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Batch and fixed bed column adsorption of tetrabromobisphenol A onto metal organic resin: Equilibrium, kinetic and mechanism studies

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The approximate loading amount of metal ion and MOF on the resin

We determined the approximate loading of metal ion on the resin during the production of Cu^{2+}, Zn^{2+} or Cr^{3+} exchanged form. Briefly, the wet resins in Na-form were added into 10% $CuCl_2$, $ZnCl_2$ or $CrCl_3$ solution to produce Cu^{2+}, Zn^{2+} or Cr^{3+} exchanged form. The resin of exchanged form was rinsed using 0.5 M HCl and the loading metal ion was rinsed into the solution. Then, the concentration of Cu^{2+}, Zn^{2+} or Cr^{3+} in eluate can be determined by a simple method- spectrophotometric method. In our preparation, approximately 29 mg/g of Cu, 29 mg/g of Zn and 24 mg/g of Cr was loaded onto the cation resin. These loading mass can serve as reference only.

According to the previous report, the total weight loss of Cu-MOF was about 43% between 25 and 700 ^{o}C [1]. From the TG analysis of Cu-MOR and cation resin, the loading amount of MOF on resin was estimated to be 31%.

Table S1 Properties of cation exchange resin

Name	cation exchange resin
Colour	light camel
Particle size range	0.315-1.250 mm
Effective grain size	0.4-0.6 mm
Basic group	styrenedivinyl benzene
Functional group	sulfonic acid group

Table S2. The main FT-IR bands for cation resin and MORs

Resin	-OH	(-S(O)$_2$-O-)	C=C aromatic ring	-CH aromatic and ring bend	Na-O
wavenumber(cm^{-1})	3430	1386/ 1098	1592	751/693	541
Cu-MOR	-OH	C=C-CO	-C-O-		Cu-O
wavenumber (cm^{-1})	3430	1633	1172		<600
Zn-MOR	-OH	imidazole ring	Zn-N		
wavenumber (cm^{-1})	3430	1098	413		
Cr-MOR	-OH	C=O	C=C	-C-O-	Cr-O
wavenumber (cm^{-1})	3430	1658	1551	1172	420

Table S3. Intra-particle diffusion constants for the binding of TBBPA by three MORs

Parameter	Cu-MOR	Cr-MOR	Zn-MOR
K_{d1}(g mg^{-1} h$^{-0.5}$)	0.86	0.75	0.36
C_1(mg g^{-1})			
r^2	0.98	0.97	0.97
K_{d2} (g mg^{-1} h$^{-0.5}$)	0.11	0.34	0.15
C_2 (mg g^{-1})			
r^2	0.99	0.99	0.94

Table S4. Calculated parameters for three isotherm models during equilibrium tests

Models	Cu-MOR	Cr-MOR	Zn-MOR	GAC	Cation resin
Langmuir					
Q_m(mg g^{-1})	24.65	26.58	14.22	8.78	2.27
b (L g^{-1})	0.09	0.05	0.02	0.03	0.02
r^2	0.99	0.96	0.98	0.98	0.99
Freundlich					
K_F (mg g^{-1})	3.95	2.79	0.78	0.82	0.09
n (g L^{-1})	2.39	2.08	1.74	1.98	1.50
1/n	0.41	0.48	0.57	0.51	0.67
r^2	0.98	0.96	0.97	0.92	0.98
Temkin					
b_T (J mol K^{-1})	509.02	534.69	911.83	1267.28	5482.74
A_T (L g^{-1})	1.35	1.03	0.37	0.40	0.25
$B=RT/b_T$ (J mol^{-1})	4.79	4.56	2.67	1.92	0.44
r^2	0.99	0.92	0.95	0.97	0.98

Table S5. Composition of synthetical water and Nanhu Lake water

Parameters	Synthetical water	Nanhu Lake water
pH	6.2	6.9
DOM (mg C L^{-1})	------	8.8
SS (mg L^{-1})	-----	30
Na^+ (mg L^{-1})	33	33
K^+ (mg L^{-1})	3.8	3.8
Mg^{2+} (mg L^{-1})	16	16.1
Ca^{2+} (mg L^{-1})	76	76.2
Cl^- (mg L^{-1})	102	48
SO_4^{2-} (mg L^{-1})	64	110

