Supporting Information

Fabrication of magnetic trimetallic metal–organic frameworks for rapid removal of tetracycline from water

Rui Xiao [a], Hassan Idris Abdu [a], Liping Wei [a], Tieying Wang [a], Shuhui Huo [a], Jing Chen [a], Xiaoquan Lu [a,b,*]

[a] Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, China

[b] Tianjin Key Laboratory of Molecular Optoelectronics, Department of Chemistry, Tianjin University, Tianjin 300072, China

E-mail: luxq@nwnu.edu.cn; luxq@tju.edu.cn

Contents:

1. Adsorption Kinetics Study.....S-2

2. Adsorption Equilibrium Isotherms.....S-3

3. Supplementary Figures.....S-4

4. Supplementary Tables.....S-10

5. References.....S-13

1. Adsorption Kinetics Study

The removal efficiency (%) of tetracycline is calculated as follows:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 (mg/L) is the initial concentration of the tetracycline solution, C_t (mg/L) is the concentration of the tetracycline solution after adsorption.

The maximum amount adsorption was assessed using the following equation:

$$Q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (2)$$

Where Q_t (mg/g) is the maximum amount of tetracycline (mg) adsorbed by the sorbent at time t. C_0 (mg/L) is the initial concentration of the Tc solution, C_t (mg/L) is the concentration of the tetracycline solution after adsorption. V (L) is the volume of contaminant stock solution. m (g) is the mass of sorbent used in the study.

The adsorbed amount at equilibrium was expressed by the following equation:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (3)$$

Where Q_e (mg/g) is the amount of Tc (mg) adsorbed by the sorbent at equilibrium. C_0 (mg/L) is the initial concentration of the Tc solution, C_t (mg/L) is the concentration of the tetracycline solution after adsorption. V (L) is the volume of pollutant stock solution. m (g) is the mass of sorbent used in the study.

The absorption rates of the two adsorbents were compared by the pseudo-second-order adsorption model of Ho and McKay (4) and the pseudo-first-order adsorption model of Lagergren (5). The linear equation can be expressed as:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{t}{k_2 Q_e^2} \quad (4)$$

$$log(Q_e - Q_t) = log(Q_e) - \frac{k_1}{2.303} t \quad (5)$$

Where Q_t and Q_e are the adsorption capacity at time t (min) and at equilibrium, respectively. k_2 and k_1 ($g.mg^{-1}.min^{-1}$) are the rate constants of pseudo-second-order and pseudo-first-order kinetic model, respectively. The relevant parameters are listed in Table S2.

2. Adsorption Equilibrium Isotherms

The Langmuir isotherm is assumed to be monolayer adsorption and all adsorption sites are identical, which can be expressed as:

$$\frac{C_e}{C_s} = \frac{1}{C_L \times C_s, max} + \frac{C_e}{C_s, max} \tag{6}$$

The Freundlich model is considered to be a multilayer adsorption with a distribution of different active sites. Usually expressed as:

$$logC_S = logK_F + \frac{1}{n} logC_e \tag{7}$$

Where C_e (mg/L) is the concentration of Tc in the residue at the equilibrium of adsorption, C_s (mg/g) is the amount of Tc adsorbed per unit weight of adsorbent in equilibrium, $C_{s,\ max}$ (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir constant, which is related to the heat of adsorption. K_F ($mg^{1-n}\ L^n/g$) and n both represent the adsorption equilibrium constant.

3. Supplementary Figures

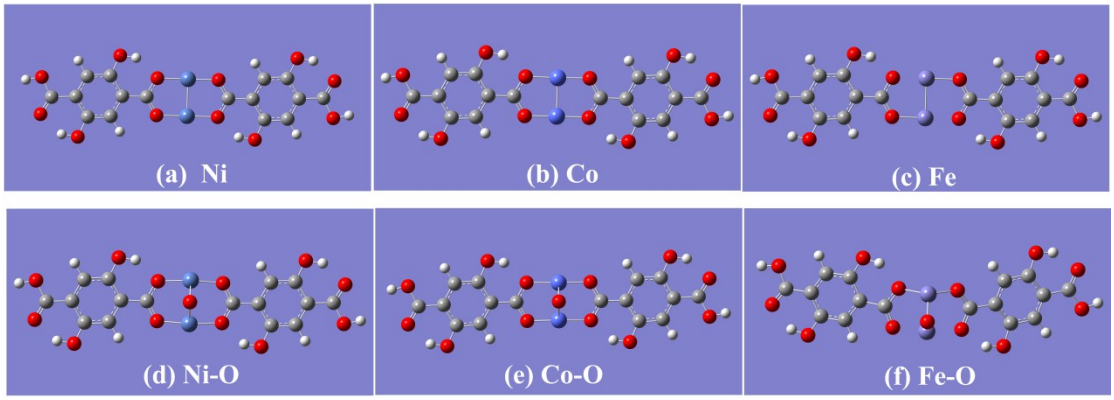

Fig. S1 The minimum energy structures obtained by B3LYP 6-31G calculations for H_4DOT-metals complexes (a, b, c). The minimum energy structures of three metals (Ni, Co, Fe) with the O atoms of organic ligands (d, e, f)

