

## Supporting information

### **Metal ion-induced separation of valuable organic acids from the depolymerized mixture of lignite without use of organic solvents**

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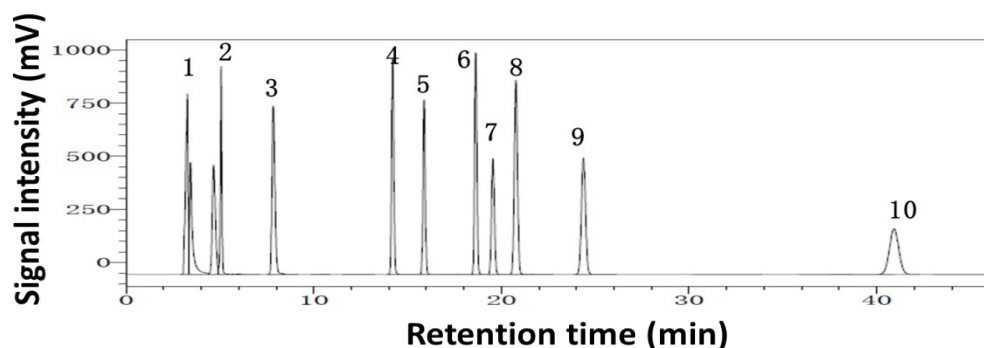
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## 1. Experimental

### 1.1 HPLC analysis of the simulated system



**Fig. S1** HPLC profile of the simulated system (mother solution). 1, *BHA*; 2, *BPA*; 3, *1,2,4,5-BTA*; 4, *1,2,4-BTA*; 5, *1,2,3-BTA*; 6, *1,3,5-BTA*; 7, *1,2-BDA*; 8, *1,4-BDA*; 9, *1,3-BDA*; 10, *BA*.

### 1.2 Separation of the simulated and real mixtures

**Mother solution:** The separation processes of the simulated system and the real lignite depolymerized mixture were similar as illustrated in Scheme S1. For the real lignite depolymerized mixture, 2.5 g of AOOs powder was totally dissolved into 100 mL deionized water to form homogeneous solution, which was used as mother solution for the following separation. A volume of 5 mL of the mother liquid was used for each separation process. For the simulated system, typical separation process was as following.

**Firstly**, 0.1 g of metal salt (M) was added into the mother solution and magnetically stirred under 50 °C for 2 h. The M-VOAs intermediate precipitate could be generally formed for most of the studied metal salts after the reaction.

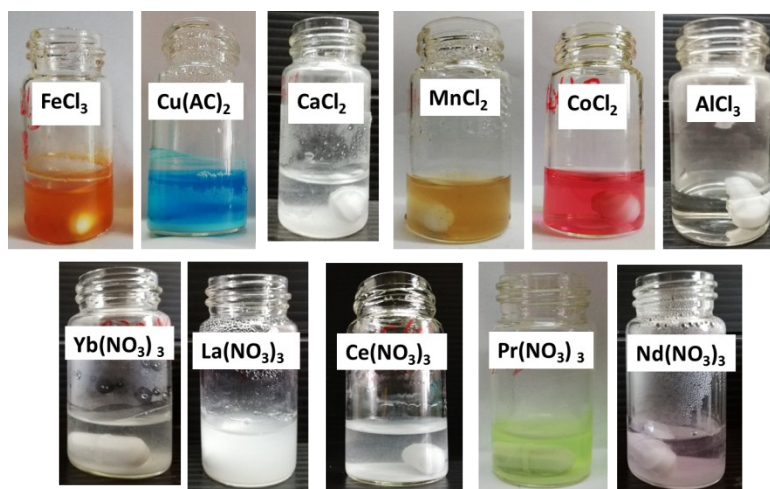
**Secondly**, the formed intermediate precipitate was collected by centrifugation (9000 rpm, 20 min) and washed by deionized water for 3 times. The washing water was combined together with the supernatant after the above centrifugation to form the Supernatant A. Supernatant A was analyzed by HPLC to detect the residual organic acids in the supernatant after separation.

**Thirdly**, the obtained M-VOAs intermediate precipitate was solubilized by 5 mL NaOH (0.5 mol/L) to release the VOAs into the solution with  $M^{n+}$  being converted into M-containing precipitate.

