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Electronic Supporting Information

for

Bromate Reduction in Water by Catalytic Hydrogenation using Metal Organic Frameworks and Sodium Borohydride

*Kun-Yi Andrew Lin** *and Shen-Yi Chen*

Department of Environmental Engineering, National Chung Hsing University,

250 Kuo-Kuang Road, Taichung, Taiwan, R.O.C.

*Corresponding Author. Tel: +886-4-22854709, E-mail address: linky@nchu.edu.tw (Kun-Yi Andrew Lin)

Text S1. Preparation of MIL-88A and ZIF-67

Materials:

All chemicals used in this study were commercially available and used as received without additional purification. Iron chloride ($FeCl_3 \cdot H_2O$) was purchased from Merck (Germany). Fumaric acid ($C_4H_4O_4$), sodium bromate ($NaBrO_3$), sodium borohydride ($NaBH_4$) and sodium phosphate dibasic (Na_2HPO_3) were obtained from Sigma-Aldrich (USA). Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) was purchased from Choneye Pure Chemicals (Taiwan). 2-methylimidazole (2-MIM), sodium nitrate ($NaNO_3$) and sodium sulfate (Na_2SO_4) were obtained from Acros Organics (USA). D.I. water was prepared to exhibit less than 18 MOhm-cm.

Synthesis and Characterization of MIL-88A and ZIF-67:

MIL-88A was prepared as illustrated in Fig. 1(a) based on the reported procedure (Horcajada et al. 2010, Xu et al. 2014). At first, 0.5 g of $FeCl_3 \cdot H_2O$ and 5 g of fumaric acid were added to 50 ml of D.I. water in a media bottle. The resultant mixture was then stirred for 2 hour to completely dissolve the two reagents in D.I. water. Next, the homogeneous solution was capped and heated at 85 °C under ambient pressure for 24 hours. The precipitate was collected via centrifugation, washed with ethanol/water, and dried at 100 °C under reduced pressure (*i.e.*, 7.8×10^{-2} atm) to obtain MIL-88A.

The preparation of ZIF-67 can be seen in Fig. 1(b) according to the reported procedure (Shao et al. 2014). Briefly, 1.16 g of $Co(NO_3)_2 \cdot 6H_2O$ was first dissolved in 100 ml of methanol, while 1.31 g of 2-MIM was added to another 100 ml of methanol. The methanol solution of cobalt was slowly added to the methanol solution of 2-MIM. The resultant mixture was stirred at ambient temperature for 2 hours. The precipitate was then collected and washed repeatedly with ethanol. The as-synthesized crystals were first dried at 60 °C

under ambient pressure for 6 hours and then under reduced pressure at 100 °C for 12 hours to obtain the final product, ZIF-67.

To characterize morphology of MOF crystals, a field emission SEM (JEOL JSM-6700, Japan) and a transmission electronic microscopy (TEM) (JEOL JEM-2010, Japan) were used. Crystalline structures of MOFs were obtained using an X-ray diffractometer (XRD) (PANalytical, the Netherlands) with copper as an anode material (40 mA, 45 kV). Absorption infrared (IR) spectra of MOFs were measured by a Fourier-Transform Infrared spectrometer (Horiba FT-730, Japan) with KBr pellets as sample holders. The chemical composition of MOFs was analyzed using a X-ray Photoelectron Spectroscopy (XPS) (PHI 5000 Versa Probe/Scanning ESCA Microprobe, ULVAC-PHI, Inc., Japan) with a monochromatized Mg Kα (1253.6 eV) X-ray source. Thermogravimetric (TG) curves of MOFs were measured using a thermogravimetric analyzer (ISI TGA i1000, USA) at a heating rate of 10 °C min^{-1} from 25 to 800 °C in nitrogen. N_2 adsorption/desorption isotherms of MOFs were measured by a volumetric sorption analyzer (Micromeritics ASAP 2020, USA) at a relative pressure (P/P_0) range of 0.0001−0.99.

Text S2. Effects of pH and co-existing anions on the bromate reduction

To investigate the effect of pH on the bromate reduction, pH of bromate solutions (C_0 = 0.781 mmol g^{-1}) was adjusted from 3 to 11 using 0.1 M of hydrochloric acid and sodium hydroxide solutions. The removal efficiency at equilibrium (q_e) for each pH-adjusted bromate solution was then determined. Since many other anions can be found in wastewater, the effect of co-existing anions was also examined by adding equal-molar concentrations of phosphate, nitrate and sulfate to bromate solutions. Removal efficiency for each anion was determined and the resulting bromide during the bromate reduction was also analyzed. Furthermore, considering that the typical range of bromate concentration ranges from ten to a

few hundreds μg L^{-1} (Matos et al. 2008), MOFs were also evaluated for removing bromate of low-level concentration (*i.e.*, 100 μg L^{-1}) from water.

Text S3. Recyclability of MIL-88A and ZIF-67 for the bromate reduction

As a heterogeneous catalyst, it is important to evaluate whether MOFs can be re-used to reduce bromate. Thus, the recyclability of MIL-88A and ZIF-67 for the bromate reduction was examined. To do so, the spent MIL-88A and ZIF-67 were directly used for subsequent reduction experiments without any regeneration treatments. The removal efficiency at equilibrium of each cycle using the spent MOFs was determined and compared with that of the pristine MOFs. The leaching-out of Fe and Co from MIL-88A and ZIF-67, respectively, during the bromate reduction was determined using an atomic absorption spectrophotometer (Perkin Elmer AA100, USA).

