Electronic Supplementary Information

Solid phase extraction based on magnetic carbon nitride/metal organic framework composite with high performance liquid chromatography for determination of tyrosine kinase inhibitors in urine samples

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S1 Material performance studies of MCN/BIF-20

The effect of solution pH

Britton-Robinson buffer (BR Buffer) was prepared by following process: 0.245 mL H_3PO_4, 0.230 mL HAC and 0.247 g H_3BO_3 was added into 100 mL volumetric flask, then distilled water was added to the tick mark. By adding different volumes of NaOH solution (0.2 mol L^{-1}) to the mixture, different pH BR buffer were acquired. 2mg MCN/BIF-20 was added to each 2 mL solution of imatinib, gefitinib or erlotinib (100 μg mL^{-1}) and 0.2 mL BR buffer with different pH (2, 4, 6, 7, 8, 10, 12). The solution was shaken at room temperature for 120 min with gas bath oscillator. After magnetically separated, the supernatant was filtered through 0.22 m membrane and tested by HPLC-DAD to detect drugs.

The adsorption kinetics

To evaluate the rate of adsorption of MCN/BIF-20, 2 mg MCN/BIF-20 was mixed with 2 mL of TKIs drugs solution at a concentration of 100 μg mL^{-1} and 0.2 mL BR buffer (pH=4). After shaking with different time (5min, 10 min, 15min, 20 min, 30 min, 40 min, 50 min, 60 min), the drugs in the supernatant were separated by a magnet and then detected by HPLC-DAD.

The adsorption isotherm

To evaluate the adsorption capacity of MCN/BIF-20, 2 mg MCN/BIF-20 was added to the 2 mL TKIs drugs solution (pH=4) in different initial concentration (100 μg mL^{-1} 200 μg mL^{-1} , 300 μg mL^{-1} , 400 μg mL^{-1} , 500 μg mL^{-1} , 600 μg mL^{-1} , 700 μg mL^{-1} , 800 μg mL^{-1}) and 0.2 mL BR buffer (pH=4). According to the results of adsorption kinetics experiment, 40 min was selected to adsorption time. After shaking with 40 min, the drugs in the supernatant were separated by a magnet and then detected by HPLC-DAD.

Comparison of single materials

To evaluate the adsorption properties of complex material and single materials including g-C_3N_4, MCN, BIF-20, gefitinib was chosen to model drug. And the

experiment process of pH, adsorption kinetics and adsorption isotherm of single materials was obtained by experiment as well as MCN/BIF-20.

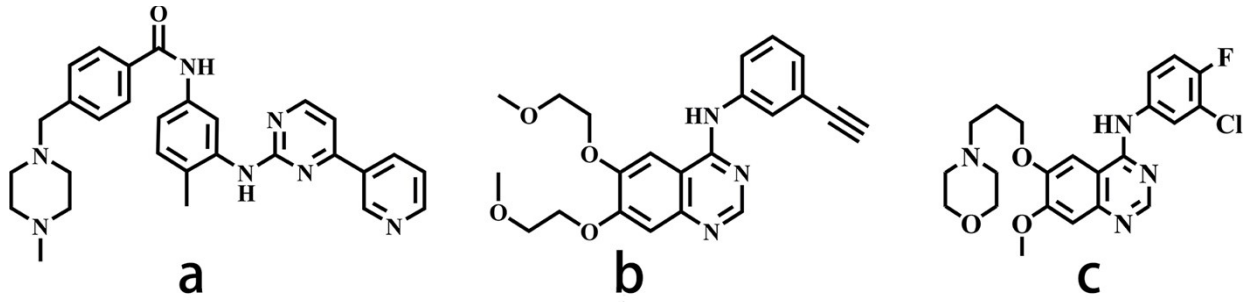

Fig.S1 The molecular structures of imatinib(**a**), erlotinib(**b**) and gefitinib(**c**)