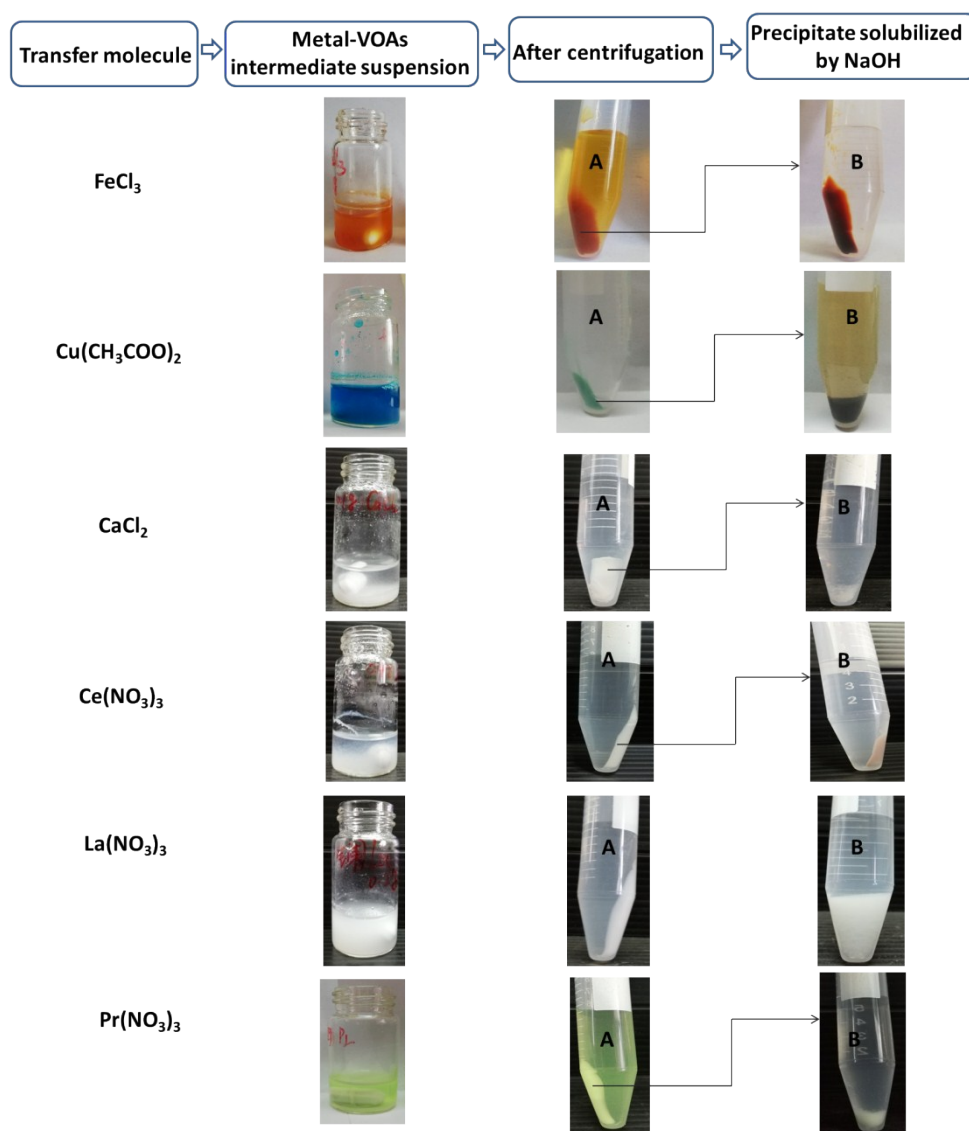
**Finally**, the supernatant B containing the target VOAs was obtained by centrifugation and detected by HPLC to analyze the organic acids separated out from the mixture solution.

For the investigation of different separation conditions, different initial pH values of real mother solution (2, 4, 6, and 8), different dosages of metal salts (0.1 g, 0.2 g, and 0.4 g), and different reaction temperatures (25 °C, 50 °C, 75 °C) were adopted,

with other processes the same as above.



**Fig. S2** Optical photographs of the phenomena after the addition of different metal salts into the simulated solution. Separation conditions: the dosages of the metal salts 0.2 g (for  $\text{MnCl}_2$  and  $\text{AlCl}_3$ , 0.4 g), temperature, 50 °C, 2 h.



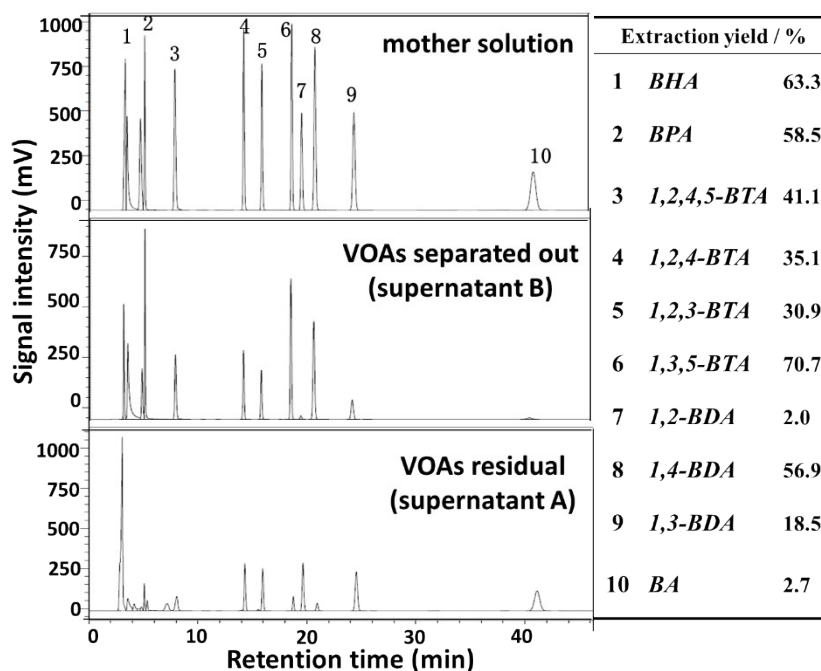
**Fig. S3** Optical photographs of the separation process using several typical metal ions.

