

**Recovery of syringic acid from aqueous solution by magnetic Fe-Zn/ZIF and its
slow-release from CA-coating carrier based on a 3Rs concept**

Huifang Zhao^a, Ting Wang^a, Dahuan Liu^{ab,}, Qing-yuan Yang^{a,*}*

^aState Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical
Technology, North Third Ring Road 15, Chaoyang District, Beijing 100029, P. R. China

^bCollege of Chemical Engineering, Qinghai University, Xining 810016, P. R. China

**E-mails: Dahuan_Liu@outlook.com (D.L.); qyyang@mail.buct.edu.cn.*

Section S1 Preparation of Materials

Fe-Zn/ZIF. According to the previous work,¹ Fe-Zn/ZIF was synthesized *via* a one-step method. Firstly, solutions A (0.6 g Zn(OAc)₂·4H₂O in 5 mL H₂O) and B (0.6 g FeSO₄·7H₂O in 5 mL H₂O) were thoroughly mixed. Then, 5 mL of the mixture of A and B was added to MeIM solution (2.24 g in 5 mL H₂O) drop by drop. After reaction for 12 h, the Yellowish brown solid was collected using magnetism. The resulting product was washed with DI water and methanol several times. At last, the solid was dried at 353 K for 12 h.

Section S2 Characterization of Materials

The sample powder X-ray diffraction (PXRD) patterns were recorded on a D8 Advance X diffractometer using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Nitrogen adsorption-desorption isotherms measurement at 77 K was performed on an Autosorb-iQ-MP surface area analyzer. The morphology of the MOFs was characterized using a Hitachi SU8010 field emission scanning electron microscope (SEM). Magnetic properties of the ZIF and Fe-Zn/ZIF were measured with a physical property measurement system (PPMS). Infrared spectra of the samples were recorded on a Nicolet iS50 FT-IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) data were obtained on an Axis Supra X-ray photoelectron spectroscope, and Al K α X-ray was selected as the excitation source. The drug concentration in the liquid solution was determined by measuring the absorbance at a wavelength of 265.5 nm using a UV-Visible spectrophotometer (TU-1901).

Section S3 SA Loading

40 mg of MOF samples were soaked in 10 mL SA-containing solution with a concentration of 1000 ppm for 12 h at 298 K constant temperature shaker (pH = 7.0). After an adsorption process, the clear filtrate was collected *via* a PES microfiltration membrane with a pore size of 0.22 μm and further

used to measure the concentration of the adsorbate *via* a UV–Vis spectrometer (TU-1901, Persee). The collected solid sample was named SA-Fe-Zn/ZIF. The drug loading capacity (Q , $\text{mg}\cdot\text{g}^{-1}$) was calculated from the following equation:²

$$Q = \frac{(C_0 - C_f)V}{m} \quad (1)$$

where C_0 and C_f are initial and final concentrations ($\text{mg}\cdot\text{g}^{-1}$) of SA in the solution, V is the volume (L) of the solution, and m is the mass (g) of the dried drug carrier.

Section S4 Release of SA

5 mg of SA-MOF was exposed to 45 mL of PBS (pH = 5.8, 7.4) solutions, respectively. And the release system was maintained at 37 °C in a shaker with a rotation speed of 150 rpm. Then, at specified time intervals, a 4 mL mixture was withdrawn and filtrated, and clear filtration solution was collected and the concentration was quantitatively analyzed by UV–vis spectroscopy. Total amounts of the drug released (F_t) were calculated as follows:²

$$F_t = V_m C_t + \sum_{i=0}^{t-1} V_a C_i \quad (2)$$

$$\text{Cumulative release\%} = \frac{F_t}{m_{SA}} \quad (3)$$

where V_m and C_t are the volume and concentration of the drug at time t , V_a is the volume of the sample withdrawn and C_i is the drug concentration at the time i ($i < t$), m_{SA} is the mass of SA loaded in adsorbents.

Section S5 Adsorption kinetics

pseudo-first-order model:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (4)$$

pseudo-second-order model:

$$Q_t = \frac{Q_e k_2 t}{Q_e + k_2 t} \quad (5)$$

where Q_t ($\text{mg} \cdot \text{g}^{-1}$) is the adsorption amount at time t (min), k_1 (min^{-1}) and k_2 ($\text{g} \cdot \text{min}^{-1} \cdot \text{mg}^{-1}$) are pseudo-first-order models and pseudo-second-order model rate constants, respectively.

