. In contrast, the corresponding adsorption energy values for the O–N (Figure 3(d)), O– π (Figure 3(e)), and π – π conjugation (Figure 3(f)) interactions are lower, which shows that their adsorption effect is weaker. For aniline, the π -complexation and hydrogen bonding interactions are stronger, effectively compensating for the disadvantage of its weaker basicity in coordinating at the active sites^[25]. Consequently, the overall adsorption capacity of aniline on MIL-101(Cr) is intermediate between those of pyridine and quinoline. The simulation results further corroborate the strength of aniline's π -complexation and hydrogen bonding. Accordingly, the adsorption temperature has a relatively large influence on the adsorption of aniline compared to the other compounds.

2.3 Mulliken charge analysis of pyridine, aniline and quinoline molecules before and after adsorption

As indicated by the preceding analysis, the adsorption process of pyridine, aniline or quinoline on MIL-101(Cr) is dominated by coordination adsorption. To further elucidate the adsorptive denitrogenation mechanism, the Dmol3 module was used to calculate the Mulliken charge of the system after the adsorption of pyridine, aniline or quinoline at the Cr^{3+} sites in MIL-101(Cr). The Mulliken charges of pyridine, aniline or quinoline after and before adsorption are

shown in Figure 4 and Figure 2, respectively. Table 2 shows the Mulliken changes of these three basic nitrogen-containing compounds before and after adsorption at the Cr^{3+} sites in MIL-101(Cr). According to the data in Table 2, the pyridine nitrogen atom gains 0.014 e, the carbon atoms at the ortho and meta positions to nitrogen atom collectively lose 0.014 e, the carbon atom at the para position gains 0.002 e, and the hydrogen atoms on the pyridine ring collectively lose 0.007 e. This charge from the hydrogen atoms on the pyridine ring is transferred through carbon atoms to nitrogen atom and then to the MIL-101(Cr) surface, forming an $H \rightarrow C \rightarrow N \rightarrow Cr^{3+}$ charge transfer pathway^[26]. The quinoline nitrogen atom gains 0.051 e, the carbon atoms adjacent to nitrogen atom loses 0.021 e, while the carbon atoms at the remaining positions collectively gain 0.033 e and the hydrogen atoms on the pyridine ring and benzene ring of quinoline collectively lose 0.066 e. The charge transfer situation is also that the charge from the hydrogen atoms on the pyridine ring and benzene ring of quinoline is transferred through carbon atoms to nitrogen atom and then to the MIL-101(Cr) surface, forming an $H \rightarrow C \rightarrow N \rightarrow Cr^{3+}$ charge transfer pathway. However, due to the high electronegativity of the nitrogen atom, not all the accumulated charge is transferred to Cr^{3+} ^[27], resulting in a net electron gain on the nitrogen atom after adsorption. Specifically, the lone pair electrons of nitrogen atom can be donated to the empty d -orbitals of Cr^{3+} and can also accept back-donated electrons from the d -orbitals of Cr^{3+} to form a coordinate bond and a back-bond. This synergistic interaction leads to strong interactions between pyridine, quinoline and the adsorbent^[28]. In the case of aniline, the charge transfer for aniline involves three distinct pathways. First, the lone pair electrons of the amino nitrogen atom in aniline are transferred to the MIL-101(Cr) surface, forming an $N \rightarrow Cr^{3+}$ charge transfer channel. Second, the amino group can provide electrons to the benzene ring through p – π conjugation and the benzene ring undergoes π -complexation with the MIL-101(Cr) surface, forming an $N \rightarrow C \rightarrow Cr^{3+}$ charge transfer channel, which leads to the amino nitrogen atom in aniline losing 0.035 e and the benzene ring carbon atoms collectively losing 0.109 e. The hydrogen atoms on the benzene ring may gain 0.105 e due to the conjugation effect. Third, the hydrogen atoms on the amino group form hydrogen bonds with oxygen atoms in MIL-101(Cr).

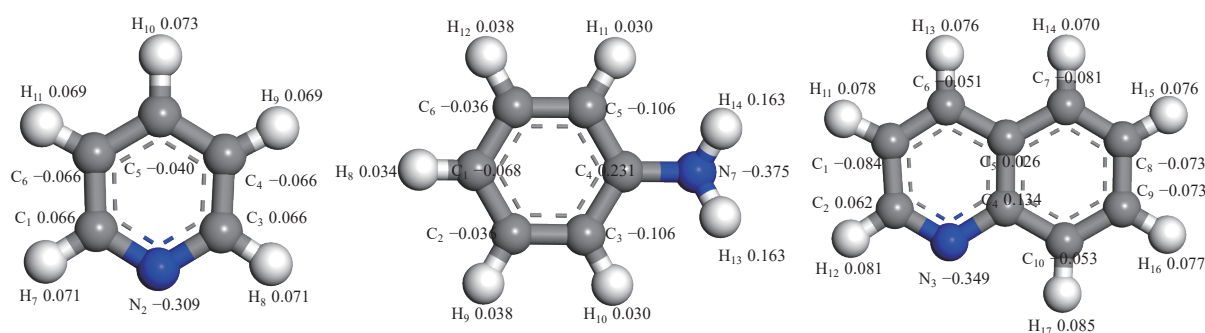


Fig. 4 Mulliken charge of each atom in pyridine, aniline or quinoline molecules after adsorption

Table 2 Mulliken charge distribution of atoms in pyridine, aniline or quinoline molecules before and after adsorption