References:

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Xu, W.-T., Ma, L., Ke, F., Peng, F.-M., Xu, G.-S., Shen, Y.-H., Zhu, J.-F., Qiu, L.-G. and Yuan, Y.-P. (2014) Metal-organic frameworks MIL-88A hexagonal microrods as a new photocatalyst for efficient decolorization of methylene blue dye. Dalton Transactions 43(9), 3792-3798.

Shao, J., Wan, Z., Liu, H., Zheng, H., Gao, T., Shen, M., Qu, Q. and Zheng, H. (2014) Metal organic frameworks-derived Co3O4 hollow dodecahedrons with controllable interiors as outstanding anodes for Li storage. Journal of Materials Chemistry A 2(31), 12194-12200.

Matos, C.T., Velizarov, S., Reis, M.A.M. and Crespo, J.G. (2008) Removal of Bromate from Drinking Water Using the Ion Exchange Membrane Bioreactor Concept. Environmental Science & Technology 42(20), 7702-7708.

Mikhail, R.S., Brunauer, S. and Bodor, E.E. (1968) Investigations of a complete pore structure analysis: I. Analysis of micropores. Journal of Colloid and Interface Science 26(1), 45-53.

Table S1. A summary of bromate reduction efficiencies using MIL-88A and ZIF-67 with $NaBH_4$ under various conditions (C_0 of bromate = 100 mg L^{-1}).

MOFs	Conditions				Reduction Efficiency at t = 60 min (mmol g^{-1})
	Temp. (°C)	$NaBH_4$ (mg L^{-1})	MOF loading (mg L^{-1})	pH	
MIL-88A	25	500	500	6.6	0.63
	40	500	500	6.6	0.63
	50	500	500	6.6	0.63
	60	500	500	6.6	0.63
	75	500	500	6.6	0.63
	25	0	500	6.6	0.00
	25	600	500	6.6	1.11
	25	1000	500	6.6	1.56
	25	500	250	6.6	1.01
	25	500	500	6.6	0.63
	25	500	1000	6.6	0.27
	25	500	500	3.0	1.26
	25	500	500	4.0	0.87
	25	500	500	5.0	0.74
	25	500	500	6.0	0.63
	25	500	500	7.0	0.59
	25	500	500	8.0	0.61
	25	500	500	9.0	0.62
	25	500	500	10.0	0.57
	25	500	500	11.0	0.53
ZIF-67	25	500	500	6.6	1.56
	40	500	500	6.6	1.56
	50	500	500	6.6	1.56
	60	500	500	6.6	1.56
	75	500	500	6.6	1.56
	25	0	500	6.6	0.00
	25	200	500	6.6	1.50
	25	400	500	6.6	1.53
	25	1000	500	6.6	1.56
	25	500	250	6.6	3.04
	25	500	500	6.6	1.56
	25	500	1000	6.6	0.78
	25	500	500	3.0	1.56
	25	500	500	4.0	1.55
	25	500	500	5.0	1.56
	25	500	500	6.0	1.51
	25	500	500	7.0	1.48
	25	500	500	8.0	1.44
	25	500	500	9.0	1.26
	25	500	500	10.0	1.11
	25	500	500	11.0	0.25

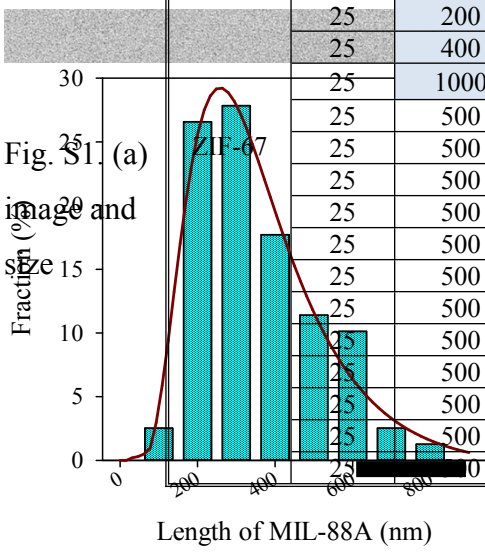

Fig. S1. (a) TEM image and (b) the size distribution of MIL-88A. The scale bar is 200 nm.