### 1.3 Characterization of the separation intermediate precipitate

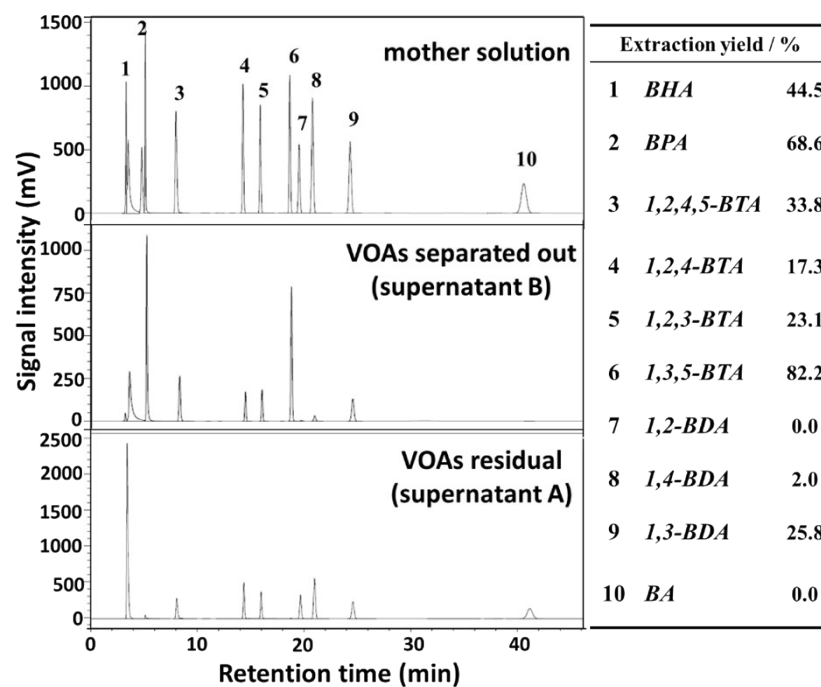
Scanning electron microscopy (SEM) measurements were performed using a Hitachi SU8220 scanning electron microscope operated at 20 kV X-ray diffraction (XRD) was carried out via an XD8 Advance-Bruker AXS X-ray diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 0.154$  nm) and Ni filter scanning at 2° per minute ranging from 5° to 90°. The tube voltage was 40 kV, and the current was 40 mA. Fourier transform-infrared spectra (FT-IR) were obtained using a PerkinElmer spectrometer. The XPS measurements were carried out via an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific) at a pressure of  $3 \times 10^{-9}$  mbar using Al K $\alpha$  as the excitation source ( $h\nu = 1486.6$  eV) and operating at 15 kV and 150 W.

## 2. Results and discussion

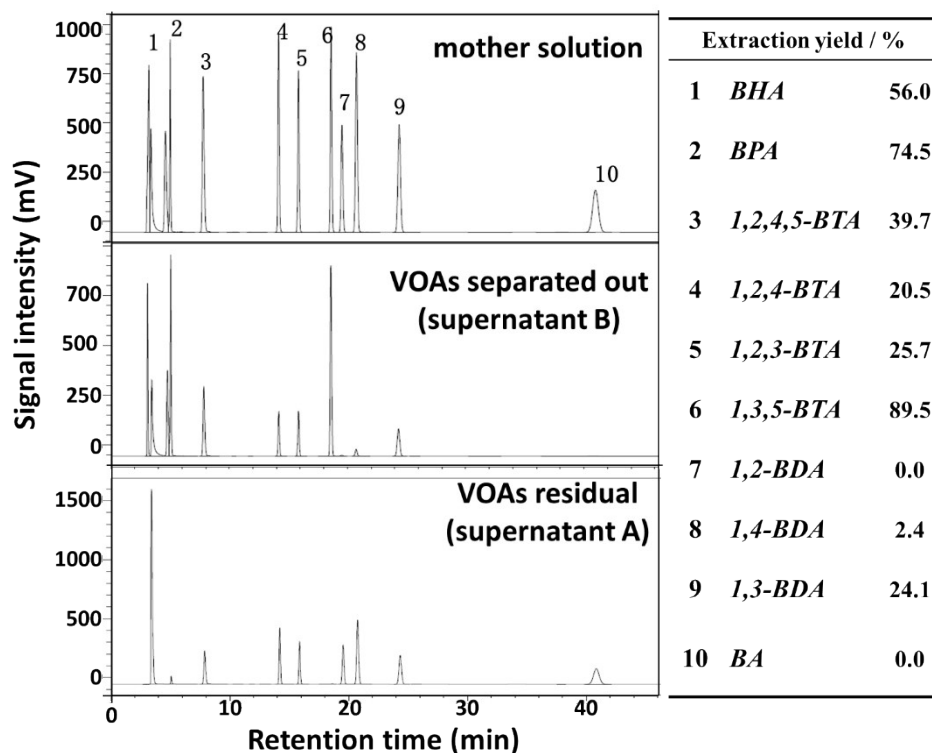
### 2.1 Separation results of the simulated system by different metal ions



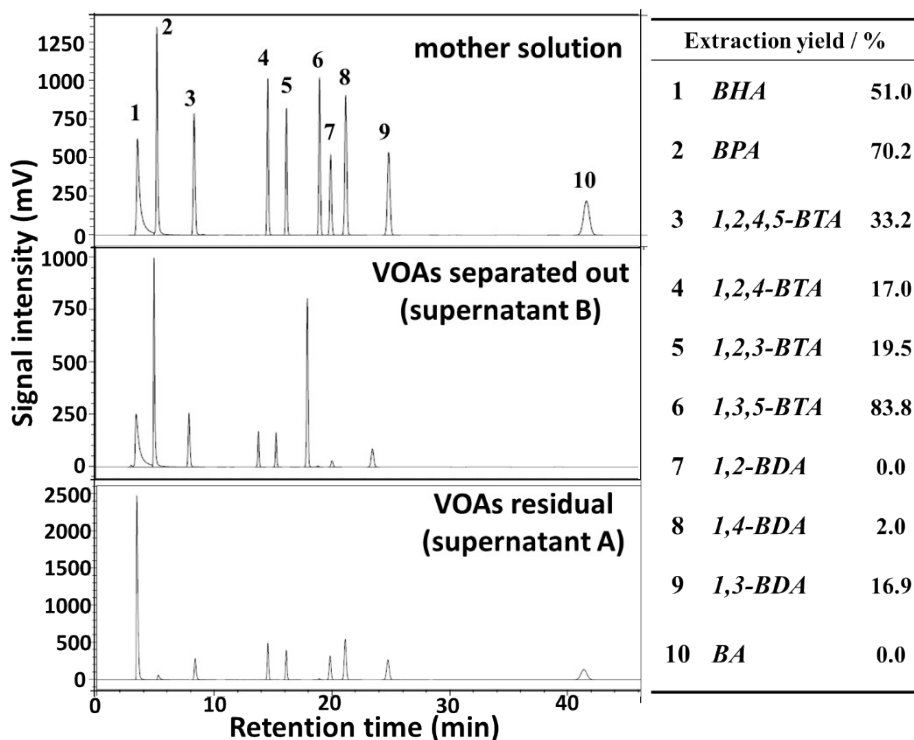
**Fig. S4** Separation results of the simulated mixture using  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ . The inserted table gave the extraction yields of each organic acid. Separation conditions: the mother solution 5 mL; the dosage of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  0.1 g; 50 °C; 2 h.