Pyridine			Aniline			Quinoline		
atomic number	atomic charge before adsorption	atomic charge after adsorption	atomic number	atomic charge before adsorption	atomic charge after adsorption	atomic number	atomic charge before adsorption	atomic charge after adsorption
C ₁	0.063	0.066	C ₁	-0.092	-0.068	C ₁	-0.082	-0.084
N ₂	-0.295	-0.309	C ₂	-0.054	-0.036	C ₂	0.046	0.062
C ₃	0.063	0.066	C ₃	-0.110	-0.106	N ₃	-0.298	-0.349
C ₄	-0.070	-0.066	C ₄	0.190	0.231	C ₄	0.129	0.134
C ₅	-0.038	-0.040	C ₅	-0.110	-0.106	C ₅	0.030	0.026
C ₆	-0.070	-0.066	C ₆	-0.054	-0.036	C ₆	-0.045	-0.051
H ₇	0.069	0.071	N ₇	-0.410	-0.375	C ₇	-0.074	-0.081
H ₈	0.069	0.071	H ₈	0.055	0.034	C ₈	-0.065	-0.073
H ₉	0.068	0.069	H ₉	0.058	0.038	C ₉	-0.069	-0.073
H ₁₀	0.072	0.073	H ₁₀	0.052	0.030	C ₁₀	-0.051	-0.053
H ₁₁	0.068	0.069	H ₁₁	0.052	0.030	H ₁₁	0.070	0.078
—	—	—	H ₁₂	0.058	0.038	H ₁₂	0.068	0.081
—	—	—	H ₁₃	0.183	0.163	H ₁₃	0.065	0.076
—	—	—	H ₁₄	0.183	0.163	H ₁₄	0.060	0.070
—	—	—	—	—	—	H ₁₅	0.068	0.076
—	—	—	—	—	—	H ₁₆	0.069	0.077
—	—	—	—	—	—	H ₁₇	0.077	0.085

When a hydrogen atom partially loses electrons due to the hydrogen bond, the adjacent nitrogen atom compensates by donating electrons to the hydrogen atoms through the covalent bond, causing the hydrogen atoms in the amino group to gain 0.04 e and forming an N→H→O charge transfer channel. This further proves that the adsorption of MIL-101(Cr) with pyridine and quinoline is mainly dominated by coordination adsorption. In contrast, the adsorption of aniline involves additional significant contributions from π -complexation and hydrogen bonding.

2.4 Charge density plot and charge differential density plot

The charge density plot and charge density difference plot (where red and blue represent an increase and decrease in electron density, respectively) for pyridine (a), aniline (b) or quinoline (c) after adsorption at the Cr³⁺ sites of MIL-101(Cr) are shown in Figure 5 and Figure 6, respectively. The cross-section plane for the charge density difference analysis was selected to the nitrogen atom and Cr atom. Owing to the non-planar configuration of the aniline molecule and its tilted adsorption geometry, its charge density difference plot (Figure 6(b)) primarily reveals the electron transfer between the amino nitrogen atom and Cr atom while the electron density changes of the benzene ring and the amino hydrogen atoms are not fully captured in this view. As shown in Figure 5, the electron clouds of the nitrogen atoms in the pyridine, aniline and quinoline molecules all have significant overlap with the electron cloud of Cr atom in MIL-101(Cr), indicating that a coordinate bond has formed between nitrogen atoms and Cr

atom. From Figure 6, it is evident that the areas around the pyridine and quinoline molecules are mainly blue, whereas the area around Cr atom is mainly red. This observation suggests that electrons from carbon atoms and hydrogen atoms in pyridine or quinoline is first polarized toward their respective nitrogen atoms before being transferred to the MIL-101(Cr) surface. In the case of aniline, the area around the amino nitrogen atom is blue, while the area around Cr atom is mainly red, demonstrating a direct electron from the aniline nitrogen atom to the MIL-101(Cr) surface. Consistently, the electron density of the nitrogen atom in the pyridine, aniline and quinoline molecules decreases, while the electron density of Cr atom in MIL-101(Cr) increases. An interaction exists between nitrogen atom and Cr atom, forming a Cr–N coordinate bond, which allows the pyridine, aniline or quinoline molecules to be stably adsorbed on the MIL-101(Cr) surface. These findings are fully consistent with the electron transfer pathways formed by pyridine, aniline or quinoline on the MIL-101(Cr) surface, as determined from the analysis of Mulliken charge before and after adsorption mentioned above.

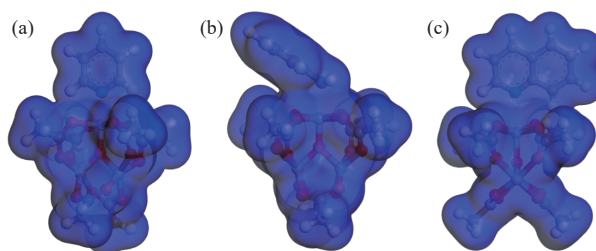


Fig. 5 Charge density plot of pyridine (a), aniline (b) or quinoline (c) adsorbed on the Cr³⁺ site of MIL-101(Cr)

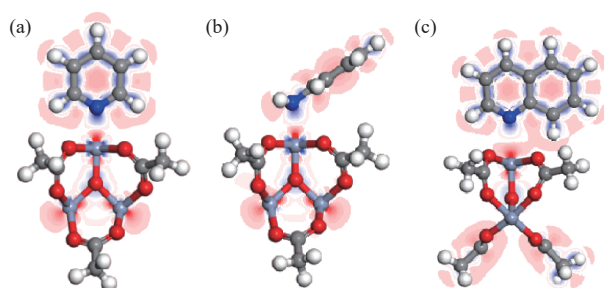


Fig. 6 Charge difference density plot of pyridine (a), aniline (b) or quinoline (c) adsorbed on the Cr^{3+} site of MIL-101(Cr)

2.5 Influence of adsorption time on the adsorptive denitrogenation over MIL-101(Cr)-0.5

The influence of adsorption time on the adsorptive denitrogenation performance of MIL-101(Cr)-0.5 is shown in Figure 7.

