

# Supplementary Information

## ***Metal-Organic Framework/ $\alpha$ -Alumina Composite with Novel Geometry for Enhanced Adsorptive Separation***

*Chenghong Wang, Melanie Lee, Xinlei Liu, Bo Wang, J. Paul Chen and Kang Li\**

## 1. Materials

Unless otherwise stated, all the chemicals were used as received without further purification. The chemicals including triethyl phosphate (TEP, HPLC grade), acetic acid (AC, HPLC grade), zirconium(IV) chloride ( $ZrCl_4$ , 99.5%), 1,4-benzenedicarboxylic acid (BDC, 98%), and sodium arsenate dibasic heptahydrate ( $Na_2HAsO_4 \cdot 7H_2O$ , 98%) were purchased from Sigma-Aldrich. Those including dimethyl sulphoxide (DMSO, HPLC grade), dimethylformamide (DMF, 99.9%), ethanol (99.9%), nitric acid (68%), and sodium hydroxide (99%) were purchased from VWR. Moreover, aluminium oxide ( $Al_2O_3$ ) (alpha, 99.9% metals basis, surface area 6-8  $m^2/g$ , mean particle size (d50) 1  $\mu m$ , Inframat Corporation) as well as Polyethersulfone (PESf) (Radal A300, Ameco Performance) and Arlachel P135 (polyethylene glycol 30-dipolyhydroxystearate, Uniqema) were used as supplied. Besides, the stock solution of 1 mg/L arsenate was obtained by dissolving  $Na_2HAsO_4 \cdot 7H_2O$  in deionized (DI) water (Analytic lab, ACEX, Imperial College London).

## 2. 3D-pore network structure of $\alpha$ -alumina hollow fibre

Pore size determination was carried out using a gas-liquid displacement technique and was undertaken according to an established method with PoroLux 100 Porometer.

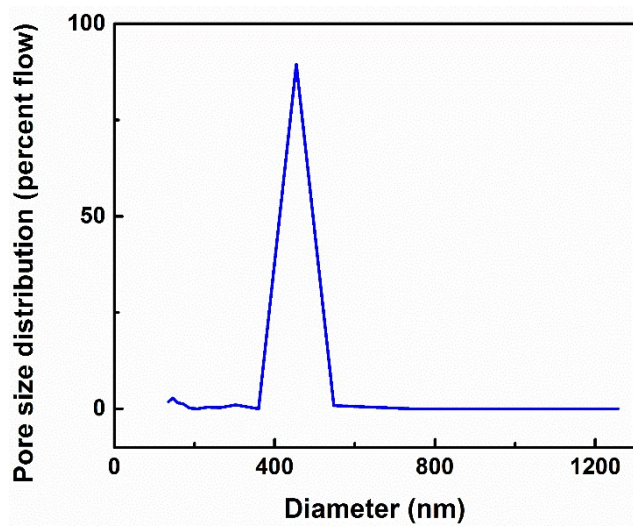


Figure S1. Pore size distribution of the 3D pore structure of  $\alpha$ -alumina hollow fibre.

### 3. Micro-channels opening of $\alpha$ -alumina hollow fibre

The outer surface morphology of the  $\alpha$ -alumina hollow fibre was studied by using a scanning electron microscope (SEM, JEOL JSM-5610).

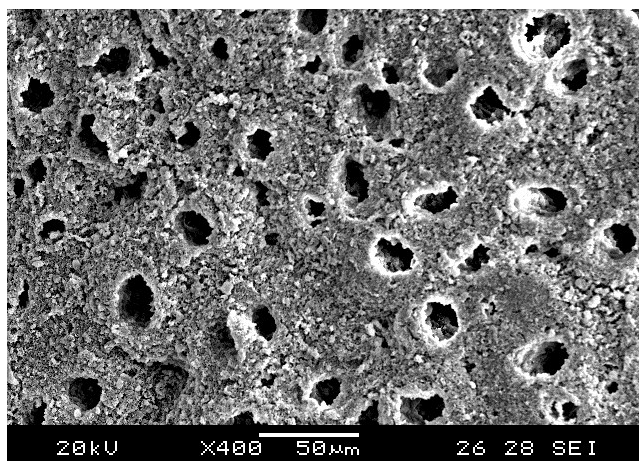


Figure S2. Outer surface of  $\alpha$ -alumina hollow fibre (micro-channel opening).