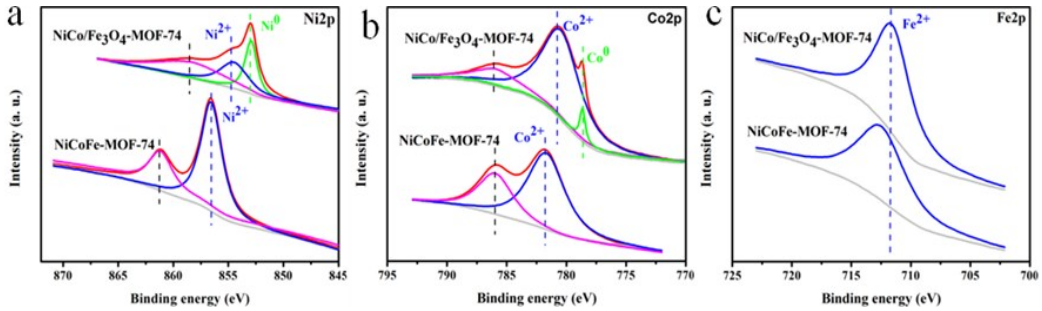

Fig. S2 Ni 2p (a), Co 2p (b), Fe 2p (c) XPS spectra of NiCoFe-MOF-74 and NiCo/Fe_3O_4-MOF-74

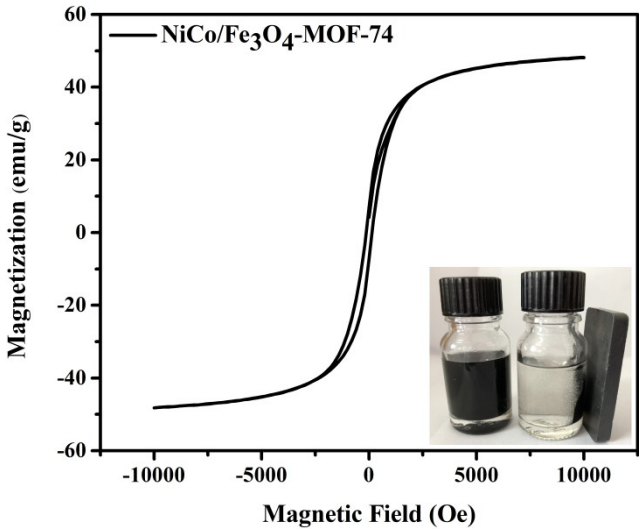

Fig. S3 Vibrating sample magnetometric (VSM) magnetization curves of NiCo/Fe_3O_4-MOF-74.

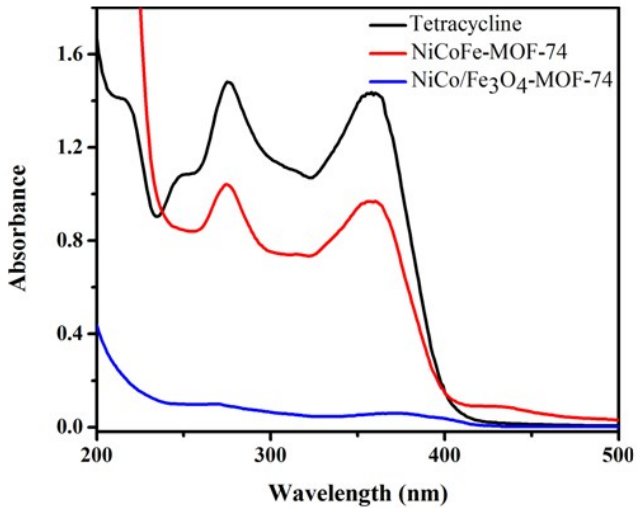

Fig. S4 Uv-vis absorbance of Tc (0.1 mM) and residual pollutant sorbed by NiCoFe-MOF-74 and NiCo/Fe_3O_4-MOF-74 at the same experimental conditions.

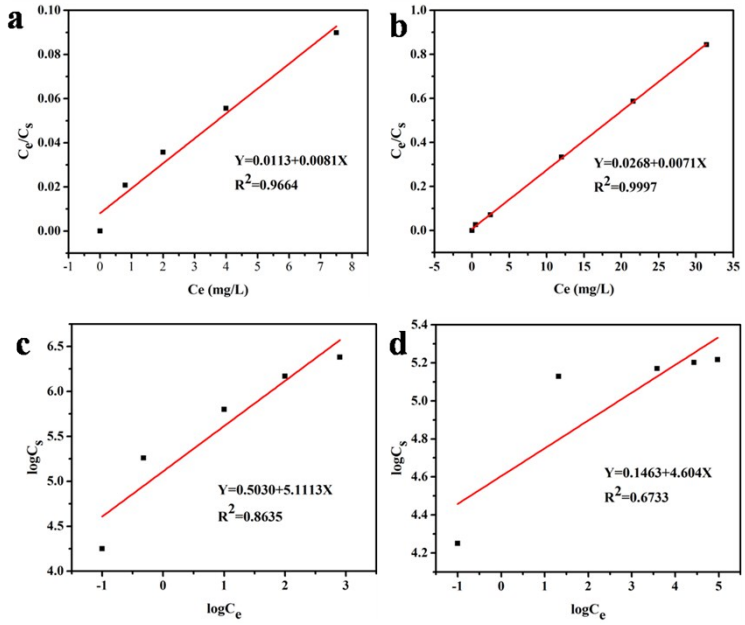

Fig. S5 Analysis of Langmuir isotherm model for the adsorption of Tc with NiCo/Fe_3O_4-MOF-74 (a) and NiCoFe-MOF-74 (b). Freundlich isotherm model for the adsorption of Tc with NiCo/Fe_3O_4-MOF-74 (c) and NiCoFe-MOF-74 (d).