Within the initial 30 min, the abundance of active sites on MIL-101(Cr)-0.5, facilitates rapid binding of basic nitrogen molecules, leading to a significant increase in adsorption capacity and removal rate. Subsequently, the adsorption capacity and removal rate for aniline tend to reach equilibrium between 30 and 50 min, followed by a sharp decrease after 50 min. After 40 min, the adsorption capacity and removal rate for pyridine tend to reach equilibrium. In contrast, the adsorption capacity and removal rate for quinoline tend to reach equilibrium between 40 and 50 min. As the adsorption time is prolonged, the basic nitrogen-containing compounds adsorbed on MIL-101(Cr)-0.5 undergo a certain degree of desorption, causing the adsorption capacity to decrease slightly before finally reaching adsorption equilibrium. This desorption behavior can be interpreted based on the simulation results.

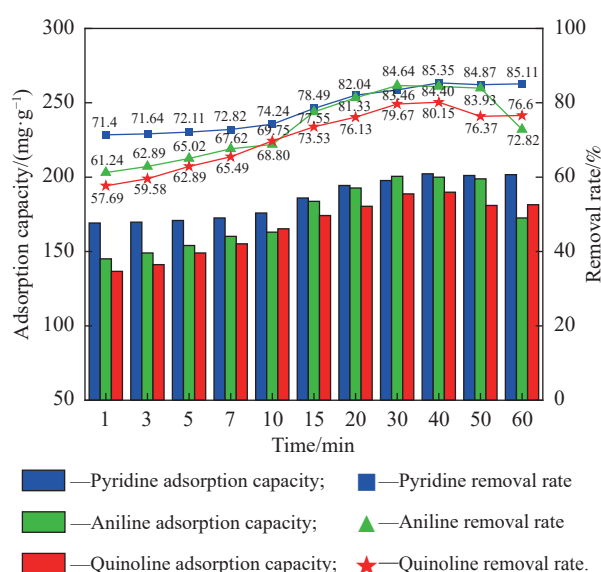


Fig. 7 Effect of adsorption time on the adsorption of pyridine, aniline or quinoline by MIL-101(Cr)-0.5

The adsorption of pyridine, aniline or quinoline on MIL-101(Cr), the order of strength for both π -complexation and hydrogen bonding between these three basic nitrogen-containing compounds and MIL-101(Cr)-0.5 is aniline > quinoline > pyridine. However, since the π -complexation and hydrogen bonding forces are relatively weak^[29], desorption becomes significant over time. Consequently, the desorption of aniline becomes more evident. Based on these findings, the optimal adsorption conditions for aniline adsorption by MIL-101(Cr)-0.5 is 30 °C with an adsorption time of 30 min. For the pyridine or quinoline, the more suitable adsorption conditions is 40 °C with an adsorption time of 40 min.

2.6 Adsorption kinetic models

The pseudo-first-order kinetic model and pseudo-second-order kinetic model are widely employed for analyzing adsorption kinetics. The pseudo-first-order kinetic model assumes that the adsorption rate is limited by diffusion, where the interaction between the adsorbate and the solid surface is relatively weak and the reaction rate is mainly influenced by the diffusion process. This model is widely used to describe the adsorption of gas or liquid molecules on a solid surface, especially for physical adsorption^[30]. In contrast, the pseudo-second-order kinetic model is suitable for describing adsorption processes that are dominated by chemisorption, particularly when the interaction between the adsorbate and the adsorbent surface is strong. Unlike the pseudo-first-order model, the pseudo-second-order model accounts not only for the change in adsorbate concentration but also for the formation of chemical bonds between the adsorbate and the surface^[31]. The linearized forms of these two kinetic models are expressed as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (1)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (2)$$

In the equations, Q_t and Q_e represent the adsorption capacity at time t and at equilibrium, respectively; t denotes the adsorption time; k_1 and k_2 are the rate constants for the pseudo-first-order and pseudo-second-order models.

The adsorption kinetics for pyridine, aniline or quinoline were linearly fitted using the pseudo-first-order and pseudo-second-order kinetic models, and the results presented in Figures 8(a), (b), respectively. The calculated parameters for the adsorption kinetic models are summarized in Table 3. As evidenced by Figures 8(a), (b) and Table 3, the R^2 values obtained from the pseudo-second-order kinetic linear fitting are closer to 1 compared to the R^2 values from the pseudo-first-order kinetic linear fitting. This indicates that the adsorption process of pyridine, aniline and quinoline on MIL-101(Cr)-0.5 are well fitted by the pseudo-second-order kinetic model and mainly dominated by chemisorption.