Table S6. Calculated parameters for Thomas model during dynamic adsorption

Thomas model	Synthetical water	Nanhu Lake water
q_e (mg g^{-1})	1.48	0.80
k_T (mL min^{-1} mg^{-1})	0.53	1.01
r^2	0.96	0.98

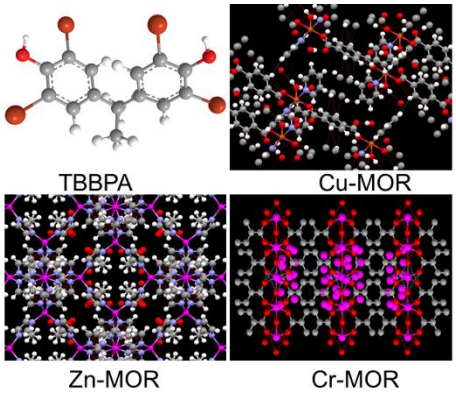

Fig. S1 Chemical structure of (a) TBBPA; (b) Cu-MOR; (c) Zn-MOR; (d) Cr-MOR.

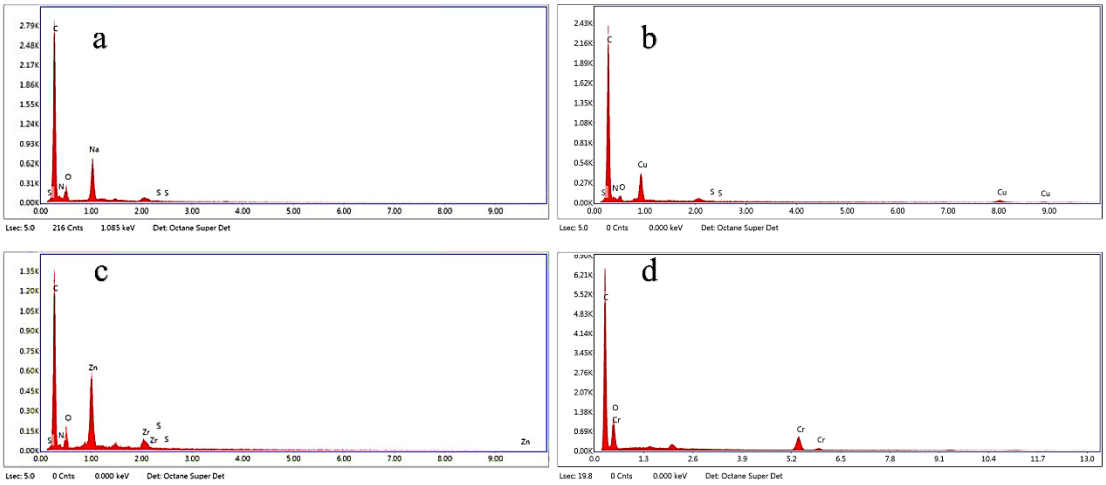

Fig. S2 EDS elemental analysis of the surface of the metal organic resins: (a) resin; (b) Cu-MOR; (c) Zn-MOR; (d) Cr-MOR.

Note: in Fig. S1c, the peak of Zr may be caused by the metal spraying process

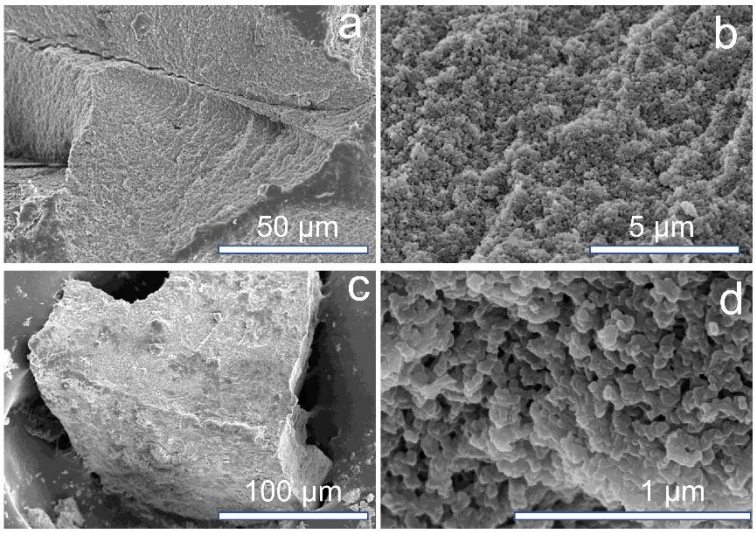

Fig. S3 Cross-section part of resin (a, ×1000; b, ×10000) and Cross-section part of Cu-MOR (c, ×500; d, ×50000)