Section S6 Adsorption isotherms models

Langmuir isotherm model:

$$Q_e = \frac{Q_m C_e}{\frac{1}{b} + C_e} \quad (6)$$

Freundlich isotherm model:

$$Q_e = KC_e^{1/n} \quad (7)$$

where b ($\text{mg} \cdot \text{g}^{-1}$) and K are Langmuir and Freundlich adsorption constants, respectively; Q_m is the theoretical equilibrium adsorption capacity for the Langmuir model; n is referred to the temperature-related constant of the adsorption system.

Table S1 Source and purity of all chemicals used in the experiment.

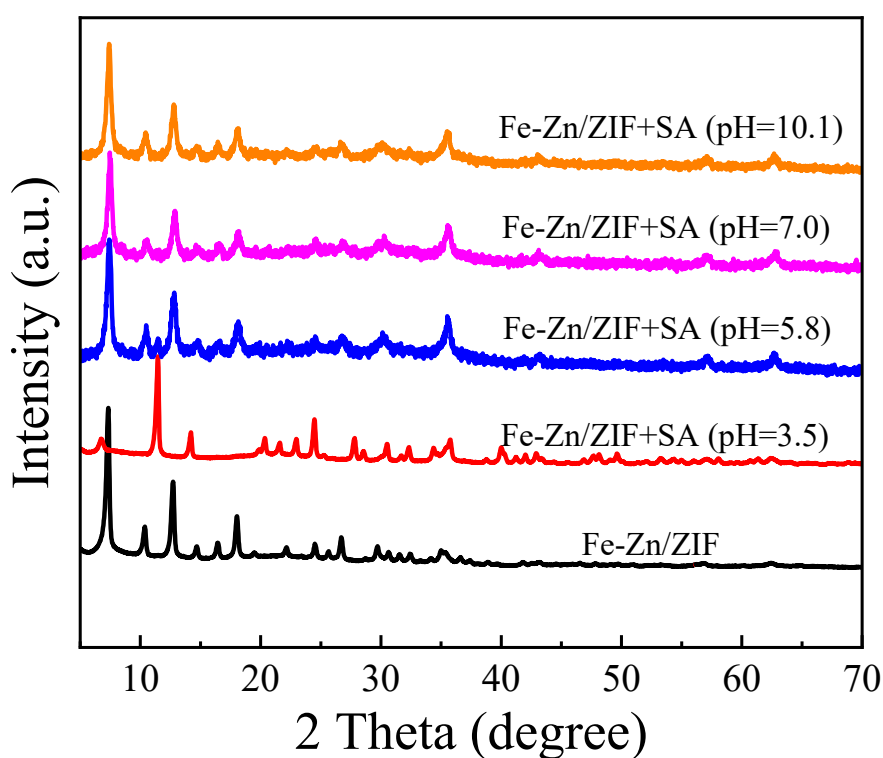
Chemicals	Source	Purity
Zn(CH ₃ CO ₂) ₂ ·2H ₂ O	Shanghai Macklin Biochemical Co., Ltd.	97 %
FeSO ₄ ·7H ₂ O	Shanghai Macklin Biochemical Co., Ltd.	98 %
MeIM	Shanghai Macklin Biochemical Co., Ltd.	98 %
SA	Shanghai Macklin Biochemical Co., Ltd.	99.5 %

Table S2 Kinetics models parameters of SA adsorbed on the Fe-Zn/ZIF.

C_0 ($\text{mg}\cdot\text{L}^{-1}$)	$Q_{e,exp}$ ($\text{mg}\cdot\text{g}^{-1}$)	Pseudo-first-order model			Pseudo-second-order model		
		$Q_{e,Cal}$ ($\text{mg}\cdot\text{g}^{-1}$)	k_1 (min^{-1})	R^2	$Q_{e,Cal}$ ($\text{mg}\cdot\text{g}^{-1}$)	k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	R^2
976.4	450.6	434.3	0.0166	0.9410	482.3	11.5864	0.9712

Table S3 Parameters in Langmuir and Freundlich models of SA adsorbed on the MOFs.