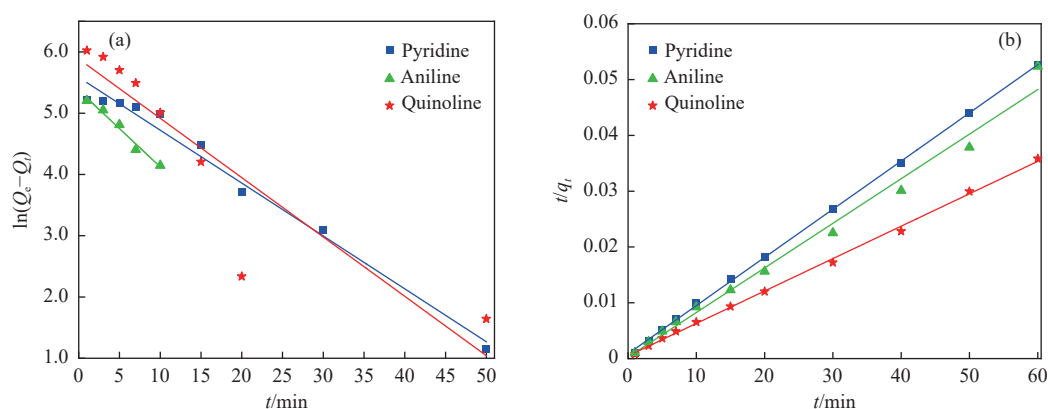


Fig. 8 (a) Quasi first order adsorption kinetics fitting curve of MIL-101(Cr)-0.5; (b) Quasi second order adsorption kinetics fitting curve of MIL-101(Cr)-0.5

Table 3 Quasi first order kinetic adsorption kinetics and quasi second order kinetic adsorption kinetics fitting parameters of MIL-101(Cr)-0.5

Adsorbate type	Quasi first order kinetic adsorption model			Quasi second order kinetic adsorption model		
	k_1	$Q_{e,1}$	R^2	k_2	$Q_{e,2}$	R^2
Pyridine	0.08633	47.19	0.98018	0.00085	205.09	0.99952
Aniline	0.12509	32.48	0.96965	0.00242	188.41	0.98645
Quinoline	0.09687	39.00	0.80393	0.00069	186.56	0.99838

The equilibrium adsorption capacity for these three basic nitrogen-containing compounds follow the order: pyridine > aniline > quinoline. In contrast, the order of the k_2 values is aniline > pyridine > quinoline. The k_2 constant represents the adsorption rate of the adsorbate per unit time^[32]; thus, larger k_2 value implies a faster adsorption rate. Consequently, the higher k_2 value for aniline indicates that its adsorption rate per unit time is faster, and the time for aniline to reach its maximum adsorption capacity is shorter than that for pyridine and quinoline, which is consistent with the experimental results mentioned above.

2.7 Effect of MIL-101(Cr) dosage on adsorptive denitrification performance

The effect of the MIL-101(Cr)-0.5 dosage on the adsorptive removal of pyridine, aniline and quinoline from model fuel is shown in Figure 9. As illustrated, with the gradual increase of the MIL-101(Cr)-0.5 dosage, the removal rate progressively increases, whereas the adsorption capacity gradually decreases. When the dosage of MIL-101(Cr)-0.5 increases from 0.02 to 0.05 g, the slope of the removal rate increase is large. However, when the dosage of MIL-101(Cr)-0.5 is greater than 0.05 g, the rate of increase in the removal efficiency diminishes significantly. This trend occurs because an increase in the MIL-101(Cr)-0.5 dosage provides more active sites for the adsorption process that can interact with the basic nitrogen-containing compounds molecules, allowing for the adsorption of more basic nitrogen-containing compounds,

thereby improving the denitrogenation efficiency. With a continued increase in the MIL-101(Cr)-0.5 dosage, there are few basic nitrogen-containing compounds left in the model fuel available for adsorption, making it impossible to further significantly increase the removal rate. From a practical standpoint, using an excessive amount of MIL-101(Cr)-0.5 not only fails to substantially improve the adsorptive denitrogenation performance but also leads to a significant increase in economic costs. Therefore, by considering the denitrogenation effect and economic cost, the optimal dosage of MIL-101(Cr)-0.5 was determined to be 0.05 g.

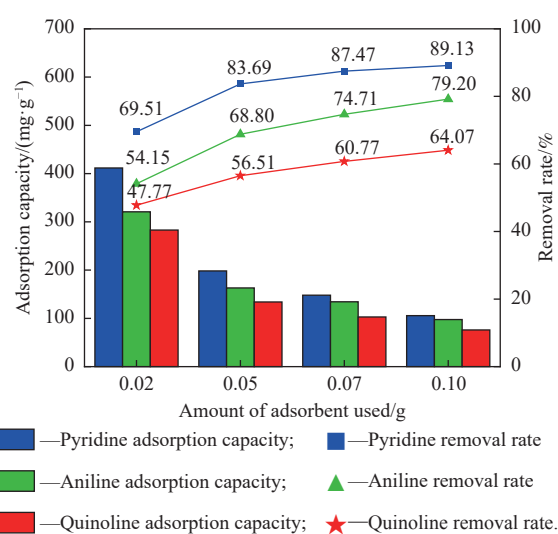


Fig. 9 Effect of MIL-101(Cr)-0.5 dosage on its adsorption of pyridine, aniline and quinoline

