



# Adsorptive removal of nitrogen-containing compounds from a model fuel using a metal–organic framework having a free carboxylic acid group



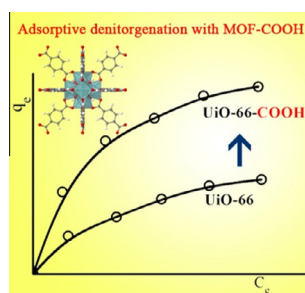
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## HIGHLIGHTS

- MOFs with COOH group were synthesized and applied in adsorptive denitrogenation.
- Denitrogenation was improved especially for neutral nitrogen containing compounds.
- Hydrogen bonding is possible mechanism for the improved adsorptive removal.
- Adsorbents (MOF-COOH) can be recycled by simple solvent washing.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Adsorptive removal of nitrogen-containing compounds from a model fuel was carried out by adsorbing indole (IND) and quinolone (QUI) over metal–organic frameworks (MOFs). UiO-66s, prototypes of MOFs, were applied as adsorbents with or without functionalization of free carboxylic groups. Even though the porosity of the functionalized UiO-66 (UiO-66-COOH) was lower than that of the pristine UiO-66, its adsorption capacity for neutral IND improved remarkably (103% and 28% based on surface area and weight, respectively) with functionalization. The enhanced performances of UiO-66-COOH could be explained by the formation of H-bond interactions between O (of –COOH) and H (of IND), which was supported by the differences in the adsorption of pyrrole vs. methylpyrrole. Curiously, the adsorbed amount (based on weight) of basic QUI decreased after the introduction of free –COOH on UiO-66, even though favorable acid–base interactions were expected. However, the amount of adsorbed QUI increased by 41% based on surface area. The adsorptive performances of UiO-66s for pyridine were very similar to those for QUI. Therefore, UiO-66-COOH might be also beneficial for the adsorption of basic NCCs, probably because of the existence of acid–base interactions (between N of NCCs and H of –COOH). However, the effect of free COOH on the adsorption of basic NCCs is generally lower than that of neutral NCCs having hydrogen atoms capable of acting as hydrogen bond donors. Based on the reusability results and the improved performances for IND and pyrrole adsorption, MOFs having free –COOH can be suggested as potential adsorbents to remove neutral NCCs, which are not easy to remove because of their lack of functionality.

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## 1. Introduction

With increasing population and development worldwide, the demand for energy is increasing continuously. To date, fossil fuel has been one of the most important sources for global energy. However, utilization of fossil fuel without adequate pre-treatment causes a serious problem, including emission of SO<sub>x</sub> and NO<sub>x</sub>, which are derived from burning of sulfur- and nitrogen-containing compounds (SCCs and NCCs, respectively) in the fuel [1–6]. SO<sub>x</sub> and NO<sub>x</sub> can be easily converted into acid rain, which has a negative effect on the environment, forests, and man-made structures. Therefore, the removal of SCCs and NCCs from fuel is very important [1–6].

SCCs in fuel have been removed mainly by a hydrodesulfurization (HDS) process which has been developed during the past few decades [1–4]. During HDS, sulfur in the SCCs is converted into gaseous H<sub>2</sub>S by hydrogenation of the SCCs at high temperature in the presence of a suitable catalyst. Removal of NCCs have started to attract attention only recently, owing to the increased NCC content in nonconventional or newly developed fuels and the enforcement of stricter environmental policies throughout the world [5,6]. Additionally, NCCs should be removed because NCCs and SCCs compete for the active sites of HDS catalysts, and NCCs generally reduce the efficiency of these catalysts [5,6]. Similar to SCCs, NCCs can be removed by hydrodenitrogenation (HDN) at high temperature in the presence of an appropriate catalyst and hydrogen. However, the efficiency of HDN is generally lower than that of HDS because successful HDN requires the destruction of the cyclic rings of NCCs. Moreover, HDN usually requires higher temperatures and pressures than HDS because of its lower reaction rate. Therefore, it is important to find a new and efficient process to remove NCCs from fuel. Recently, a technique called adsorptive denitrogenation (ADN) [5,6] has been developed to replace conventional HDN. ADN does not require the usage of hydrogen and a catalyst. Moreover, ADN can be carried out under ambient conditions if suitable adsorbents are available [5,6]. Several adsorbents such as activated carbon [5,7], Ti-HMS [8], silica–zirconia [9], ion exchange resins [10], and mesoporous silica [11] have been employed to this end.

There have been remarkable developments to porous materials in recent days thanks to the emergence of new advanced materials such as metal–organic frameworks (MOFs) [11–19] and other functional materials [20,21]. In particular, MOFs are very attractive materials for adsorption because of their high porosity, designable pore structure, ease of modification, and various pore sizes (ranging from microporous to mesoporous) [22–26]. Various MOFs have been employed in both ADS [27–35] and ADN [36–39] mainly due to the high hydrophilicity shown by MOFs and their ability to be readily modified. Not only pristine MOFs but also functionalized MOFs (such as composites [40]) have been used for both processes to obtain clean fuel.