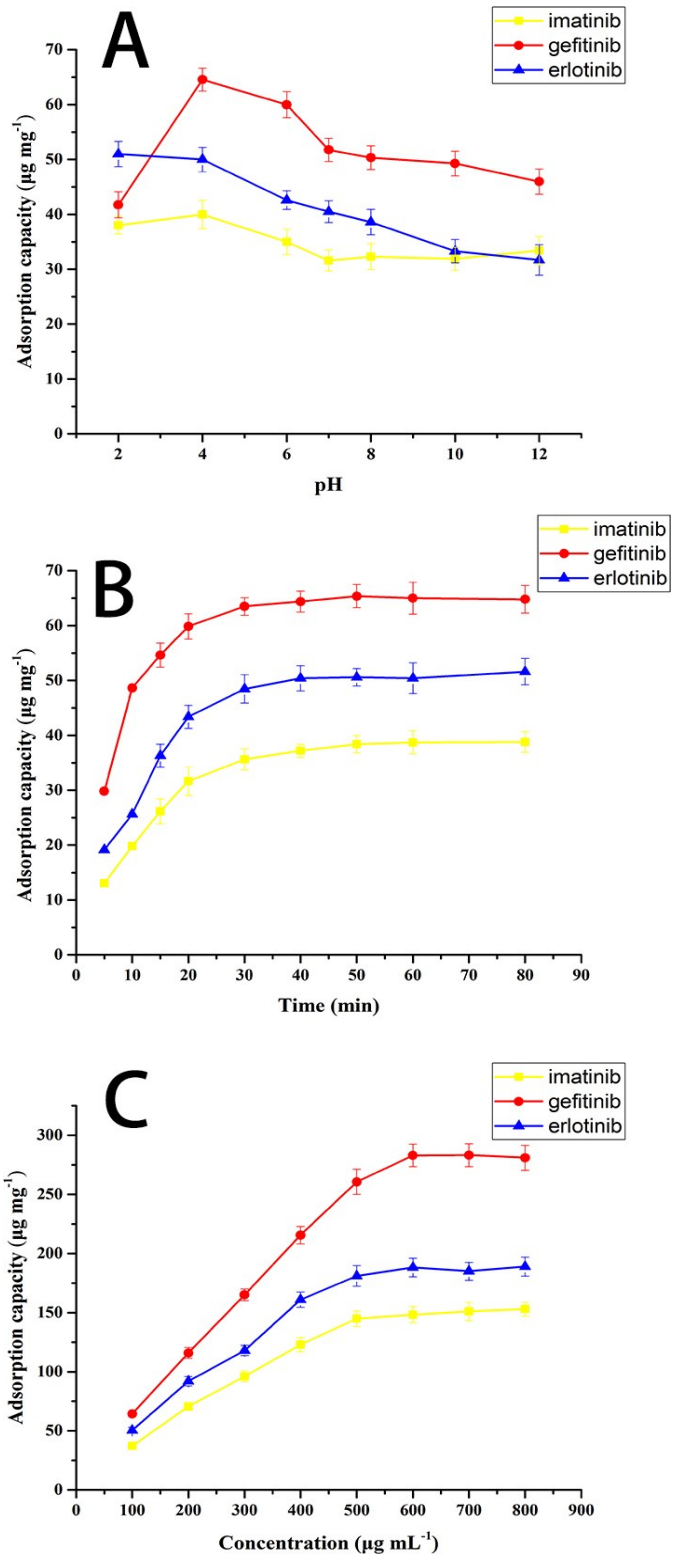

Fig. S2. Material science performance studies of MCN/BIF-20. The effect of pH (**A**) , adsorption kinetics curves of TKIs (**B**) and adsorption isotherm curves of TKIs (**C**).