Materials	Q_m ($\text{mg}\cdot\text{g}^{-1}$)	Langmuir parameters			Freundlich parameters		
		Q_m ($\text{mg}\cdot\text{g}^{-1}$)	b ($\text{L}\cdot\text{g}^{-1}$)	R^2	K ($\text{mg}^{1-1/n}\cdot\text{g}^{-(1-1/n)}$)	n	R^2
Fe-Zn/ZIF	450.6	466.6	0.02561	0.9594	115.3478	4.6003	0.9330

**Fig. S1** The PXRD patterns of Fe-Zn/ZIF after soaking in SA solutions at different pH values.

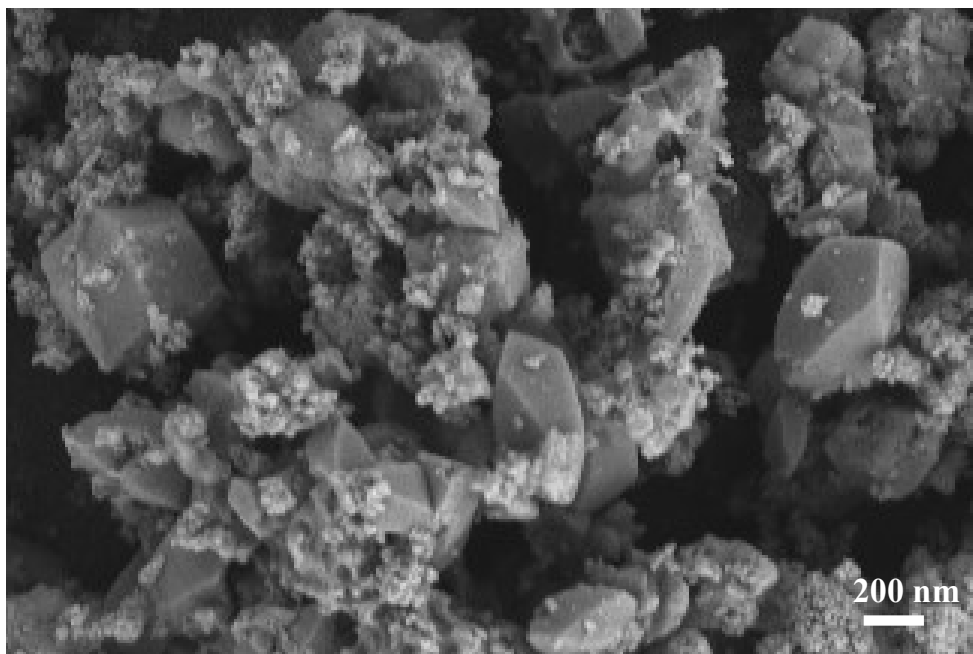


Fig. S2 SEM image of SA-Fe-Zn/ZIF.