#### 4. XRD study of UiO-66

The crystal structure of UiO-66 samples was analysed by a powder X-ray diffractometer (PXRD, Panalytical Xpert). The X-Ray diffractometer is operated with Ni-filtered Cu  $K\alpha$  radiation at a voltage of 40 mV and a current of 40 mA. To be ready for XRD study, the samples were dried at 120 °C overnight under vacuum condition.

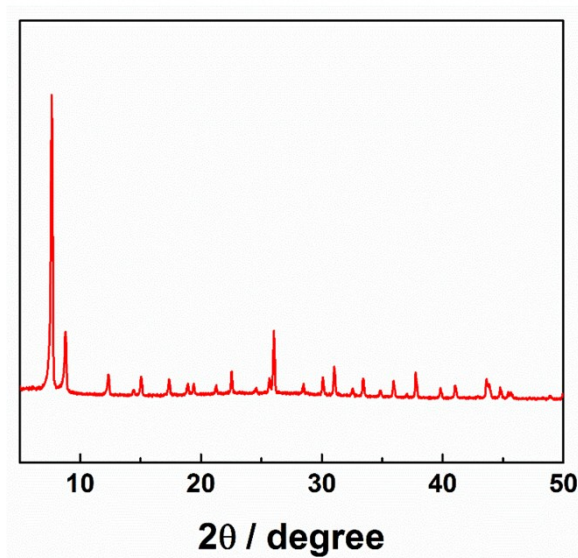


Figure S3. XRD pattern of as-synthesized UiO-66 sample.

## 5. Nitrogen physisorption measurement of UiO-66

The specific surface area of UiO-66 samples was determined by N<sub>2</sub> adsorption–desorption isotherms which was measured by gas adsorption analyser instrument (3Flex, Micrometrics) at 77 K.

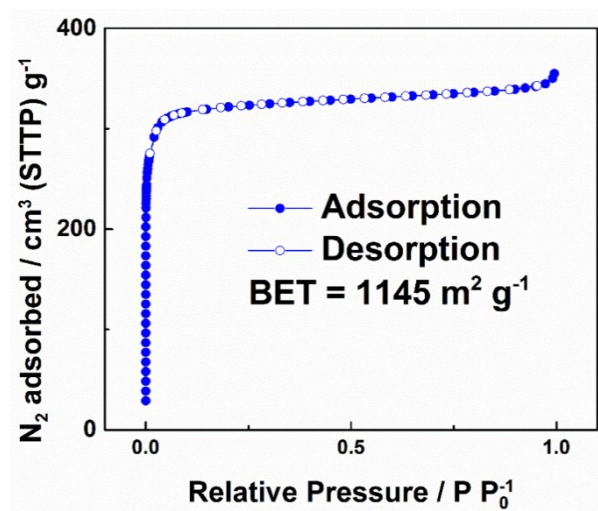


Figure S4. Nitrogen adsorption (filled circles)-desorption (open circles) isotherms of as-synthesized UiO-66 sample.

## 6. Vacuum filtration method

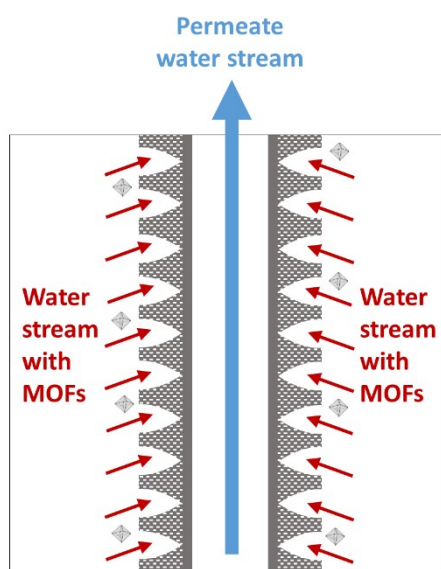


Figure S5. Scheme of vacuum filtration process.