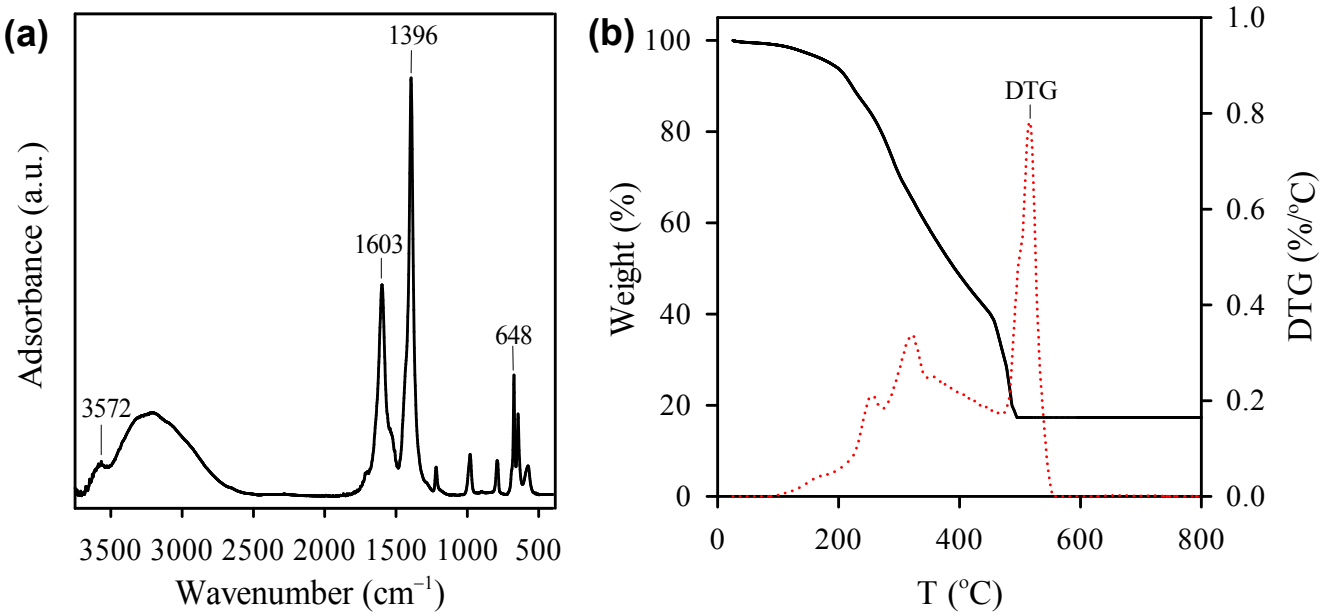

Fig. S2. Characterization of the as-synthesized MIL-88A: (a) FT-IR spectrum and (b) TGA.

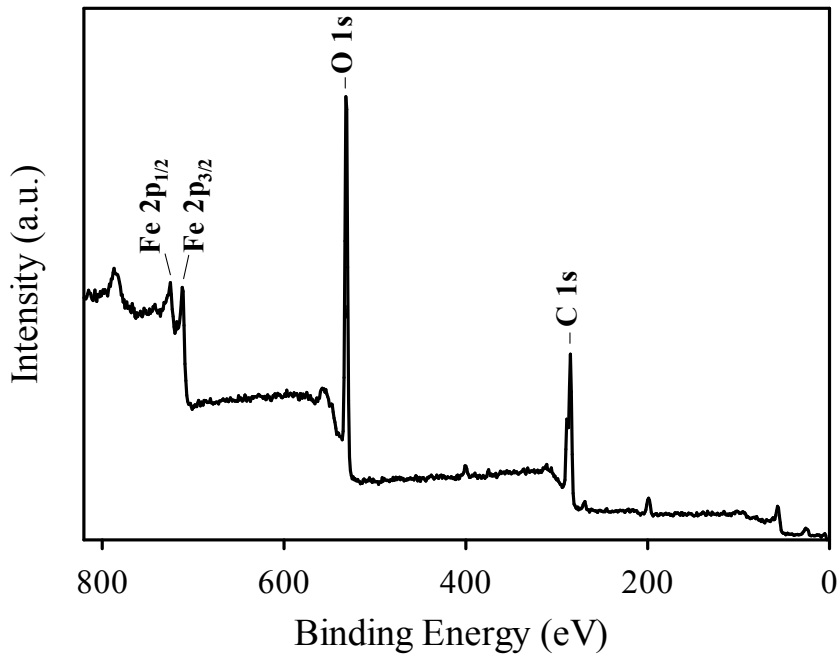

Fig. S3. Full-survey XPS spectrum of MIL-88A

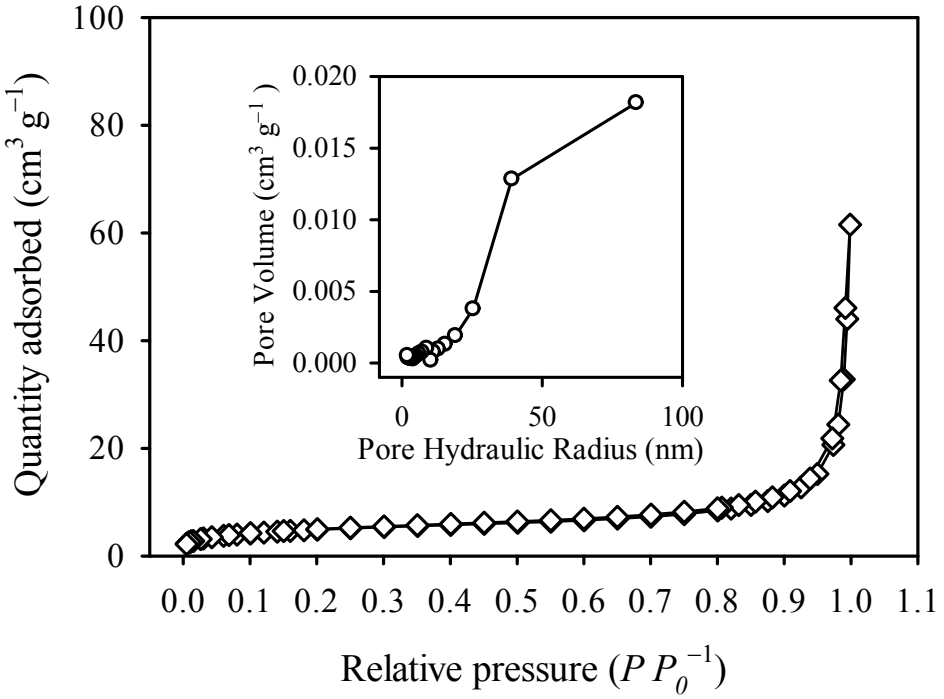

Fig. S4. N_2 sorption/desorption isotherms of MIL-88A at 77K. The inset represents the pore size distribution, ranging from 1.7 to 300 nm, based on the BJH desorption pore distribution report.