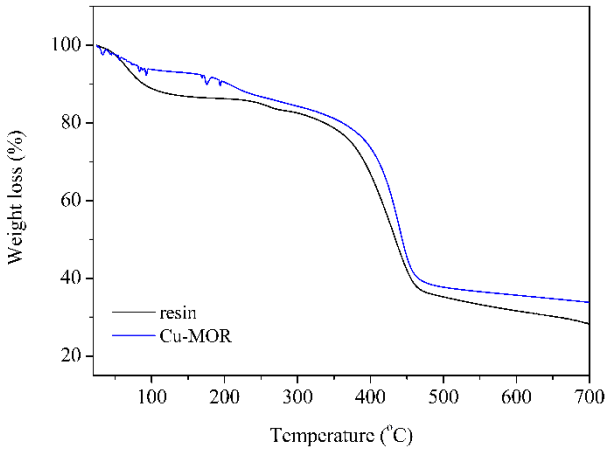

Fig. S4 TG analysis for resin and MOR

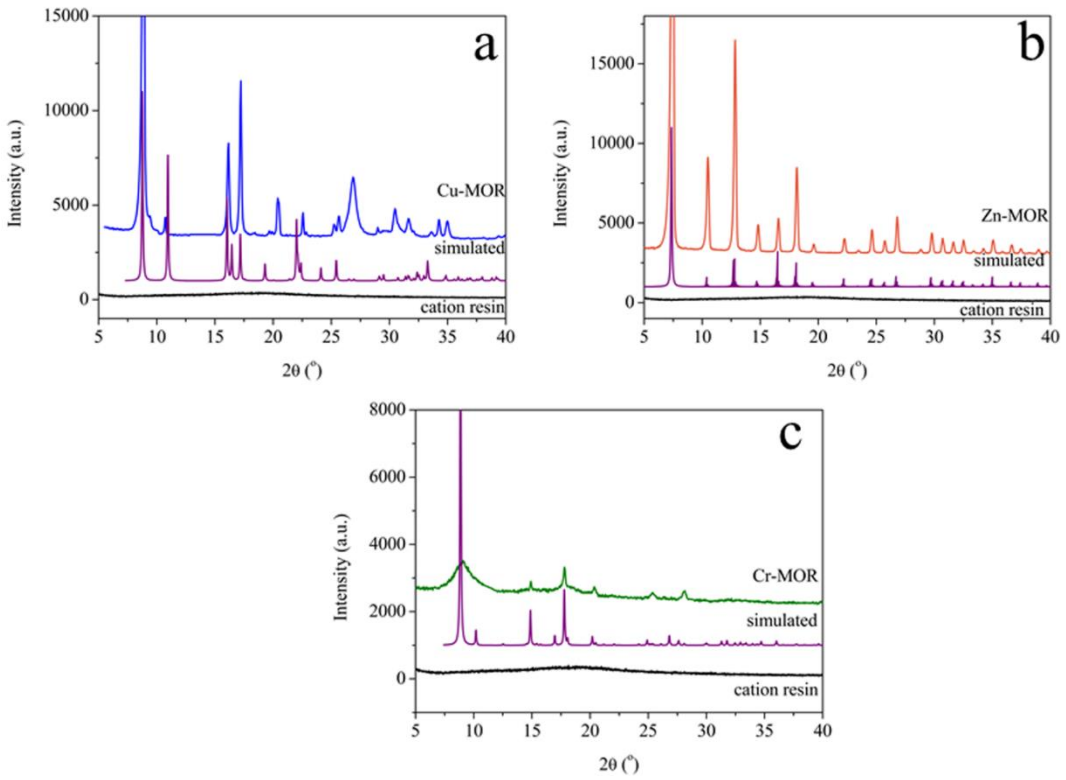

Fig. S5 XRD patterns of MOF materials

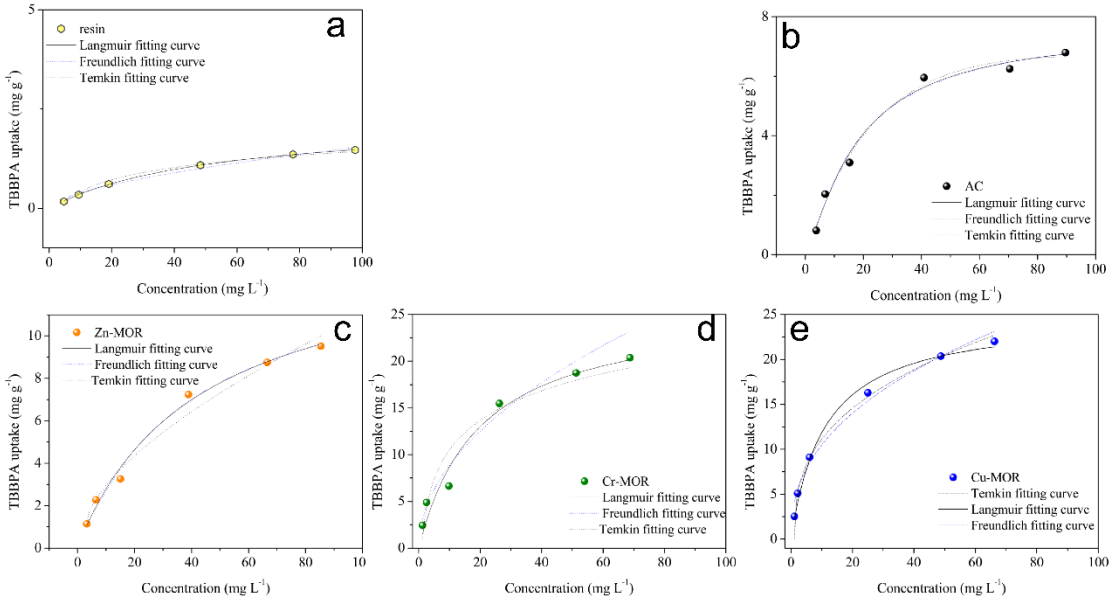

Fig. S6 Langmuir, Freundlich and Temkin model fitting curves of five sorbents