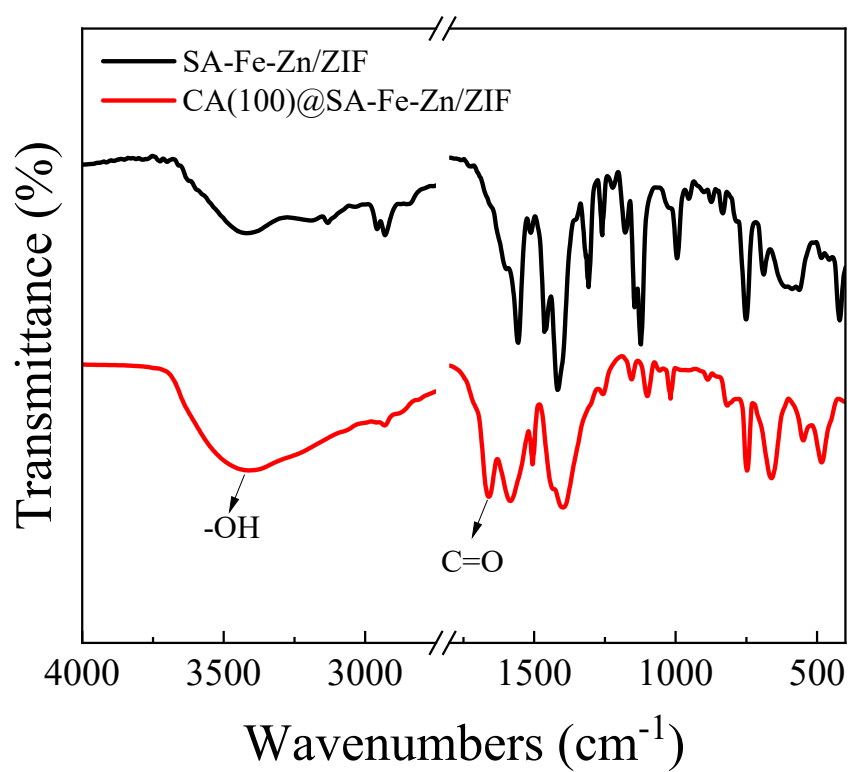


Fig. S3 The FT-IR spectra of SA-Fe-Zn/ZIF and CA(100)@SA-Fe-Zn/ZIF.

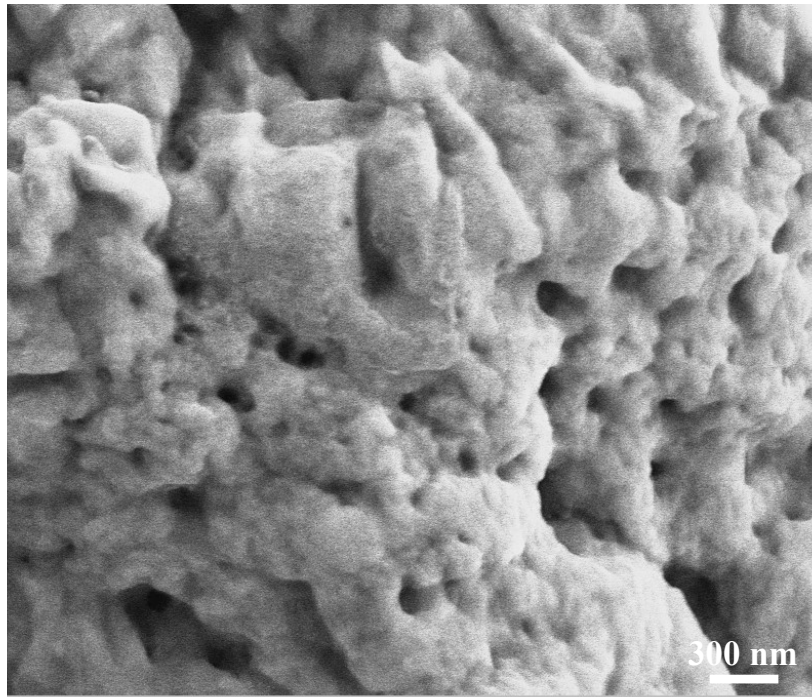


Fig. S4 SEM image of CA(100)@SA-Fe-Zn/ZIF.

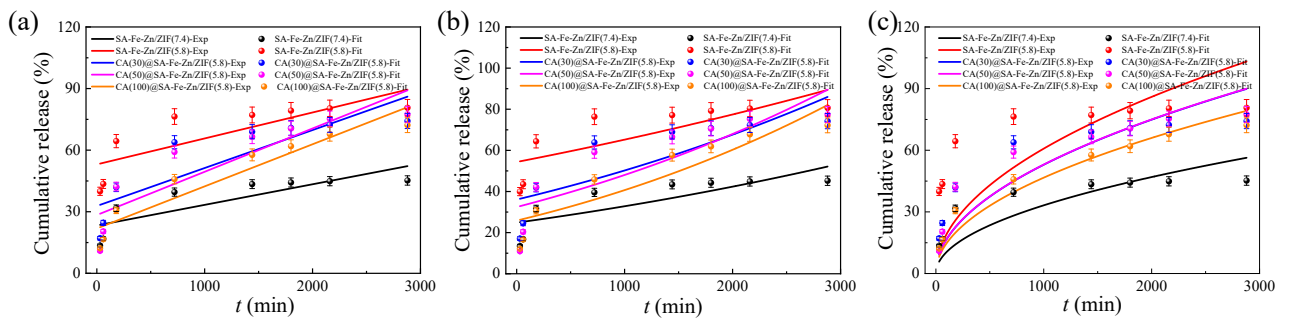


Fig. S5 (a) Zero-order, (b) Hixson-Crowell, (c) Higuchi kinetic models fitting of data of release curves.