2.8 Competitive adsorption

Real oils typically contain a certain amount of aromatic compounds, such as benzene, toluene, etc. These compounds may interact with MIL-101(Cr)-0.5 during the adsorption process, potentially affecting the selectivity of MIL-101(Cr)-0.5 for basic nitrogen-containing compounds. Previous studies have shown that when MIL-101(Cr)^[33] or MIL-101(Cr)-NH₂^[34] adsorbs benzene or toluene molecules, the process is dominated by the π - π conjugation effect formed between the large π -bond on the benzene or toluene molecules and the π -bond on the H₂BDC in the material, leading to a tendency for preferential adsorption on the H₂BDC benzene ring. Therefore, the effect of benzene on the adsorptive denitrogenation performance of MIL-101(Cr)-0.5 was investigated and the experimental results are shown in Figure 10. The equimolar amount of benzene was added to the model fuels containing pyridine, aniline or quinoline, respectively, in order to ensure the equal number of molecules of benzene and the basic nitrogen-containing compounds in the model fuel^[35]. The experimental results demonstrate that although the denitrogenation efficiency for all compounds slightly decreased, the overall performance order remained pyridine > aniline > quinoline. This finding further indicates that the adsorption of these three basic nitrogen-containing compounds by MIL-101(Cr)-0.5 is mainly dominated by the coordination between nitrogen atom and Cr³⁺, with π - π stacking playing a secondary role. Figure 10 also reveals that the effect of benzene on the adsorption of aniline by MIL-101(Cr)-0.5 is the greatest, followed by quinoline and the least for pyridine. This is attributed to benzene being adsorbed on MIL-101(Cr)-0.5 mainly through π - π conjugation and van der Waals forces^[36]. According to the simulation and calculation results for the adsorption of pyridine, aniline or quinoline

on MIL-101(Cr), the order of π - π conjugation strength between these three basic nitrogen-containing compounds and H₂BDC in MIL-101(Cr) is aniline > quinoline > pyridine. As shown by the electrostatic potential of the benzene molecule shown in Figure 11, the benzene ring has a higher electron cloud density which can lead to a stronger π - π conjugation with H₂BDC and competitive adsorption on H₂BDC. In addition, as shown in Figure 11, the order of molecular size for benzene and these three basic nitrogen-containing compounds is quinoline (0.7094 nm × 0.4992 nm) > aniline (0.5820 nm × 0.4965 nm) > benzene (0.4972 nm × 0.4972 nm) > pyridine (0.4905 nm × 0.3899 nm). The molecular size of benzene is relatively small, making it easier to diffuse into the pores of MIL-101(Cr)-0.5, thereby hindering the entry of the larger-sized aniline or quinoline molecules into the pores of MIL-101(Cr)-0.5. Consequently, the effect of benzene on the adsorption of aniline by MIL-101(Cr)-0.5 is the greatest, followed by quinoline and the least for pyridine.

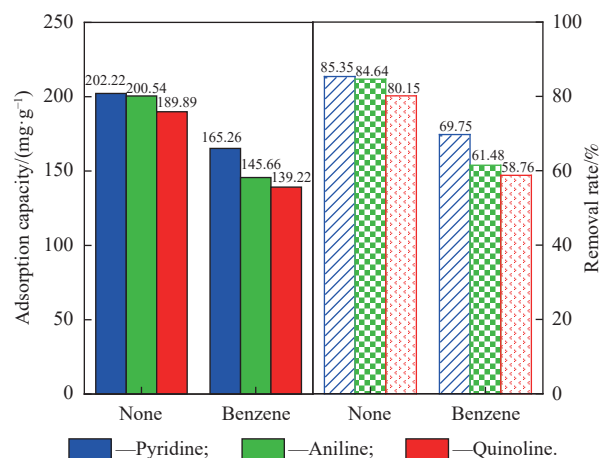


Fig. 10 Effect of benzene on adsorptive denitrification performance of MIL-101(Cr)-0.5

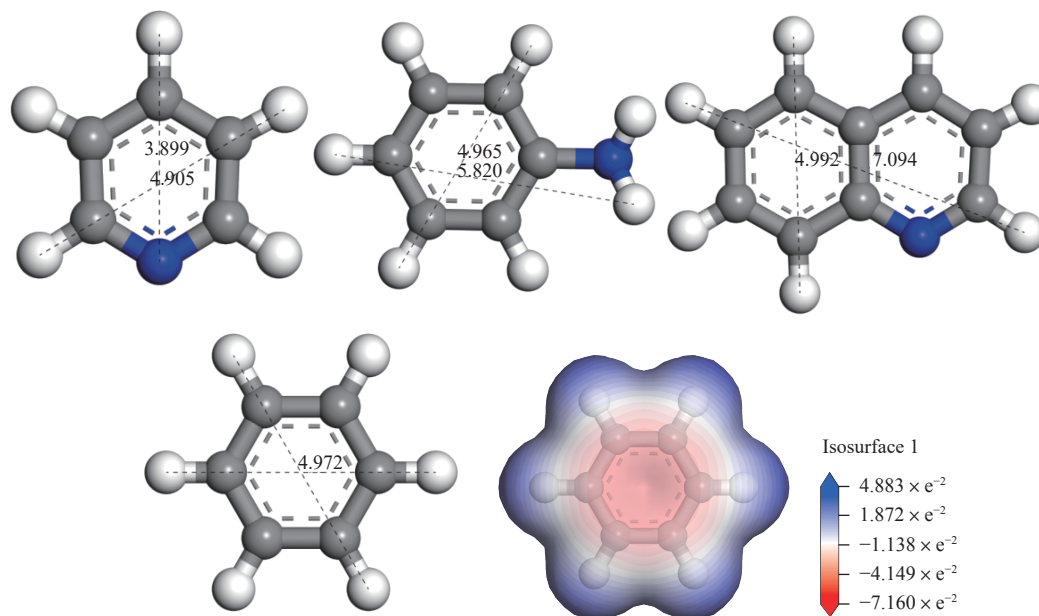


Fig. 11 Molecular size and electrostatic potential of pyridine, aniline, quinoline and benzene