Table S1. Optimized parameters for vacuum filtration process

Optimized experimental parameters	
Particle size of UiO-66	600 nm
Micro-channels length in $\alpha$ -alumina hollow fibres	500 $\mu\text{m}$
MOF concentration in the water solution	0.5 g/L
Magnetic stirrer speed for dispersing MOF crystals in the water solution	160 rpm
Duration of the vacuum filtration process for each composite	5 min



## 7. SEM study

The surface morphology of all the samples was studied by using a scanning electron microscope (SEM, LEO Gemini 1525) coupled with Energy-dispersive X-ray (EDX), as well as a transmission electron microscope (TEM, JEOL JEM-2000FX).

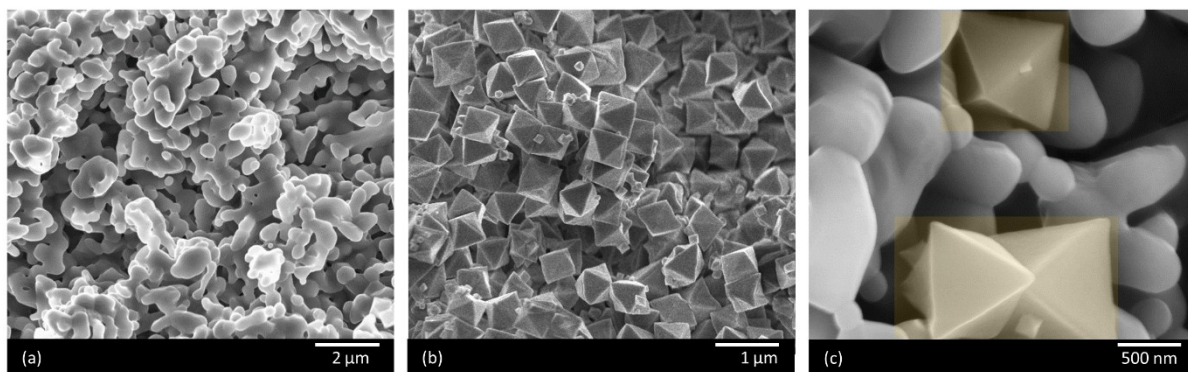


Figure S6. SEM images: (a) Alumina particles constituting the walls of ceramic hollow fibre micro-channels. (b) UiO-66 crystal particles. (c) Enlarged view inside the micro-channel showing UiO-66 crystals stay with alumina particles. Yellow shades indicate the octahedral UiO-66 crystals.

8. Arsenic contaminated water remediation studies: **composite-1**

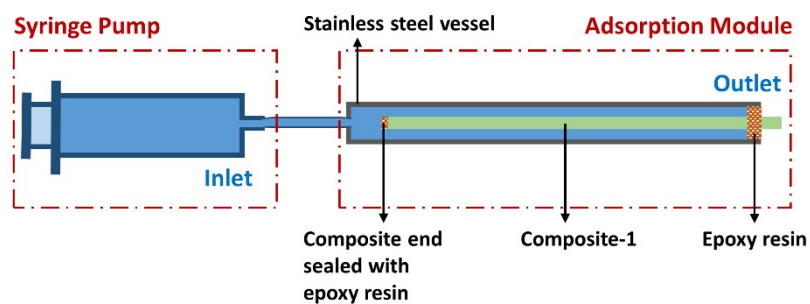


Figure S7. The prototype of experiment setup, using **composite-1** for arsenic contaminated water remediation.