Table S4 Release kinetic parameters for the data of release curves.

Kinetic model	Equations	Sample	pH	a	b	c	R^2
First-order	$y=a+b\exp(-x/c)$	SA-Fe-Zn/ZIF	7.4	43.7212	-36.288	177.3302	0.9840
		SA-Fe-Zn/ZIF	5.8	78.94325	-48.557	159.7291	0.9901
		CA(30)@SA-Fe-Zn/ZIF	5.8	71.32489	-58.485	288.0121	0.9928
		CA(50)@SA-Fe-Zn/ZIF	5.8	71.75963	-63.332	306.2497	0.9658
		CA(100)@SA-Fe-Zn/ZIF	5.8	72.97901	-58.831	947.50356	0.9813
Second-degree polynomial	$y=a+bx+cx^2$	SA-Fe-Zn/ZIF	7.4	18.70482	0.0272	-6.517×10^{-6}	0.8685
		SA-Fe-Zn/ZIF	5.8	47.04435	0.0351	-8.522×10^{-6}	0.8323
		CA(30)@SA-Fe-Zn/ZIF	5.8	24.88506	0.0481	-1.121×10^{-6}	0.9118
		CA(50)@SA-Fe-Zn/ZIF	5.8	20.96713	0.0489	-1.052×10^{-5}	0.9080
		CA(100)@SA-Fe-Zn/ZIF	5.8	16.65511	0.0400	-7.364×10^{-6}	0.9691
Korsmeyer–Peppas	$y=ax^b$	SA-Fe-Zn/ZIF	7.4	8.2539	0.2230		0.9230
		SA-Fe-Zn/ZIF	5.8	27.0176	0.1439		0.9041
		CA(30)@SA-Fe-Zn/ZIF	5.8	9.63206	0.2653		0.9492
		CA(50)@SA-Fe-Zn/ZIF	5.8	6.89353	0.3106		0.9541
		CA(100)@SA-Fe-Zn/ZIF	5.8	4.35537	0.3551		0.9937
Zero-order	$y=a+bx$	SA-Fe-Zn-ZIF	7.4	23.2974	0.01004		0.63896
		SA-Fe-Zn-ZIF	5.8	53.0499	0.01265		0.65053
		CA(30)@SA-Fe-Zn-ZIF	5.8	32.7839	0.01850		0.74369
		CA(50)@SA-Fe-Zn-ZIF	5.8	28.3771	0.02109		0.78749
		CA(100)@SA-Fe-Zn-ZIF	5.8	21.8443	0.02052		0.89784
Hixson-Crowell	$y=(a+bx)^3$	SA-Fe-Zn-ZIF	7.4	2.9182	2.8383×10^{-4}		0.63896
		SA-Fe-Zn-ZIF	5.8	3.78785	2.3739×10^{-4}		0.61799
		CA(30)@SA-Fe-Zn-ZIF	5.8	3.30418	3.8533×10^{-4}		0.68294
		CA(50)@SA-Fe-Zn-ZIF	5.8	3.18931	4.4585×10^{-4}		0.72363
		CA(100)@SA-Fe-Zn-ZIF	5.8	2.95683	4.8216×10^{-4}		0.83427
Higuchi	$y=ax^{1/2}$	SA-Fe-Zn-ZIF	7.4	1.04979			0.38315
		SA-Fe-Zn-ZIF	5.8	1.92255			-1.2126
		CA(30)@SA-Fe-Zn-ZIF	5.8	1.6748			0.66715
		CA(50)@SA-Fe-Zn-ZIF	5.8	1.67694			0.82039
		CA(100)@SA-Fe-Zn-ZIF	5.8	1.47562			0.93307

Reference

- 1 H. Zhao, Y. Zhao, X. Zhao and D. Liu, *ACS Appl. Bio Mater.*, 2019, **64**, 18, 51-1858.
- 2 H. Zhao, Y. Zhao, X. Zhao and D. Liu, *J. Mol. Struc.*, 2022, **1263**, 133121.