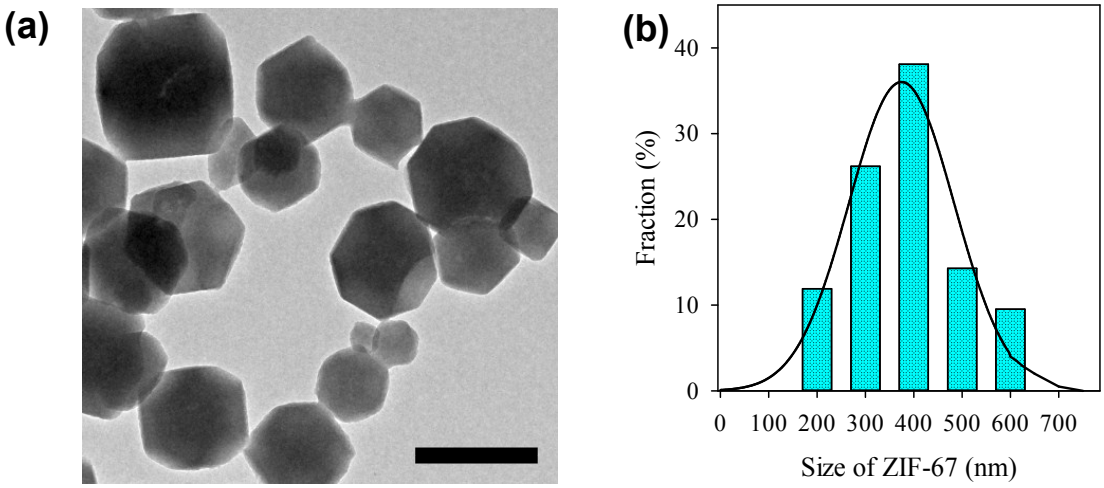

Fig. S5. (a) TEM image and (b) the size distribution of ZIF-67. The scale bar is 500 nm.

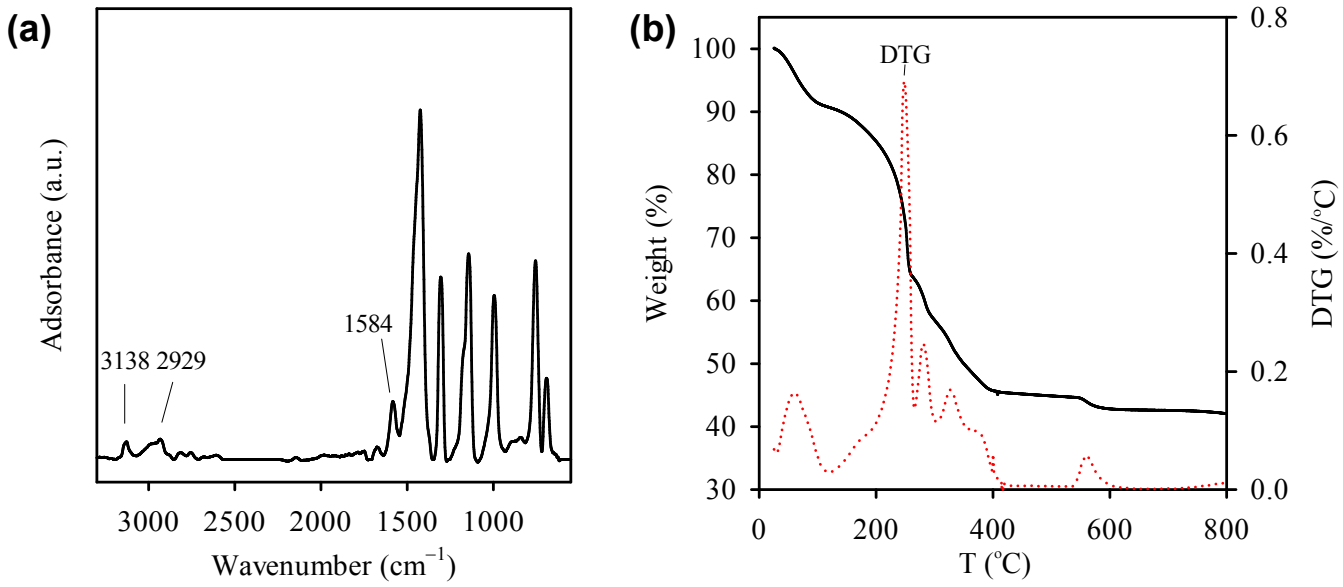

Fig. S6. Characterization of the as-synthesized ZIF-67: (a) FT-IR spectrum and (b) TGA.