Table S2. Optimized experimental parameters for arsenic contaminated water remediation using **composite-1**

Optimized experimental parameters	
Active Loading of UiO-66 in $\alpha$ -alumina hollow fibre	0.68 mg g <sup>-1</sup>
Outer/inner diameter of $\alpha$ -alumina hollow fibre	1.8 mm/1.1 mm
Composite length	5 cm
Syringe pump flow rate	0.6 mL min <sup>-1</sup>
Recovery permeate rate	1.74 L min <sup>-1</sup> m <sup>-2</sup>
Feed concentration	1 mg L <sup>-1</sup>
Time duration before breakthrough	60 min

## 9. Arsenic contaminated water remediation studies: packed columns

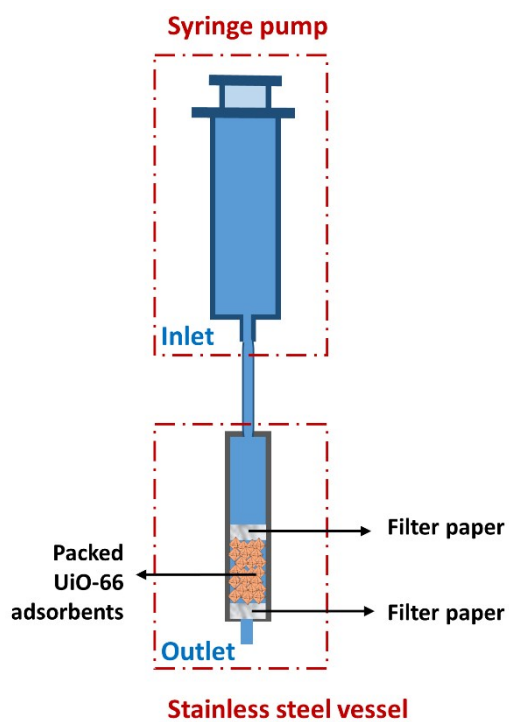


Figure S8. The prototype of experiment setup, using packed column bed setup for arsenic contaminated water remediation.

Table S3. Experimental parameters for arsenic contaminated water remediation using packed column beds

Experimental parameters for packed columns	
Equivalent amount of UiO-66 in the composite	15 mg (1X); 30 mg (2X); 75 mg (5X); 120 mg (8X)
Packed column diameter	3.175 mm
Packed column heights	0.6 cm (1X); 1.2 cm (2X); 3 cm (5X); 4.8 cm (8X)
Recovery outflow rate	0.6 mL min <sup>-1</sup>
Filter paper pore size	0.45 μm
Feed concentration	1 mg L <sup>-1</sup>

## 10. Composite FTIR analysis

To understand the interaction between UiO-66 and alumina, the samples were analysed by a FTIR spectrometer (Spectrum 100, PerkinElmer) equipped with diamond ATR (attenuated total reflection) crystal. As shown in Fig. S9, all the characteristic peaks of **composite-1** can be correlated with the ones of alumina and UiO-66. In other words, the FTIR spectrum of **composite-1** is a simple superimposition of the spectra of alumina and UiO-66. This suggests there is only physical attachment between alumina particles and UiO-66 crystals in the composite. The main reason (mechanism) that UiO-66 crystals stay well within the composite is attributed to the size-exclusion effect provided by the conical shape micro-channels as well as the thin barrier layer at the lumen side.