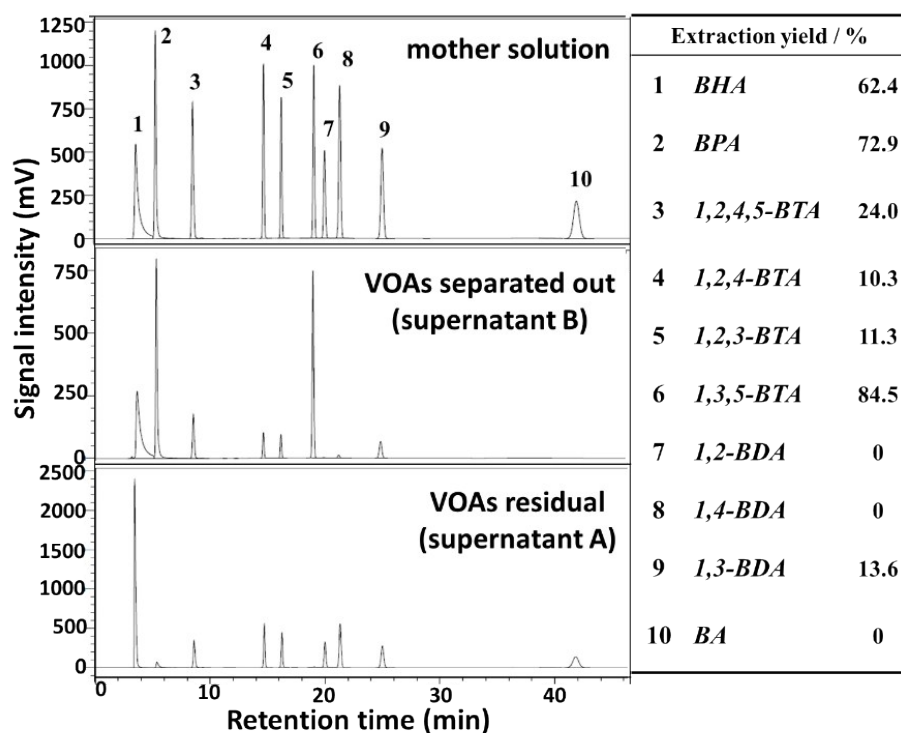
**Fig. S5** Separation results of the simulated mixture using  $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ . The inserted table gave the extraction yields of each organic acid. Separation conditions: the mother solution 5 mL; the dosage of  $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  0.1 g; 50 °C; 2 h.



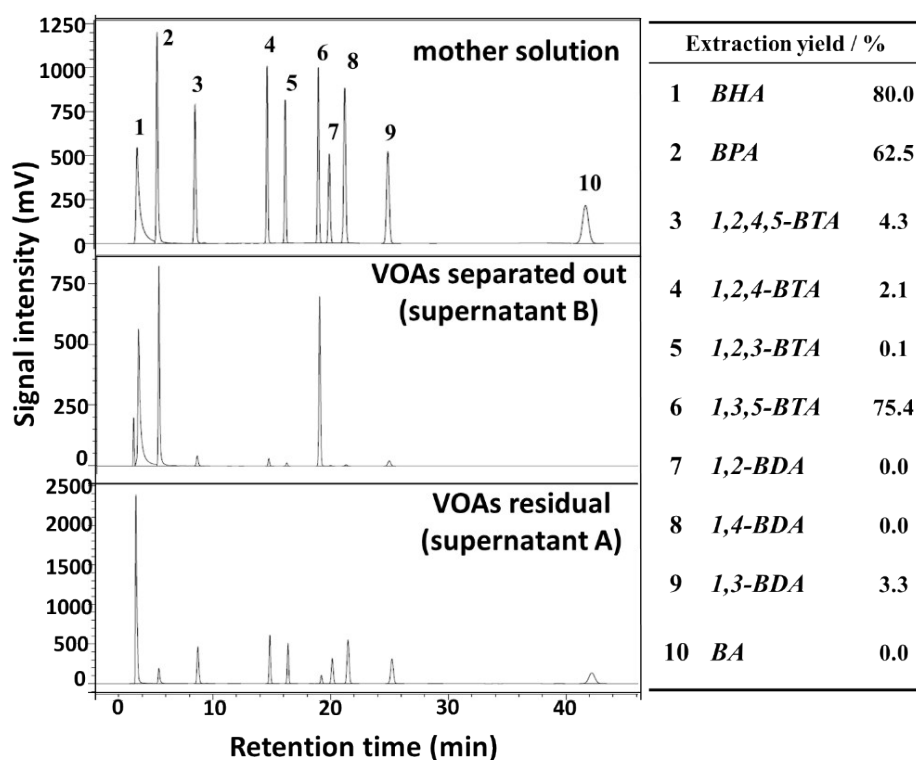
**Fig. S6** Separation results of the simulated mixture using  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The inserted table gave the extraction yields of each organic acid. Separation conditions: the mother solution 5 mL; the dosage of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  0.05 g; 50 °C; 2 h.