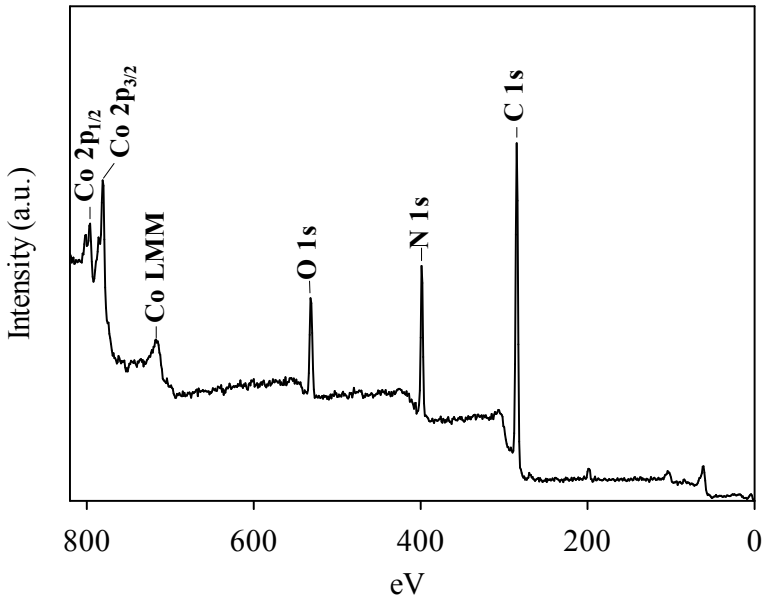

Fig. S7. Full-survey XPS spectrum of ZIF-67

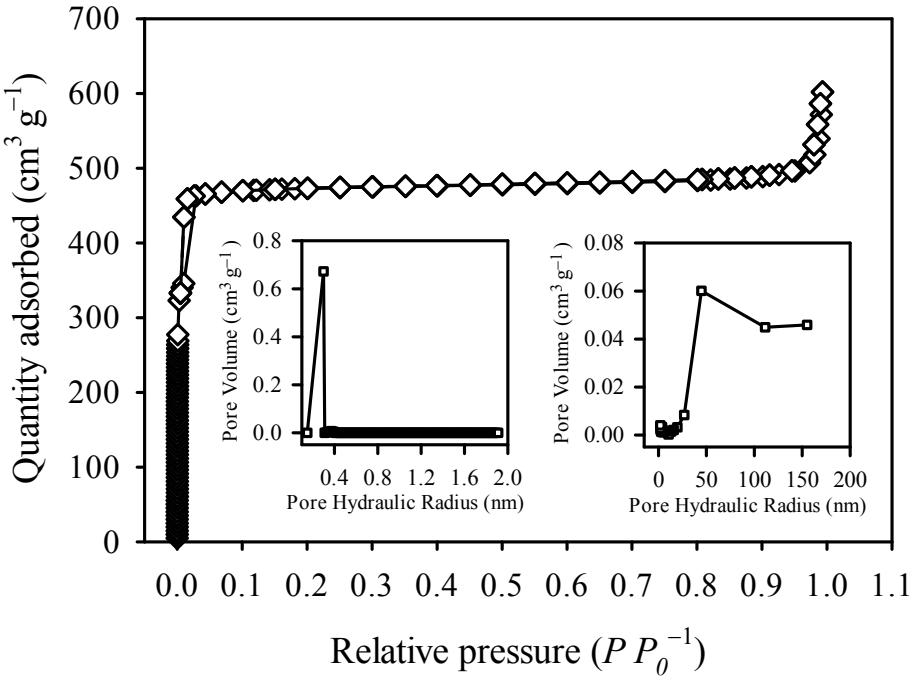

Fig. S8. N_2 sorption/desorption isotherms of ZIF-67 at 77K. The inset on the left side represents the micropore size distribution based on the MP-method (*i.e.*, the micropore analysis method developed by Brunauer et al. (Mikhail et al. 1968)). The inset on the right side represents the pore size distribution, ranging from 1.7 to 300 nm, based on the BJH desorption pore distribution report.

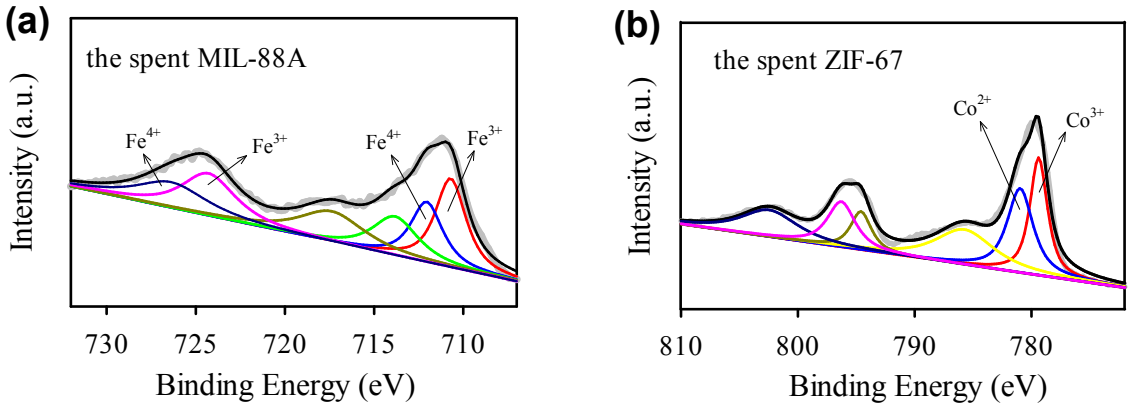

Fig. S9. XPS analyses of the spent MOFs recovered from the bromate reduction: (a) Fe core-level XPS spectrum of MIL-88A and (b) Co core-level XPS spectrum of ZIF-67