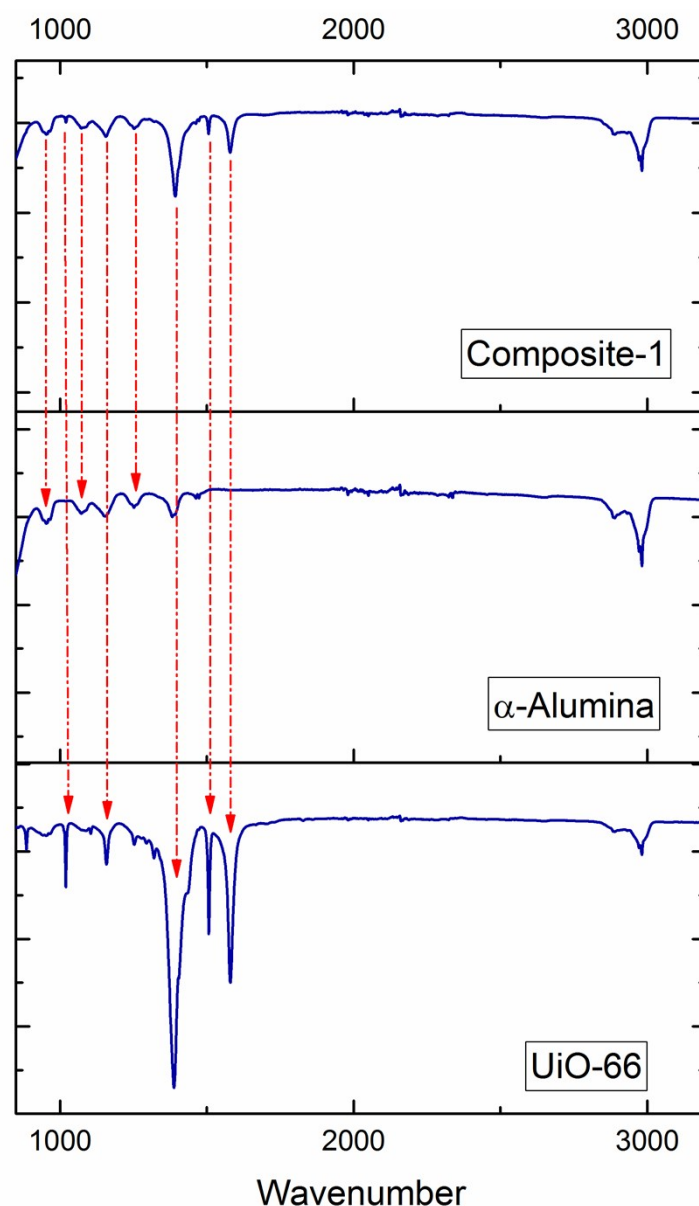


Figure S9. FTIR spectra of **composite-1**, alumina and UiO-66.

## 11. Composite TGA analysis

The thermal analysis was carried out using a thermogravimetric analyzer (TGA Q500, TA Instruments). Characteristic patterns of weight change were obtained with respect to **composite-1**, alumina, UiO-66, respectively. It shall be noted that **composite-1** only exhibited one obvious weight drop (~ 1%, at 500 °C) along with an increase of temperature (from room temperature to 1000 °C). This weight drop is corresponding with the thermal degradation of UiO-66 crystals that were incorporated within the composite.