**Fig. S7** Separation results of the simulated mixture using  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The inserted table gave the extraction yields of each organic acid. Separation conditions: the mother solution 5 mL; the dosage of  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  0.1 g; 50 °C; 2 h.

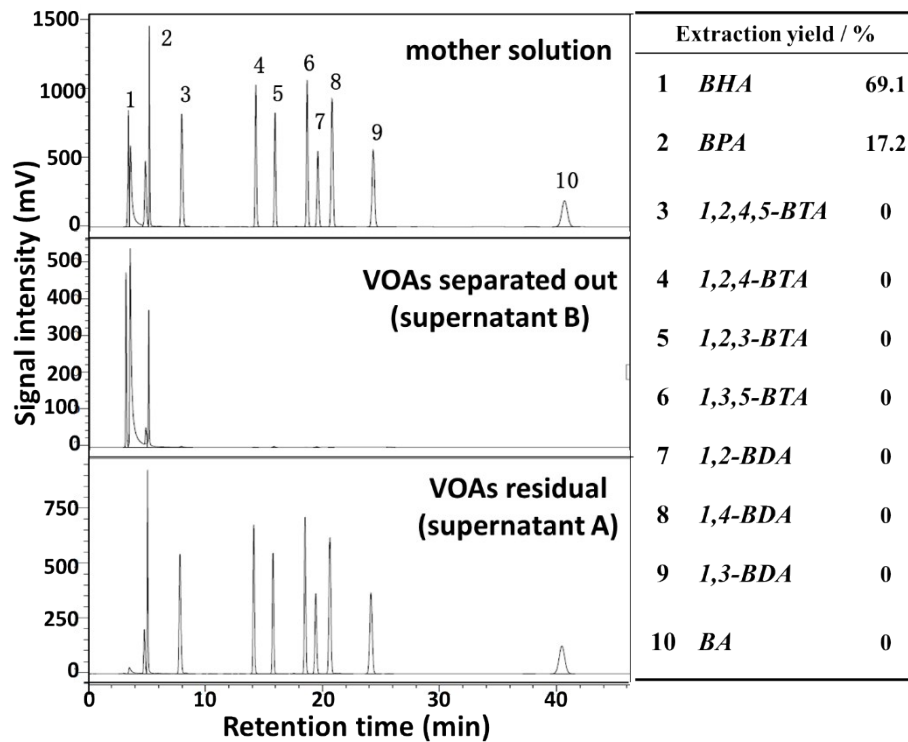


**Fig. S8** Separation results of the simulated mixture using  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The inserted table gave the extraction yields of each organic acid. Separation conditions: the mother solution 5 mL; the dosage of  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  0.1 g; 50 °C; 2 h.

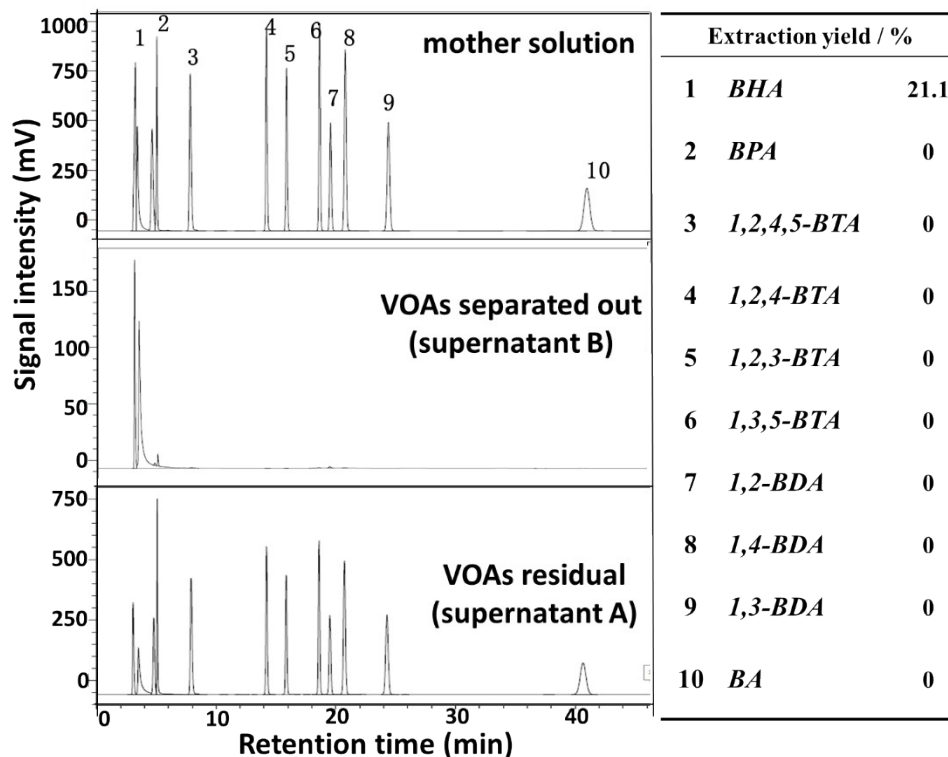


**Fig. S9** Separation results of the simulated mixture using  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ . The inserted table gave the extraction yields of each organic acid. Separation conditions: the mother solution 5 mL; the dosage of  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  0.1 g; 50 °C; 2 h.