2.9 Regeneration performance

The regeneration performance of an adsorbent is a crucial factor for its practical application. Pyridine, aniline and quinoline are all polar molecules. Ethanol, a moderate polarity, can effectively dissolve these organic substances^[37] while causing minimal damage to the structure and performance of MIL-101(Cr)-0.5. Additionally, ethanol is relatively safe and volatile and serves as an efficient and mild regeneration solvent^[38]. Therefore, the spent MIL-101(Cr)-0.5 was regenerated using ethanol reflux and the adsorptive denitrogenation results of the regenerated MIL-101(Cr)-0.5 are shown in Figure 12. As shown in Figure 12, the adsorption capacity and removal rate of MIL-101(Cr)-0.5 did not change significantly after two regeneration cycles. Interestingly, after the first regeneration, the adsorption capacity and removal rate of MIL-101(Cr)-0.5 for these three basic nitrogen-containing compounds slightly increased. This enhancement may be because after regeneration with ethanol reflux, most of these three basic nitrogen-containing compounds adsorbed on MIL-101(Cr)-0.5 were removed and simultaneously, some residual H₂BDC in the pores of the fresh MIL-101(Cr)-0.5 was also washed away. With the removal of these organic molecules, the once-regenerated MIL-101(Cr)-0.5 possesses more active sites, causing a slight increase in its adsorption capacity and removal rate. Following the second regeneration cycle, the adsorption capacity and removal rate showed only a slight decrease. This indicates that the structure of MIL-101(Cr)-0.5 remains stable and resistant to damage. However, it is inferred that a small fraction of the strongly adsorbed nitrogen compounds persists on the adsorbent surface after regeneration, which reduces the number of active sites and thus leads to a slight decrease in adsorption capacity and removal rate.

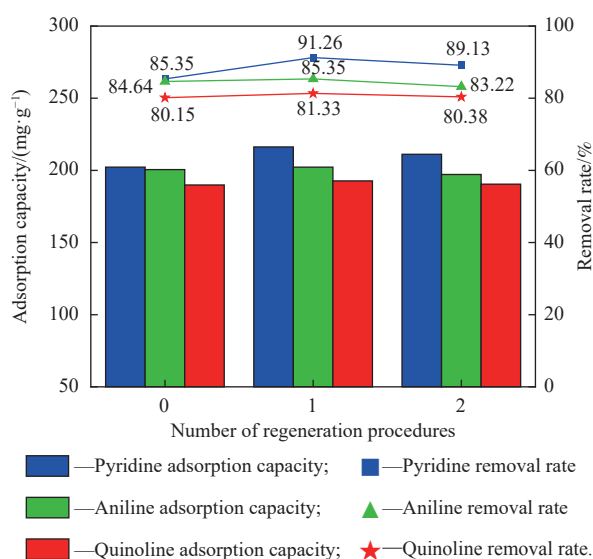


Fig. 12 Effect of MIL-101(Cr)-0.5 cycle regeneration times on adsorption denitrification performance

3 Conclusions

MIL-101(Cr)-0.5 was employed for the adsorptive denitrogenation on model fuels containing pyridine, aniline or quinoline, respectively. The optimal adsorption performance for aniline was achieved at 30 °C with 30 min contact time, whereas the optimal conditions for pyridine and quinoline were 40 °C and 40 min. The order of the adsorptive denitrogenation performance for MIL-101(Cr)-0.5 is pyridine > aniline > quinoline. This trend is attributed to the higher affinity of the Lewis acidic sites in MIL-101(Cr)-0.5, for the stronger basic pyridine. Conversely, the lower adsorption capacity for quinoline compared to aniline results from its greater steric hindrance, which impedes effective contact with the Cr³⁺ active sites of MIL-101(Cr)-0.5.

The MS software was used for simulation and calculation to conduct an in-depth study of the adsorption mechanism of MIL-101(Cr) for pyridine, aniline or quinoline. The simulation results show that the interaction of pyridine with MIL-101(Cr) is dominated by coordination adsorption, while the interaction of aniline or quinoline with MIL-101(Cr) is dominated by coordination adsorption, supplemented by π -complexation and hydrogen bonding. The overall adsorption strength follows the order: pyridine > aniline > quinoline, which correlates with the basicity of these three basic nitrogen-containing compounds. The basicity of pyridine is stronger, and the strength of the Cr–N bond formed between nitrogen atom and Cr³⁺ is greater. For aniline, however, its stronger π -complexation and hydrogen bonding compensate for the disadvantage of its weaker basicity, resulting in an intermediate overall adsorption capacity between that of pyridine and quinoline. Combining the Mulliken changes of pyridine, aniline and quinoline before and after adsorption at the Cr³⁺ sites of MIL-101(Cr), along with the charge density maps and charge density difference maps after adsorption, indicates that transfer electrons to the MIL-101(Cr) surface during the adsorption process, pyridine and quinoline via the H→C→N→Cr³⁺ pathway. In contrast, aniline transfers electrons through multiple pathways, including N→Cr³⁺, N→C→Cr³⁺ and N→H→O.

The adsorption kinetics analysis indicates that the adsorption of pyridine, aniline or quinoline on MIL-101(Cr)-0.5 is better described by the pseudo-second-order kinetic model, which shows that the adsorption process is dominated by chemisorption. The equilibrium adsorption capacity for these three basic nitrogen-containing compounds follows the order: pyridine > aniline > quinoline. The order of the adsorption rate constant k_2 is aniline > pyridine > quinoline, which indicates that the time for aniline to reach its maximum adsorption capacity is the shortest.