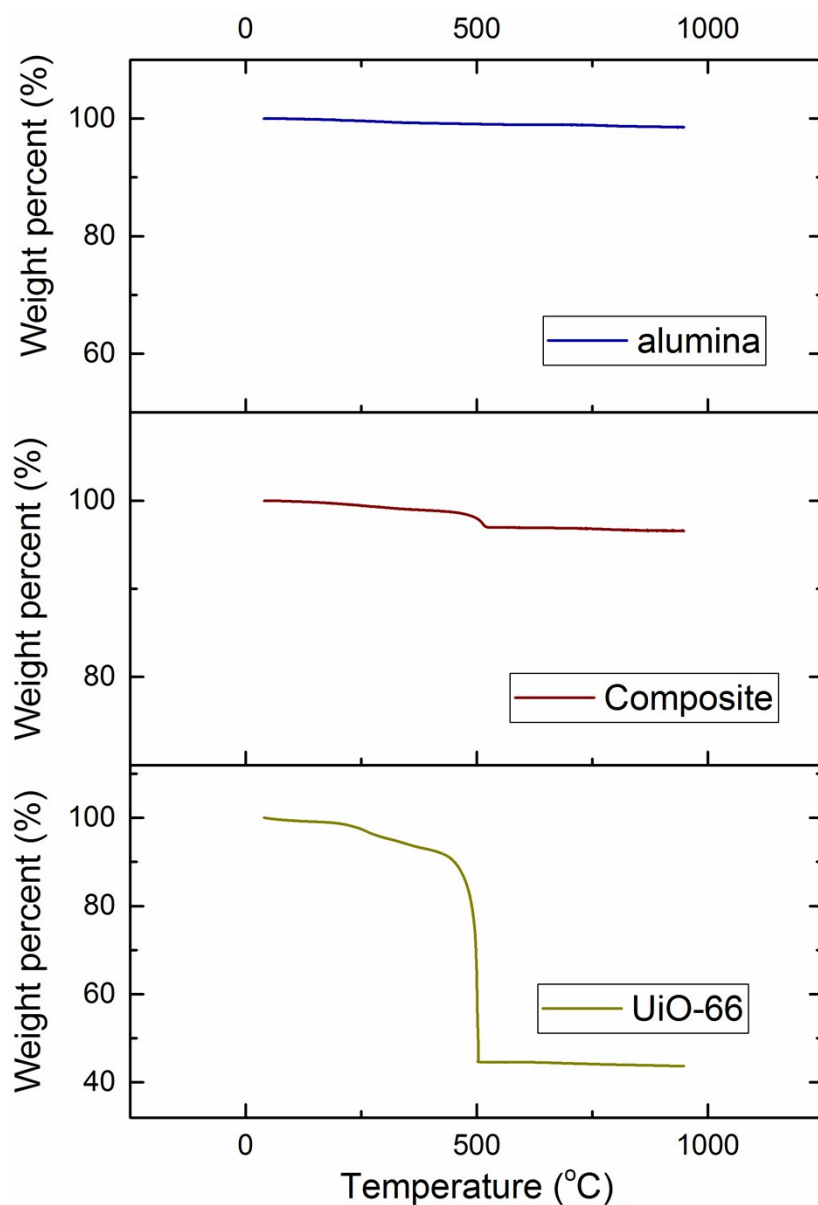


Figure S10. TGA analyses for weight changes with temperature on **composite-1**, alumina and UiO-66.

## 12. UiO-66 loss test

After the adsorptive separation tests, the outflow from **composite-1** was collected and sent for centrifugation. No appearance of UiO-66 particles was observed after centrifugation. The outflow samples were then put for ICP analysis to detect Zr signal, which should be due to the presence and/or decomposition of UiO-66 particles if there is any. Both visible observation and element detection together prove that the loss of UiO-66 crystals from the composite throughout the adsorptive separation tests is negligible.



### 13. Regeneration study

The regenerability of UiO-66 after the adsorption of arsenate was studied using the typical approaches (Tab. S5), which were reported in literature to have successfully regenerated the arsenic adsorbents with similar adsorption mechanisms (containing Zr-OH adsorption sites).<sup>15</sup> The experiment results suggest that the arsenic adsorption by Zr-MOF UiO-66 is, however, an irreversible sorption process. This restricts the arsenic decontamination capability of **composite-1** in repeated use. Despite that, if a regenerable adsorbent is used and loaded within the micro-channels to form the composite, repeated use can be realised in such cases.

Table S5. Arsenate desorption using typical approaches from the spent UiO-66 after first cycle adsorption.