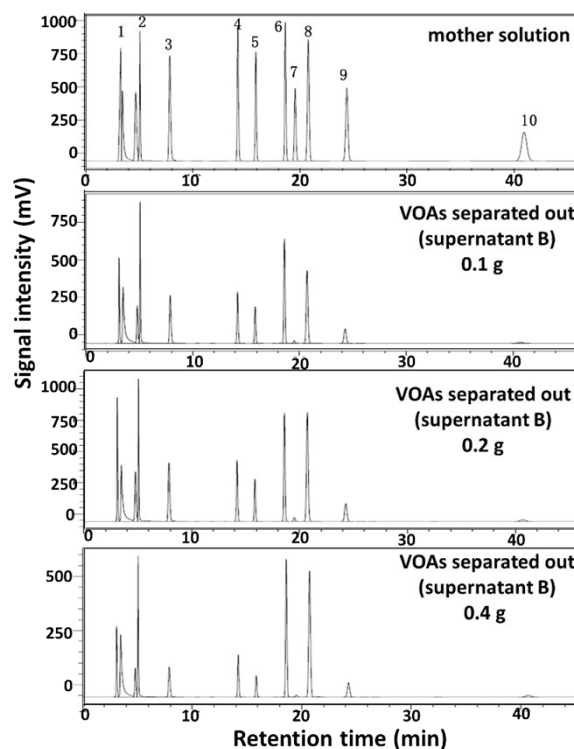


**Fig. S10** Separation results of the simulated mixture using  $\text{CaCl}_2$ . The inserted table gave the extraction yields of each organic acid. Separation conditions: the mother solution 5 mL; the dosage of  $\text{CaCl}_2$  0.1 g; 50 °C; 2 h.



**Fig. S11** Separation results of the simulated mixture using  $\text{MnCl}_2$ . The inserted table gave the extraction yields of each organic acid. Separation conditions: the mother solution 5 mL; the dosage of  $\text{MnCl}_2$  0.4 g; 50 °C; 2 h.

## 2.2 Effects of separation conditions for the simulated system

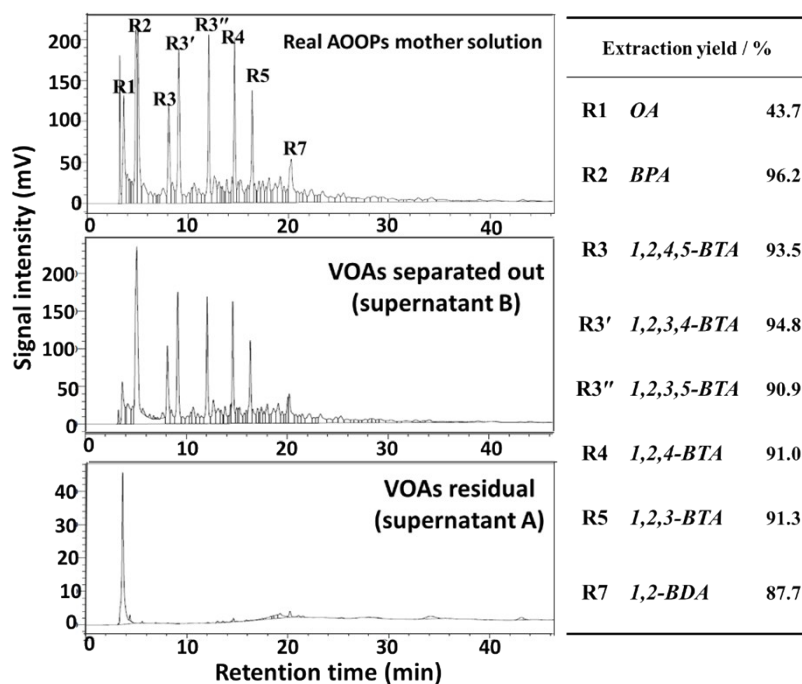


**Fig.S12** Effects of the dosage of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  on the separation result of the simulated system: comparison of the HPLC profiles. Separation conditions: mother solution 5 mL, 50°C, 2h.

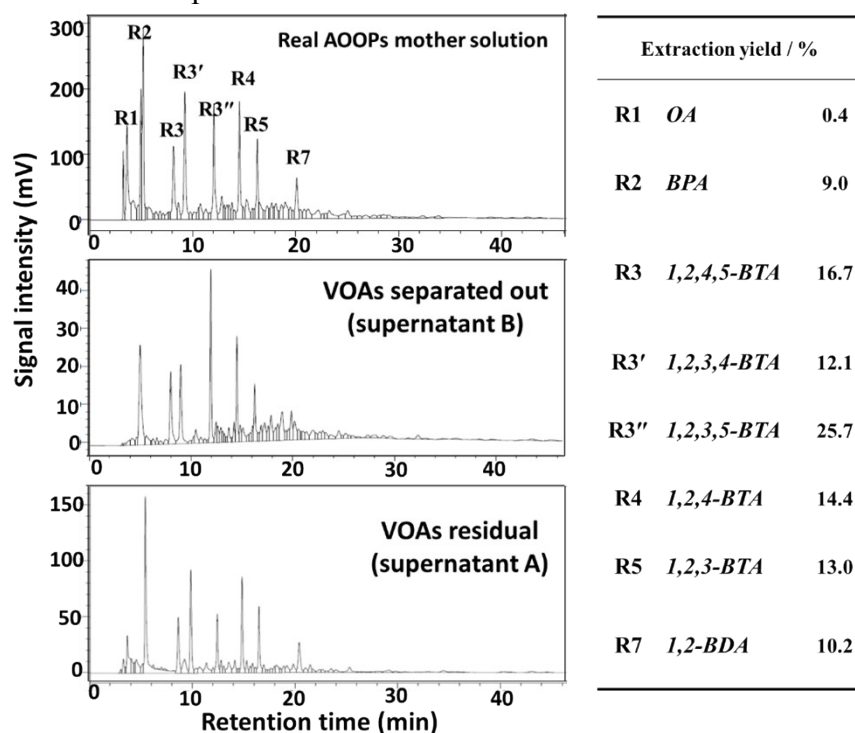
**Table S1** Effects of the pH value of the mother solution on the extraction yields using  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ . The separation conditions were given in above Fig. S19.