NCCs can generally be removed by adsorbents having high porosity because of common interaction of van der Waals force [38].  $\pi$ -complexation has been also reported as an effective mechanism to adsorb NCCs having  $\pi$ -electrons [41,42]. The removal of basic NCCs such as quinolone (QUI), in which the formation of acid–base interactions is expected to play an important role, has also been described [43,44]. However, neutral NCCs such as indole (IND) do not have active functionalities for adsorption; therefore, the efficiency of adsorption of neutral NCCs is generally lower than that of basic NCCs. Recently, H-bond formation has been suggested as a way to adsorb neutral NCCs in cases where there is a hydrogen atom bound to a nitrogen atom in the NCC structure [45]. In this study, we investigated the adsorptive removal of NCCs from a model fuel by using functionalized MOFs that contain, in

particular, a free carboxylic acid in their structure (UiO-66-COOH) [46], as –COOH groups may be effective in adsorption because of their acidity or polarity. Both neutral and basic NCCs (such as IND and QUI, respectively) were adsorbed over UiO-66-COOH and pristine UiO-66 in order to understand the factors influencing the selectivity of the adsorption. Moreover, the adsorption of similar NCCs such as pyrrole (PYR), methylpyrrole (MPYR), and pyridine (PY) was studied in order to understand the plausible mechanism of adsorption of NCCs. Additionally, the reusability of UiO-66-COOH was evaluated after washing the used adsorbents with simple solvents.

## 2. Experimental

### 2.1. Chemicals and synthesis of adsorbents

Zirconium chloride (ZrCl<sub>4</sub>, 99.5%), IND (98.0%) and QUI (98.0%) were purchased from Sigma–Aldrich Co. Terephthalic acid (TPA, 99.0%) and PY (95.0%) were procured from Junsei Chemical Company and Duksan Pure Chemicals Co. Ltd., respectively. Dimethylformamide (DMF, 99.0%) and hydrochloric acid (HCl, 35.0%) were obtained from OCI Company Ltd. PYR (99.0%) and MPYR (99.0%) were purchased from Alfa Aesar. *n*-Octane (C<sub>8</sub>H<sub>14</sub>, 97%) and oxalic acid (99.0%) were obtained from Yakuri Pure Chemicals Co. Ltd. All of the obtained chemicals were used without further purification. Activated carbon, used as standard adsorbent, was obtained from Duksan chemical company (granule; size: 2–3 mm; BET surface area: 953 m<sup>2</sup>/g) and ground to fine particles before use.

The pristine UiO-66 and the functionalized UiO-66 with free –COOH (named UiO-66-COOH) were synthesized by conventional electric heating, following a protocol previously reported [46]. The detailed process for UiO-66 synthesis is as follows: ZrCl<sub>4</sub> (1.129 g), TPA (1.626 g), HCl (1.009 g), and DMF (27.04 g) were mixed in a beaker. Then, the mixture, with a molar ratio of 1:2:2:76 (ZrCl<sub>4</sub>:TPA:HCl:DMF) was transferred to a 100 mL Teflon-lined autoclave and heated at 180 °C in an electric oven for 24 h. The solid product was recovered by filtration, washed with DMF, and dried (24 h, 30 °C) under vacuum.

UiO-66-COOH was obtained via a two-step synthesis using oxalic acid [46]. In the first step, ZrCl<sub>4</sub> (0.117 g), 1.0 mL of HCl, and 5.0 mL of DMF were added to a 20 mL vial. In order to dissolve ZrCl<sub>4</sub>, the vial was subsequently sonicated for 20 min. TPA (0.123 g) and 10 mL DMF were further added to the vial. The final ZrCl<sub>4</sub>:TPA:HCl:DMF molar ratio was 1:1.5:6:40. The vial was further sonicated until all the TPA was dissolved. Subsequently, the mixture was placed in an autoclave and heated at 80 °C for 15 h. The obtained solid was filtered and washed with DMF twice, and then washed again twice with isopropanol. In the second step, 0.11 g of oxalic acid and the solid obtained in the first step (~0.25 g) were dispersed in DMF (~50 mL) and subsequently stirred for 2 h at room temperature. The resulting slurry was filtered to obtain a solid, and this solid was recovered following a process similar to that described in the case of pristine UiO-66. The dried adsorbents (UiO-66 and UiO-66-COOH) were stored in a desiccator until the adsorption experiments were initiated.

### 2.2. Characterization

The crystal structures of the UiO-66s were determined by X-ray diffraction (XRD) analysis (D2 Phaser X-ray diffractometer, Bruker, CuK $\alpha$  radiation). The nitrogen adsorption of the MOFs was measured at –196 °C using a surface area and porosity analyzer (Micromeritics, Tristar II 3020) after evacuation of the samples at

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