Arsenate desorption percentage	
DI water wash	0.299 %
60 °C DI water wash	0.506 %
100 °C DI water wash	0.776 %
DMF wash	No detectable
Methanol wash	No detectable
Ethanol wash	0.448 %
pH shift to basic range (pH 11)	2.23 %
pH shift to basic range (pH 13)	6.60 %

## 14. Methods

### *UiO-66 preparation*

UiO-66 was prepared based on the procedure described by Cavka *et al.*,<sup>11, 25, 26</sup> with some modifications. Acetic acid (AC), 1,4-benzenedicarboxylic acid (BDC) and ZrCl<sub>4</sub> were dissolved in DMF one after another under stirring in a glass bottle at room temperature, according to a specific molar composition: Zr/BDC/AC/DMF = 1:1:160:870. The solution was then transferred to Teflon-lined stainless steel autoclaves and heated at 120 °C for 24 h in a convective oven (UF30, Memmert). Afterwards, the autoclaves were cooled down to room temperature. The UiO-66 powders were washed by ethanol with the assistance of centrifuge (Thermo Scientific Legend X1R) and dried at 120 °C overnight under vacuum condition (Fistream Vacuum Oven) for further use.

### *α-Alumina hollow fibre preparation*

The α-alumina hollow fibres were fabricated by the combined phase-inversion and sintering method, described by Lee *et al.* with some modifications,<sup>23</sup> using a triple-orifice spinneret. To start with, a uniform suspension was prepared via ball milling, which composed of alumina particles (59.9 wt. %), NMP solvent (33.6 wt. %) and PESf polymeric binder (6.0 wt. %), as well as an additive (Arlacel P135) acting as a dispersant (0.5 wt. %). This suspension was then degassed under vacuum with stirring to fully remove bubbles, and then transferred into a 200 mL stainless steel syringe that was controlled by a syringe pump (Harvard PHD22/200 HPsi and KDS410). NMP solvent was transferred into a 100 mL stainless steel syringe controlled by another syringe pump. DI water was used as the bore fluid, and was extruded together with the α-alumina suspension in the centre layer and NMP solvent in the outer layer through the spinneret into the external coagulation bath (see Table S4). When phase-inversion was complete, the hollow fibre precursors were removed from the external coagulant bath,

and were then dried and straightened at room temperature. Afterwards, they were cut into the required length for subsequent calcination and sintering (at 1500 °C).

Table S6. Spinning parameters for  $\alpha$ -alumina hollow fibre

Spinning parameters		
<b>Flow rate (mL/min)</b>	Ceramic layer	7
	Solvent layer	5
	Bore fluid	40
<b>Air gap (cm)</b>	25	

#### *MOF/ $\alpha$ -alumina composite preparation*

0.5 gram UiO-66 crystals were suspended in 1 litre water, and it was under constant agitation to ensure a homogeneous distribution. The lumen of  $\alpha$ -alumina hollow fibre was in vacuum condition, and the water solution carrying MOFs flowed from the shell side into the lumen (see Supplementary Figure S5). Each composite required 5 minute of the vacuum filtration process. Afterwards, the composites were left in ambient atmosphere for drying. The solid residuals attached to the outer surface of the  $\alpha$ -alumina hollow fibres were carefully wiped off using delicate task wipers (Kimtech Science KimWipes).

#### *Adsorption kinetics experiments*

The adsorption kinetics experiment was carried out at initial arsenate concentration of 20 mg/L with adsorbent dosage of 0.1 g/L, and the solution pH value was controlled at 2.0 during adsorption process by adding a certain amount of NaOH or HNO<sub>3</sub>. After adsorption experiments, the solution was filtered using 0.22  $\mu$ m syringe filter and arsenate concentration was measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 2000 DV, PerkinElmer).

### *Breakthrough study experiments*

The feed solution used in breakthrough experiments had arsenic concentration of 1 mg/L and a pH of 2.0. It was introduced to both **composite-1** and equivalent packed columns from a syringe pump (Nexus 6000, Chemyx). In the case of composite-1, one end was sealed and the other end served as the outlet, as shown in Supplementary Figure S7. In the case of packed columns, active MOF adsorbents were packed and held by the filter papers, as shown in Supplementary Figure S8. After collecting recovery samples, an aliquot of each sample was analysed using ICP-OES for residual arsenic concentration measurement.