To simulate a real oil environment, an equimolar amount of benzene was added to the model fuel. The experimental results show that the order of the adsorptive denitrogenation effect is still pyridine > aniline > quinoline. However, the

adsorptive denitrogenation effect for all was slightly reduced, and the degree of this influence was in the order of aniline > quinoline > pyridine. This indicates that coordination to the Cr³⁺ sites remains the primary adsorption mechanism, with competitive π - π stacking also playing a role. The order of the π - π conjugation strength between these three basic nitrogen-containing compounds and H₂BDC in MIL-101(Cr) is aniline > quinoline > pyridine. Because benzene has a stronger π - π conjugation effect and a smaller molecular size, the influence of benzene on the adsorption of aniline by MIL-101(Cr)-0.5 is the greatest, followed by quinoline, and the least for pyridine.

The adsorbent was successfully regenerated by washing with ethanol, and it maintained a stable denitrogenation performance after two regeneration cycles.

Acknowledgement

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Declaration of Competing Interest

The authors declare no conflict of interest.

References

- PRADO G H C, RAO Y, DE K A. Nitrogen removal from oil: A review[J]. Energy Fuels, 2017, 31(1): 14–36.
- HUNOVÁ I, BÄUMELT V, MODLÍK M. Long-term trends in nitrogen oxides at different types of monitoring stations in the Czech Republic[J]. Sci Total Environment, 2020, 699: 134378.
- GAO S, CHEN X, XI X, et al. Coupled oxidation-extraction desulfurization: A novel evaluation for diesel fuel[J]. ACS Sustainable Chem Eng, 2019, 7(6): 5660–5668.
- LIMA F, DAVE M, SILVESTRE D J A, et al. Concurrent desulfurization and denitrogenation of fuels using deep eutectic solvent[J]. ACS Sustainable Chem Eng, 2019, 7(13): 11341–11349.
- WANG Y, LIU W, YUAN Q, et al. Technology of oxidative denitrification combined with extraction for coking diesel[J]. Appl Chem Ind, 2011, 40(8): 1430–1433.
- PRERANA S, MEENA N, VIJAYALAKSHMI G, et al. Adsorptive denitrogenation of indole from model fuel oil over Co-MAC: Adsorption mechanisms and competitive adsorption[J]. J Indian Chem Soc, 2023, 100(1): 100801.
- LI Y, HONG X, LI X, et al. Preparation of molecular sieve Ni-MCM-41 and its adsorptive denitrogenation performance of simulated diesel[J]. Pet Ref Chem Ind, 2019, 50(6): 40–45.
- QIN Y, TANG K, WANG H, et al. Preparation and adsorption denitrification performance of MOFs material MIL-101(Cr)[J]. J Fuel Chem Technol, 2025, 53(6): 943–953.
- ZHANG J. Preparation and characterization of thiophenecompounds removal materials from simulated gasoline[D]. Hanzhong: Shanxi University of Technology, 2024.
- HONG X, LI Y, ZHAO Y, et al. Preparation of mesoporous Co-MCM-41 and its performance in adsorption removal of various basic nitrogen compounds[J]. J Fuel Chem Technol, 2018, 46(2): 243–250.
- LI T. Study on the effect of basic nitrogen compounds on coking reactions in fluid catalytic cracking[D]. Qingdao: China University of Petroleum, 2015.
- WANG Z. Adsorptive denitrogenation from liquid fuel by metal-organic frameworks[D]. Dalian: Dalian University of Technology, 2013.
- ALAHABADI A, REZAI Z, SANI A R, et al. Efficacy evaluation of NH₄Cl-induced activated carbon in removal of aniline from aqueous solutions and comparing its performance with commercial activated carbon[J]. Desalin Water Treat, 2016, 57(50): 23779–23789.
- WANG C. Research of electric catalytic oxidation technology on typical nitrogen heterocyclic compounds and its application in the pharmaceutical wastewater[D]. Nanjing: Nanjing University, 2016.
- FU T, HONG X, TIAN Y, et al. Preparation of Ag⁺ modified NaY molecular sieve and its adsorption and denitrogenation properties[J]. J Fuel Chem Technol, 2024, 52(3): 384–394.
- WANG H, TANG K, HONG X, et al. Characterization of nanometer-Scale Co₃O₄ with two morphologies and its absorption performance for quinoline[J]. Acta Pet Sin (Pet Process), 2025, 41(2): 466–476.
- ZOU L Z, SHAO P H, ZHANG K, et al. Tannic acid-based adsorbent with superior selectivity for lead(II) capture: Adsorption site and selective mechanism[J]. Chem Eng J, 2019, 364: 160–166.
- WANG J, TANG K, SHUN X, et al. Imulation calculation of the adsorption of typical basic nitrogen compounds in diesel by anatase TiO₂[J]. Pet Ref Chem Ind, 2025, 56(1): 66–75.
- WU Y, XIAO J, WU L, et al. Adsorptive denitrogenation of fuel over metal organic frameworks: Effect of N-Types and adsorption mechanisms[J]. J Phys Chem C, 2014, 118(39): 22533–22543.
- ZHAO W, ZHENG Y, WANG G, et al. Organic Chemistry[M]. Beijing: Higher Education Press, 2019.
- ZHU Q. Classification and structural characteristics of conjugated system[J]. Univ Chem, 2021, 36(6): 2007029.
- WANG J, WANG H, TANG K, et al. Density functional theory for adsorption of pyridine by graphene oxide[J]. Acta Pet Sin (Pet Process), 2025, 41(5): 1399–1408.
- SAEED A, HÖKELEK T, BOLTE M, et al. Intra-and intermolecular N–H...O=C hydrogen bonds in 1-acyl urea compounds: synthesis, X-ray structure, conformational and Hirshfeld surface analyses of 1-(2, 3-dichlorophenyl)-3-pivaloylurea[J]. J Mol Struct, 2021, 1245: 131271.
- SAMINATHAN K, JAGAN R, SIVAKUMAR K, et al. N–H...O, C–H...O hydrogen-bonded supramolecular frameworks in 4-fluoroanilinium and dicyclohexylammonium picrate salts[J]. Struct Chem, 2019, 31(3): 1–10.
- TANG F. Preparation, characterization of adsorbents modified by amino MIL-101 and the study of the adsorption desulfurization/denitrogenation performance[D]. Beijing: Beijing University of Chemical Technology, 2018.
- ZHANG W J, HOU M L, ZHOU X, et al. A theoretical study of H₂S adsorption and dissociation mechanism on defected graphene doped with Pt[J]. J. Fuel Chem. Technol., 2022, 50: 1211.