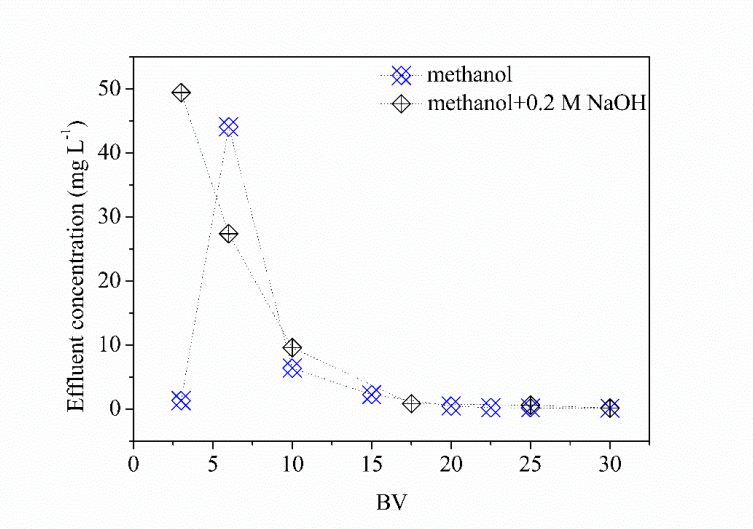

Fig. S7 Regeneration of TBBPA

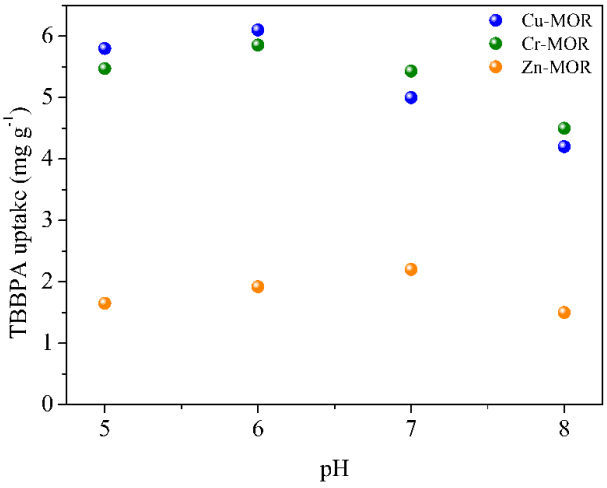

Fig. S8 Effect of pH on adsorption of TBBPA

Reference

1. Zhen Yang, Liqin Cao, Jing Li, Jiangli Lin, Jide Wang, *Polymer*, 2018, **153**, 17-23.