	pH	Extraction yield / %		
		5.7	3.6	1.5
1	<i>BHA</i>	68.3	34.5	1.8
2	<i>BPA</i>	58.2	50.8	0.0
3	<i>1,2,4,5-BTA</i>	31.1	21.6	0.0
4	<i>1,2,4-BTA</i>	25.7	9.4	0.0
5	<i>1,2,3-BTA</i>	20.0	8.4	0.0
6	<i>1,3,5-BTA</i>	67.6	58.1	56.0
7	<i>1,2-BDA</i>	1.2	0.0	0.0
8	<i>1,4-BDA</i>	69.2	0.0	0.0
9	<i>1,3-BDA</i>	13.8	3.3	0.0
10	<i>BA</i>	1.6	0.0	0.0

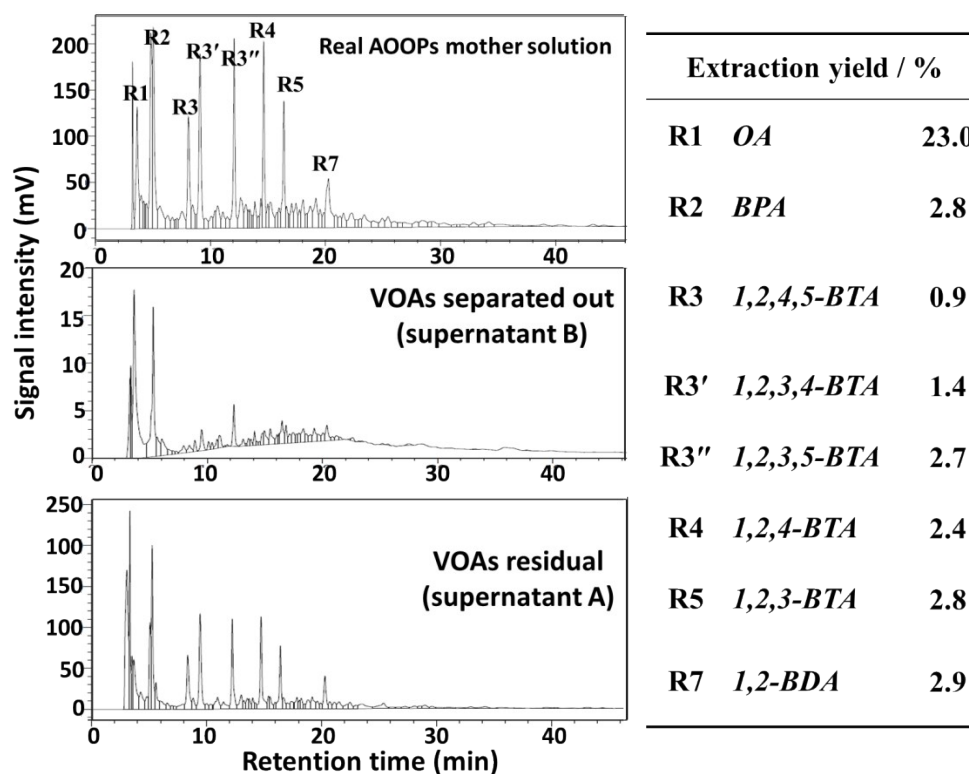
### 2.3 Separation results of the real AOOPs from lignite by different metal ions



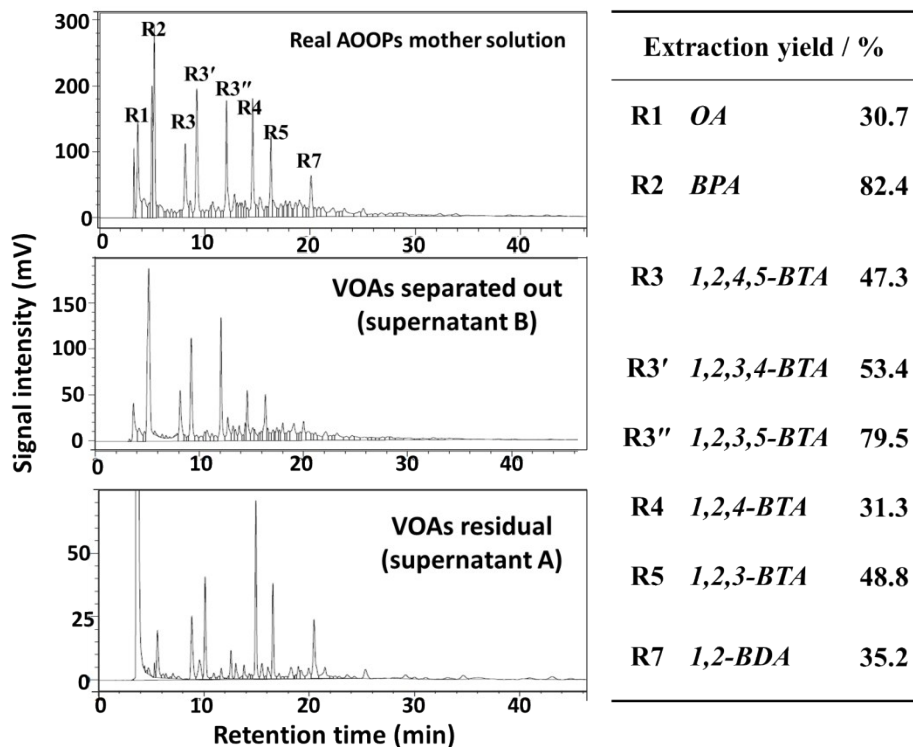
**Fig. S13** Separation results of the real AOOPs from lignite using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as transfer molecules. Separation conditions:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  0.05 g. Temperature: 50 °C. time: 2h AOOPs: 5 mL. pH=8.



