Electronic Supplementary Information (ESI)

Ionic liquid@MIL-101 prepared via the ship-in-bottle technique: Remarkable adsorbents for removal of benzothiophene from liquid fuel

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Experimental:

Materials: Terephthalic acid (TPA, C₆H₄-1,4-(CO₂H)₂, 98%), chromium chloride (CrCl₃·6H₂O, 96%), n-octane (C₈H₁₈, 99%), benzothiophene (BT, C₈H₆S, 98%), diallyldimethylammonium chloride (C₈H₁₆ClN, 97%), 1,4-butane sultone (C₄H₈O₃S, 98%), cysteamine (C₂H₇NS, ≥98.0%) were purchased from Sigma Aldrich. 4,4’-Azobis(4-cyanovaleric acid) (AVCA, C₁₂H₁₆N₄O₄, 98%) was obtained from Alfa Aesar. Methanol (CH₄O, 99.5%), ethanol (C₂H₅O, 78%), toluene (C₇H₈) and dichloromethane (CH₂Cl₂, 99.5%) were purchased from OCI company Ltd. Triethylenediamine (C₆H₁₂N₂, >98%) was obtained from Tokyo Chemicals Ltd. All chemicals were used without further purification.

Synthesis of MIL-101: MIL-101 was synthesized from CrCl₃·6H₂O, TPA and deionized water similar to a reported method.¹ The reactants composition was 1.0 CrCl₃·6H₂O : 1.0 TPA : 300 H₂O. The precursor of 30 g was loaded in a Teflon-lined autoclave and put in a preheated electric oven at 210 °C for 8 h. After the reaction, the autoclave was cooled to room temperature and solid green-colored products were recovered by filtration. After synthesis, the MOF was purified in three steps. In the first step, 1.0 g MIL-101 was added to 300 mL water and stirred magnetically for 5 h at 70 °C. Then the MOF was filtered and dried overnight in a drying oven. In the second step, the dried MOF was added to 250 mL ethanol; stirred magnetically at 60 °C for 3 h and then filtered. In the third step, the dried MOF from the second step was added to 150 mL 30 mM NH₄F solution and stirred for 10 h at 60 °C. After that, it was filtered and washed at least five times with hot water and then dried in a drying oven again. Finally, the purified MIL-101 was dehydrated at 150 °C overnight and stored in a desiccator.
Synthesis of IL/MIL-101-imp: The acidic chloroaluminate IL was prepared by mixing of 1-butyl-3-methylimidazolium chloride (10 mmol) and AlCl₃ (10 mmol) in a vial to follow the previous report.¹ The vial was sealed and a colorless thick liquid was observed by stirring the mixture for 24 h at 70 °C. IL supported MIL-101 adsorbents were prepared by impregnating IL (33 wt.%) to MIL-101 using dichloromethane as solvent. For example, an exact amount of IL was taken into a vial containing 5 mL of dichloromethane. Dehydrated MIL-101 (0.2 g) was added to that solution and stirred magnetically for 10 min at room temperature. The solvent was evaporated by using a rotary evaporator and the solid was dried overnight in a vacuum oven at 100 °C. Finally, the adsorbent was designated as IL/MIL-101-imp. The handling of IL and IL/MIL-101-imp adsorbents prior to adsorption experiments was carried out under inert conditions in a glove box.