- [27] WEN Y, WANG Y, WANG J, et al. Adsorptive denitrogenation of fuel with C-ZrO₂: Theoretical calculation research[J/OL]. J At Mol Phys, 2026, (02): 157-162[2025-01-23]/[2025-07-07]. <https://link.cnki.net/doi/10.19855/j.1000-0364.2026.026005>.
- [28] HU S, JIA X, HU J, et al. Quantum chemical analysis on molecular structures and inhibitive properties of imidazoline inhibitors[J]. J China Uni Pet (Nat Sci Ed), 2011, 35(1): 146-150.
- [29] WANG X. Study of the synthesis and adsorption and nitrogen removal properties of Ti-based porous material[D]. Tianjin: Tianjin University of Science and Technology, 2022.
- [30] CUI H, HONG X, TIAN Y, et al. Properties of adsorption quinoline from simulated fuel by AgY molecular sieve[J/OL]. J At Mol Phys, 2026, (02): 60-66[2025-01-23]/[2025-07-07]. <https://link.cnki.net/doi/10.19855/j.1000-0364.2026.022002>.
- [31] GENG J, YU Q, ZHAO R, et al. Study on adsorption denitrification of NaY molecular sieve modified by Cr³⁺, Ni²⁺[J]. Jiangxi Chem Ind, 2021, 37(1): 43-45.
- [32] LI X. Adsorption study of sulfamethoxazole and Cr(VI) co-existing pollutants in water by modified UiO-66[D]. Fuxin: Liaoning Technical University, 2023.
- [33] CAO J, LI Y, QI M, et al. Engineering porosity of MIL-101(Cr) using solvation effect[J]. J Environ Chem Eng, 2024, 12(3): 112753.
- [34] CHEN W, GUO W, XIE Y, et al. Simulation study for VOC adsorption in amino-functionalized metal-organic frameworks[J]. Funct Mater, 2023, 54(11): 11206-11214.
- [35] HONG X, LI Y, YUAN J, et al. Various basic nitrogen compounds removal from model diesel by adsorption with allochroic silica gel[J]. J Fuel Chem Technol, 2018, 46(3): 298-304.
- [36] PAN T. Design and synthesis of MIL-101(Cr)-based adsorbent and study on its adsorption performance of toluene[D]. Qingdao: China University of Petroleum (East China), 2022.
- [37] LU Y, LIANG R, YAN G, et al. Solvothermal synthesis of TiO₂@MIL-101(Cr) for efficient photocatalytic fuel denitrification[J]. J Fuel Chem Technol, 2022, 50(4): 456-463.
- [38] AHMED I, HASAN Z, KHAN N A, JHUNG S H. Adsorptive denitrogenation of model fuels with porous metal-organic frameworks (MOFs): Effect of acidity and basicity of MOFs[J]. Appl Catal B: Environ, 2013, 129: 123-129.

MIL-101(Cr) 吸附脱氮性能及其理论计算研究

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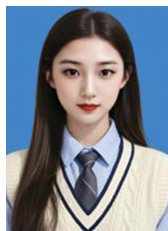
摘要: 研究 MIL-101(Cr)-0.5 对碱氮含量均为 1732 μg/g 的模拟燃料中吡啶、苯胺或喹啉的吸附脱氮性能, 考察了吸附温度、吸附时间以及吸附剂用量对其吸附脱氮性能的影响。实验结果表明, 当 MIL-101(Cr)-0.5 用量为 0.05 g、模拟燃料用量为 10 mL 时; 30 ℃、30 min 条件下, 吸附脱除苯胺的效果较好, 40 ℃、40 min 条件下, 吸附脱除吡啶或喹啉的效果较好。利用 Materials Studio (MS) 软件, 采用密度泛函理论 (DFT) 计算研究 MIL-101(Cr) 对三种碱性氮化物的吸附脱氮机理。模拟计算结果表明, 吡啶与 MIL-101(Cr) 的相互作用以配位吸附为主, 苯胺或喹啉与 MIL-101(Cr) 的相互作用以配位吸附为主, π 络合和氢键作用为辅, 整体吸附作用强弱顺序为吡啶 > 苯胺 > 喹啉。在吸附过程中, 吡啶和喹啉通过 H→C→N→Cr³⁺ 路径, 苯胺通过 N→Cr³⁺、N→C→Cr³⁺ 及 N→H→O 多种路径将电子转移到 MIL-101(Cr) 表面。吸附动力学研究表明, 三种碱性氮化物吸附过程均符合准二级动力学模型。苯对 MIL-101(Cr)-0.5 吸附脱氮性能影响的实验结果表明, 苯对苯胺和喹啉的吸附影响更显著。利用乙醇对 MIL-101(Cr)-0.5 清洗再生, 经两次再生后仍保持稳定的脱氮性能。

关键词: MIL-101(Cr); 吸附脱氮; 竞争吸附; 再生性能; 模拟计算

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