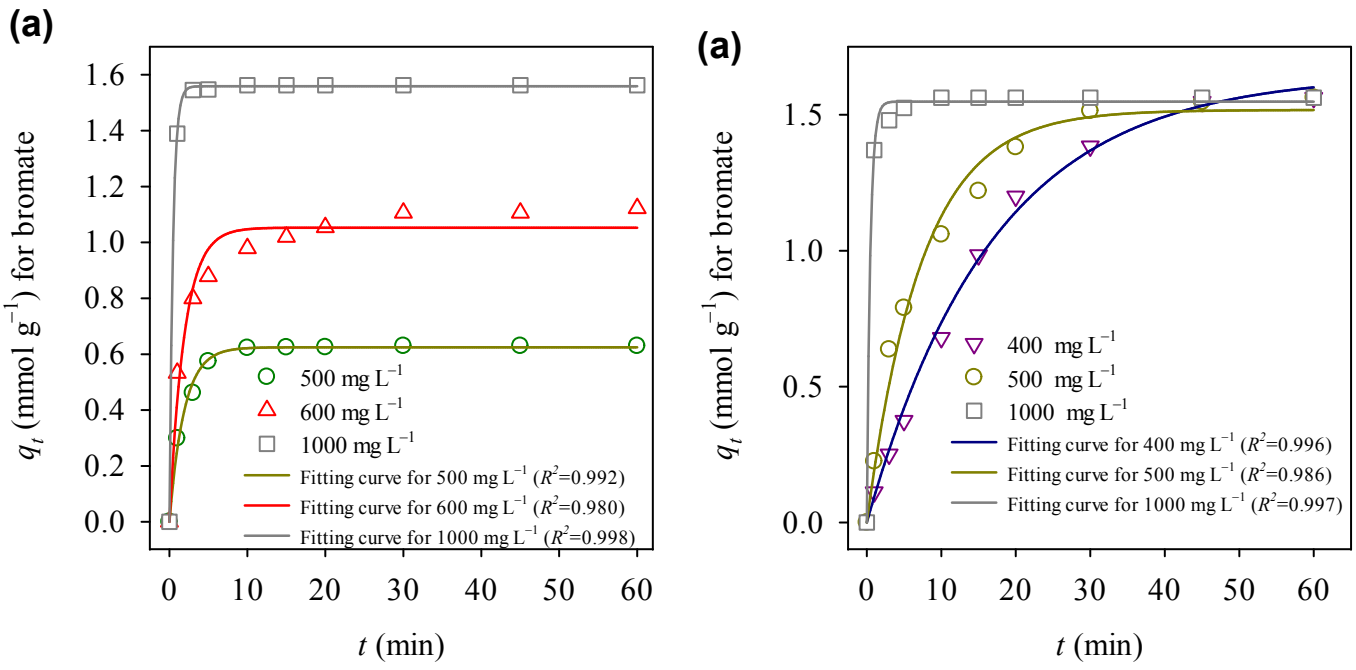

Fig. S10. Fitting results of the kinetics for investigating the effect of $NaBH_4$ dosage using (a) MIL-88A and (b) ZIF-67. The solid fitting curves are obtained using a curve-fitting function in Sigmaplot®, a scientific graphing software, to correlate q_t with t employing an "Exponential Rise to Max" ($q_t = q_e \times (1-\exp(-k_1 \times t))$ function.

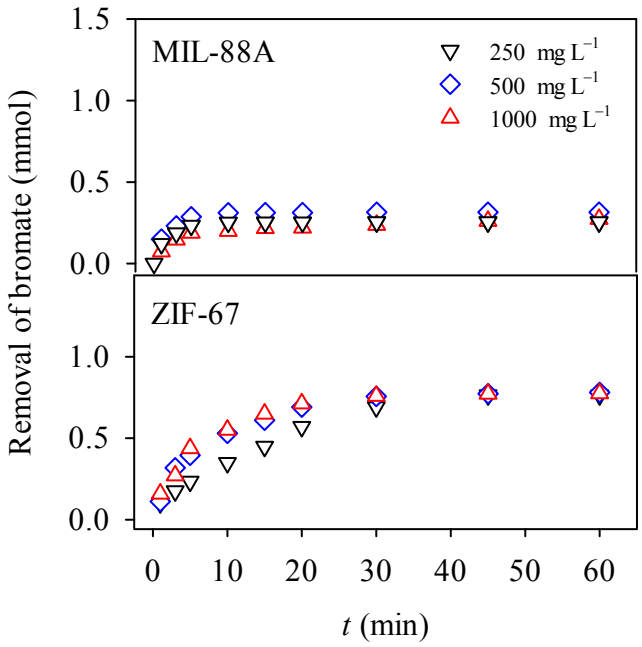

Fig. S11. Effect of MOF loading on the total amount of bromate removed using (a) MIL-88A and (b) ZIF-67.