Synthesis of IL/MIL-101-cov: The synthesis of covalently bound IL/MIL-101 was carried out according to the reported method with a small modification.² In brief, 0.5 g of MIL-101 (dehydrated at under vacuum 150 °C for 12 h), 40 mL of anhydrous toluene, and 2.5 mmol of triethylenediamine were taken in an 100 mL round bottom flask and the mixture was refluxed at 80 °C for 12 h with continuous magnetic stirring. The solids were separated by filtration, washed thoroughly to remove excess triethylene diamine, and again dispersed in 40 mL of anhydrous toluene in a 100 mL round bottom flask. 2.5 mmol of 1,4-butane sultone was added and the solution was refluxed at 80 °C for 12 h with continuous magnetic stirring. The solids were filtered and dried under vacuum at 120 for 4 h. In the final step, the dried solids were suspended in 30mL of ethanol, equivalent of concentrated H₂SO₄ (98%) was added drop by drop at 50 °C for 24 h. Finally, the catalyst was separated by filtration and dried under vacuum at 60 °C for 12h.
Synthesis of IL/MIL-101-click: The IL-functionalized MIL-101 was synthesized using the concept of click chemistry reported by Shaplov et al. with small modification. In brief, 0.5 g of MIL-101 (dehydrated at under vacuum 150 °C for 12 h), 30 mL of anhydrous toluene, and 1.0 mmol of cysteamine were taken in an 100 mL round bottom flask and the mixture was refluxed at 110 °C for 12 h with continuous magnetic stirring. The solids were separated by filtration and termed as MIL-101-SH. 0.4 g MIL-101-SH, 6 mL H₂O, 0.01 g AVCA (initiator) and 0.5 g diallyldimethylammonium chloride was taken in around bottom flask and the solution was stirred magnetically for 4 h at 70 °C. The solids were collected after vacuum drying at 70 °C. The obtained solids (0.5 g) were dispersed in 5 mL dichloromethane and 0.005 g AlCl₃ was added. The mixture was stirred magnetically for 10 min at room temperature. The solvent was evaporated by using a rotary evaporator and the solid was dried overnight in a vacuum oven at 100 °C.

Adsorption experiments: All the adsorption capacities (mg/g) were calculated from the difference between final and initial concentrations of an adsorbate by using following equation:

\[ q_t = \frac{(C_i - C_f) \cdot V}{m} \]

Where,

\( q_t \) = adsorbed amount in time \( t \) (mg/g)

\( C_i \) = initial concentration of the adsorbate (mg/ml)

\( C_f \) = final concentration after adsorption (mg/ml)

\( V \) = volume of the solution subjected to a single adsorption (ml)

\( m \) = mass of the adsorbent taken during a single adsorption (g)
Calculation of maximum adsorption capacity ($Q_0$): The maximum adsorption capacity ($Q_0$) was calculated using the Langmuir adsorption isotherm. The adsorption isotherms for different adsorbents were plotted according to the Langmuir equation\textsuperscript{4,5}

\[
\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_0 b}
\]

Where,

$C_e$: the equilibrium concentration of the adsorbate (mg/L)

$q_e$: the amount adsorbed at equilibrium (mg/g)

$Q_0$: the Langmuir constant (maximum adsorption capacity, mg/g)

$b$: the Langmuir constant (L/mg)

Therefore, the maximum adsorption capacity, $Q_0$, could be obtained from the reciprocal of the slope of a plot of $C_e/q_e$ against $C_e$.

Separation factor: The separation factor ($R_L$) was calculated using the following equation that describes the adsorption process:\textsuperscript{6-8}

\[
R_L = \frac{1}{1 + bC_o}
\]

Where,

$R_L$: separation factor

$b$: the Langmuir constant (L/mg)

$C_o$: initial concentration of adsorbate (mg/L)

Adsorbent regeneration: The used adsorbents were reactivated for further utilization following the two consecutive procedure. Firstly, the used adsorbet was soaked into n-octane solvent and allowed to stir 12 h at room temperature. While, the solvent was exchanged three times with fresh n-octane to wash out the adsorbed BT from the adsorbent. In next step,
the solid adsorbent was filtered and dried at 100 °C for 12 h. Then the dried adsorbent was heated at 230 °C under vacuum to evaporate the remaining adsorbed materials.
Reference:


Fig. S1. (a) XRD patterns; (b) nitrogen adsorption-desorption isotherms and (c) BJH pore size distributions of the adsorbents.
Fig. S2. (a) Langmuir plots and (b) effect of initial BT concentrations on the separation factor $R_L$ for the adsorption.
Fig. S3. Reusability of the adsorbents for the adsorption of BT. The initial BT concentration was 1000 ppm.
**Fig. S4.** Results of thermogravimetric analyses of the fresh and regenerated (after use once) IL@MIL-101.
**Fig. S5.** Effect of co-presence of toluene in solvent on the adsorption of BT with MIL-101 and IL@MIL-101. The initial BT concentration was 1000 ppm.