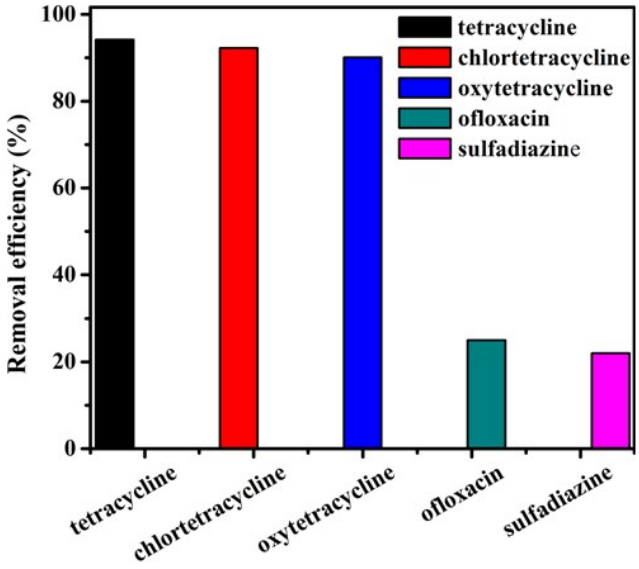

Fig. S6 The removal efficiency of NiCo/Fe_3O_4-MOF-74 to different antibiotics.

4. Supplementary Tables

Table S1 Adsorption energy of three metal atoms with oxygen atom

Metal atoms	Pre-adsorption energy (a.u.)	Post-adsorption energy (a.u.)	Adsorption energy (a.u.)	Adsorption energy (eV)
Ni	−1857.18	−1932.35	−0.21	−5.78
Co	−1808.62	−1883.87	−0.29	−7.81
Fe	−1765.29	−1840.56	−0.31	−8.42

Oxygen atom energy: −74.96 (a.u.)

Table S2 Adsorption Kinetics parameters for Tc

Adsorbents	pseudo-first-order			pseudo-second-order		
	$Q_{1,cal}$ ($mg.g^{-1}$)	k_1 ($g.mg^{-1}.min^{-1}$)	R^2	$Q_{2,cal}$ ($mg.g^{-1}$)	k_2 ($g.mg^{-1}.min^{-1}$)	R^2
NiCoFe-MOF-74	39.14	0.224	0.5673	33.27	0.317	0.9938
NiCo/Fe_3O_4-MOF-74	91.66	0.486	0.8648	85.47	0.024	0.9994

Table S3 Adsorption isotherms parameters for Tc

Adsorbents	Langmuir			Freundlich		
	$C_{s,\,max}$ (mg/g)	K_L (L/mg)	R^2	n	K_F ($mg^{1-n}L^n/g$)	R^2
NiCoFe-MOF-74	44.35	1.503	0.9997	2.6364	24.74	0.6733
NiCo/Fe_3O_4-MOF-74	102.94	0.5714	0.9664	1.5625	23.00	0.8635

5. References

(1) Ho, Y.; McKay, G. Pseudo-second Order Model for Sorption Processes. *Process biochem.* **1999**, 34, 451−465.

(2) Lagergren, S. About the Theory of so-called Adsorption of Soluble Substances. *Handl*. **1898**, 24, 1–39.

(3) Saunders, D. L.; Pecsok, R. L. Calculation of Distribution Coefficients in Inorganic Gel Chromatography. *Anal. Chem.* **1968**, 40, 44−48.

(4) Umpleby, R. J.; Baxter, S. C.;, Chen, Y.; Shah, R. N.; Shimizu, K. D. Characterization of Molecularly Imprinted Polymers with the Langmuir−Freundlich Isotherm. *Anal. Chem.* **2001**, 73, 4584−4591.

(5) Liu, Q.; Zhong, L. B.; Zhao, Q. B.; Frear, C.; Zheng, Y. M. Synthesis of Fe_3O_4/Polyacrylonitrile Composite Electrospun Nanofiber Mat for Effective Adsorption of Tetracycline. *ACS Appl. Mater. Interfaces* **2015**, 7, 14573−14583.

(6) Dong, H. R.; Jiang, Z.; Zhang, C.; Deng, J. M.; Hou, K. J.; Cheng, Y. J.; Lihua Zhang, L. H.; Zeng, G. M. Removal of Tetracycline by Fe/Ni Bimetallic Nanoparticles in Aqueous Solution. *J Colloid. Interface Sci.* **2018**, 513, 117−125.