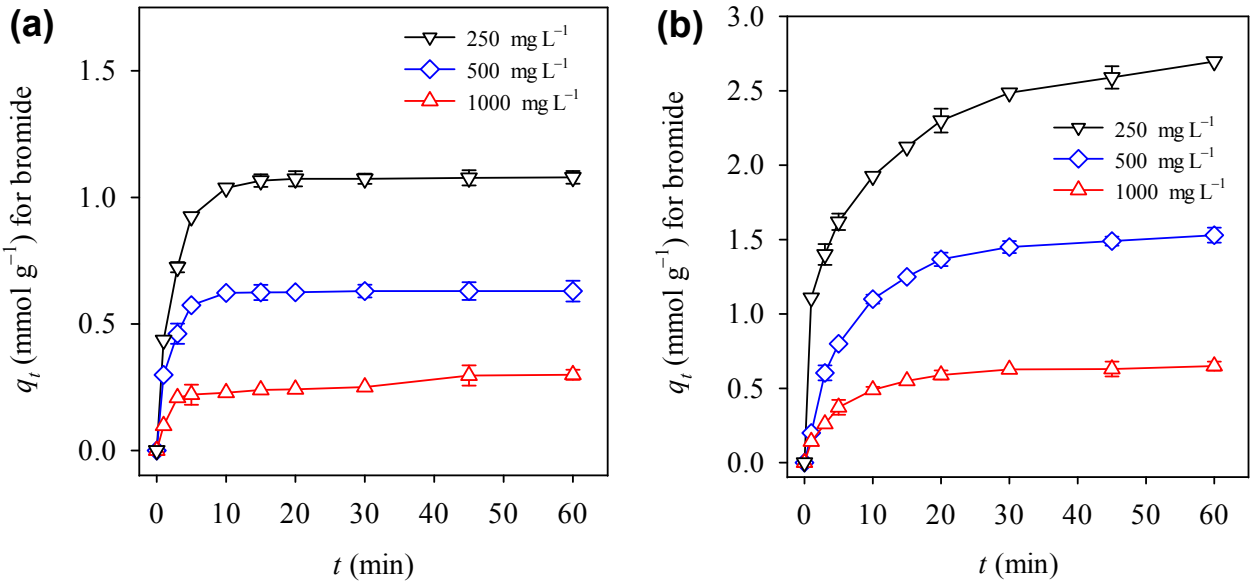

Fig. S12. Effect of MOF loading on the generation of bromide using (a) MIL-88A and (b) ZIF-67.

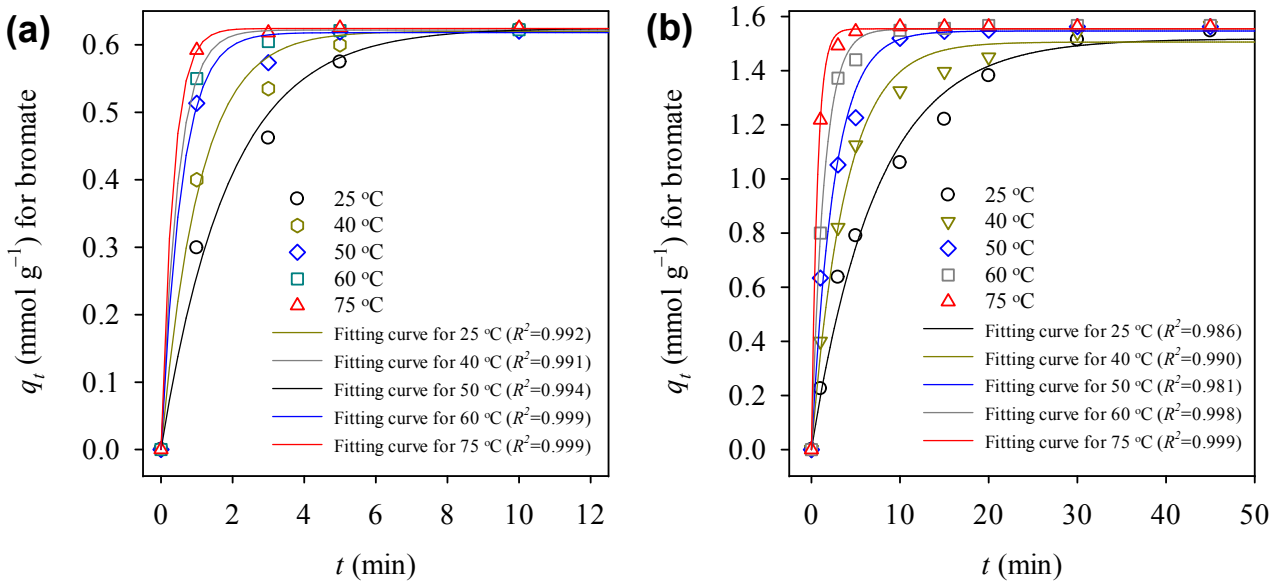

Fig. S13. Fitting results of the kinetics for investigating the effect of temperature using (a) MIL-88A and (b) ZIF-67. The solid fitting curves are obtained using a curve-fitting function in Sigmaplot®, a scientific graphing software, to correlate q_t with t employing an "Exponential Rise to Max" ($q_t = q_e \times (1-\exp(-k_1 \times t))$ function.