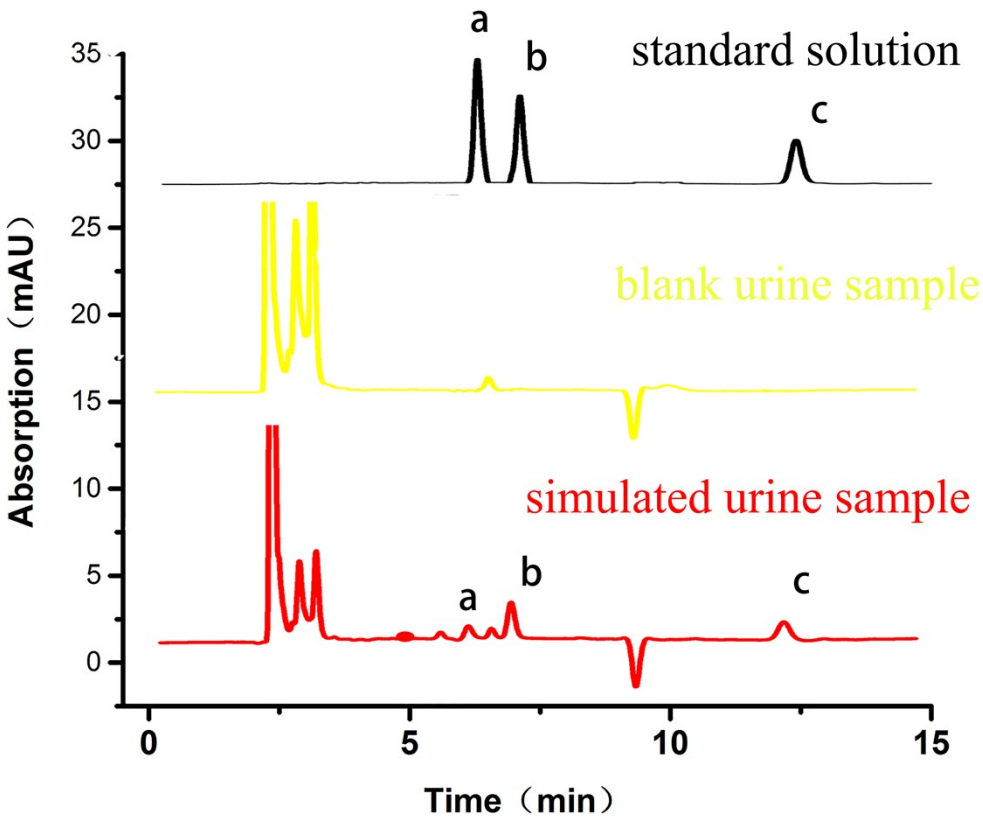

Fig.S3 the HPLC chromatogram of imatinib(**a**), erlotinib(**b**) and gefitinib(**c**) in the standard solution, blank urine sample and simulated urine sample.

Table S1 Constants of adsorption kinetic models for adsorption of TKIs on MCN/BIF-20.

		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	$Q_{e,exp}$ (mg g^{-1})	$Q_{e,cal}$ (mg g^{-1})	K_1 (min^{-1})	R^2	$Q_{e,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2
imatinib	37.20	42.89	0.0898	0.9966	52.36	0.0013	0.9904
gefitinib	64.37	62.71	0.1244	0.9971	80.65	0.0017	0.9929
erlotinib	50.40	56.93	0.0904	0.9936	69.93	0.0010	0.9808

Table S2 Constants of adsorption isotherm model parameters for adsorption of TKIs on MCN/BIF-20.

		Freundlich model			Langmuir model		
	$Q_{e,exp}$ (mg g^{-1})	1/n	K_f (mg g^{-1})	R^2	$Q_{e,cal}$ (mg g^{-1})	K_l (g mg^{-1})	R^2
imatinib	148.33	0.783	1.4952	0.9969	384.62	0.0017	0.9866
gefitinib	283.25	0.710	5.1725	0.9941	555.56	0.0034	0.9567
erlotinib	188.17	0.691	3.4586	0.9898	357.14	0.0032	0.9249

Table S3 The experimental results of adsorption studies of gefitinib on g-C_3N_4, MCN, BIF-20 and MCN/BIF-20.

Materials	pH	Adsorption equilibrium time (min)	Adsorption capacity (mg g^{-1})
g-C_3N_4	4	40	50.63
MCN	4	40	55.29
BIF-20	4	50	179.46
MCN/BIF-20	4	40	283.25