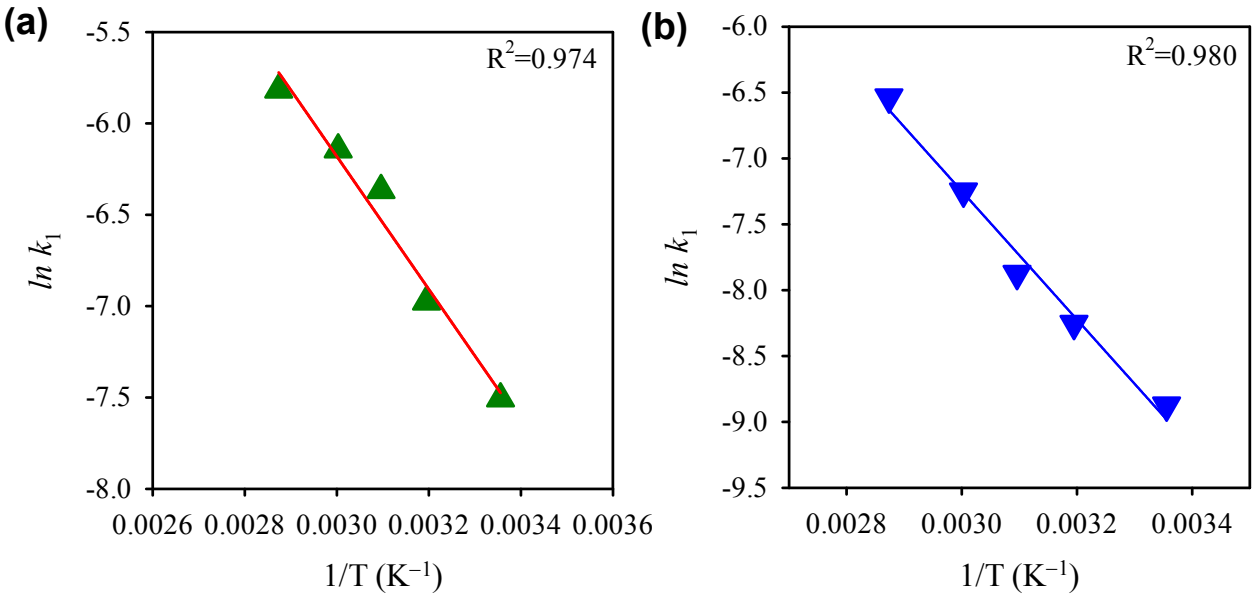

Fig. S14. Plots for determining the activation energy E_a and the temperature-independent factor k for the bromate reduction using (a) MIL-88A/$NaBH_4$ and (b) ZIF-67/$NaBH_4$.

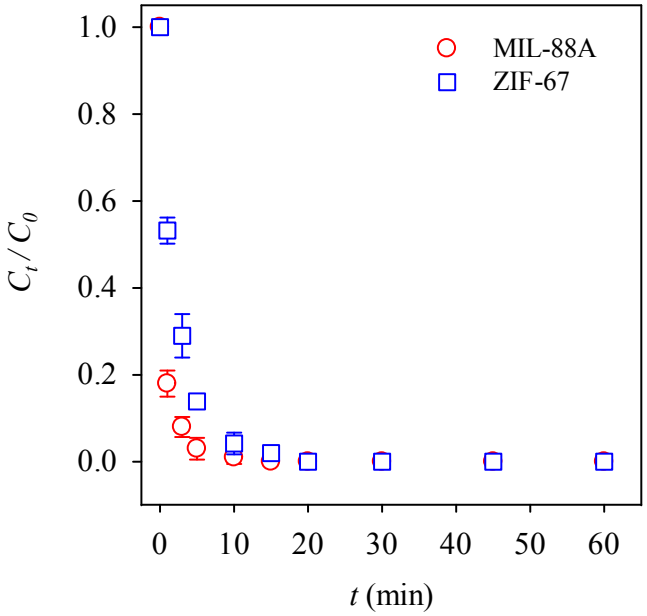

Fig. S15. Removal of low-level bromate (100 μg L^{-1}) from water using MIL-88A and ZIF-67 with $NaBH_4$.

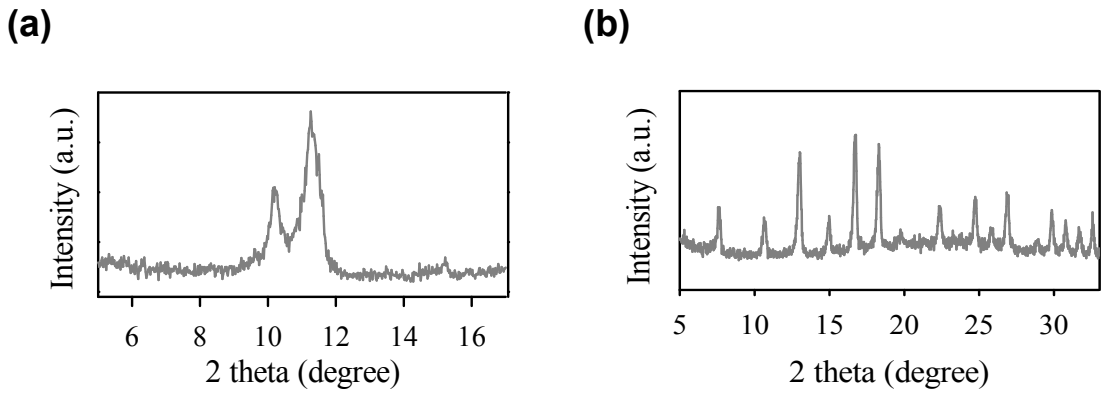

Fig. S16. XRD patterns of the spent MOFs recovered from the bromate reduction: (a) MIL-88A and (d) ZIF-67.