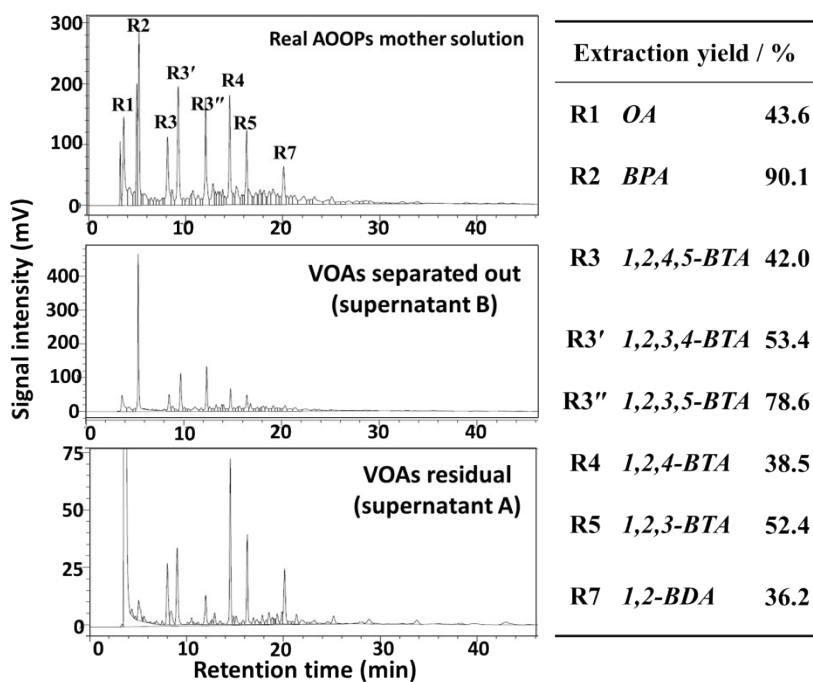
**Fig. S14** Separation results of the real AOOPs from lignite using  $\text{AlCl}_3$  as transfer molecules. Separation conditions:  $\text{AlCl}_3$  0.05 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=6.



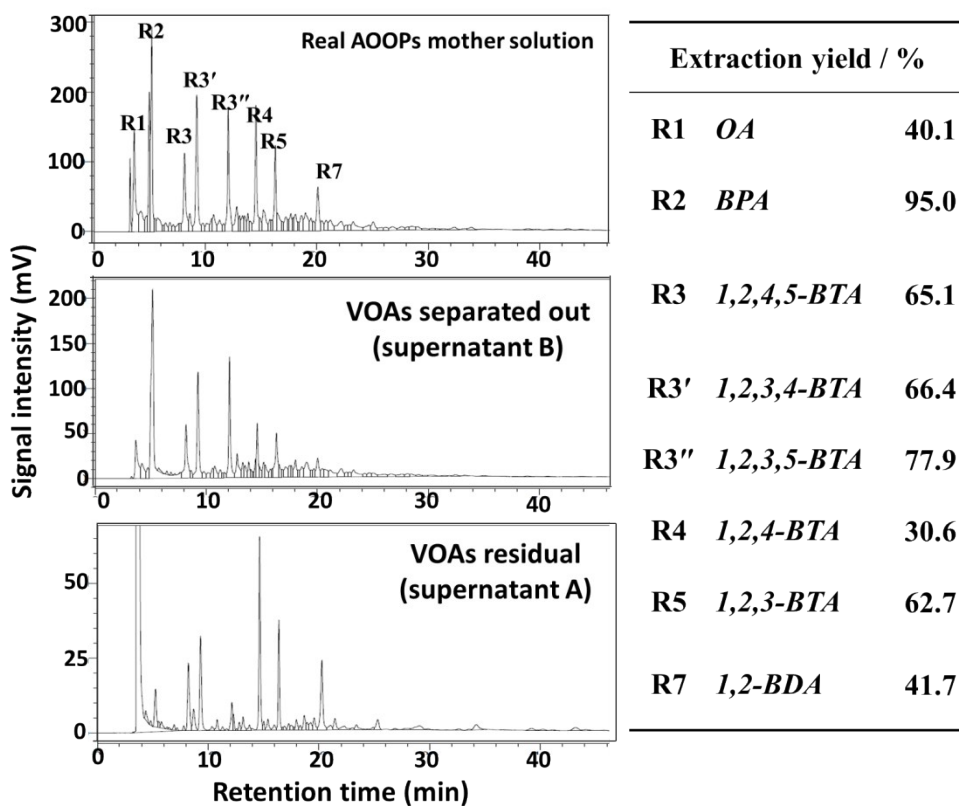
**Fig. S15** Separation results of the real AOOPs from lignite using  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  as transfer molecules. Separation conditions:  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  0.05 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=2.



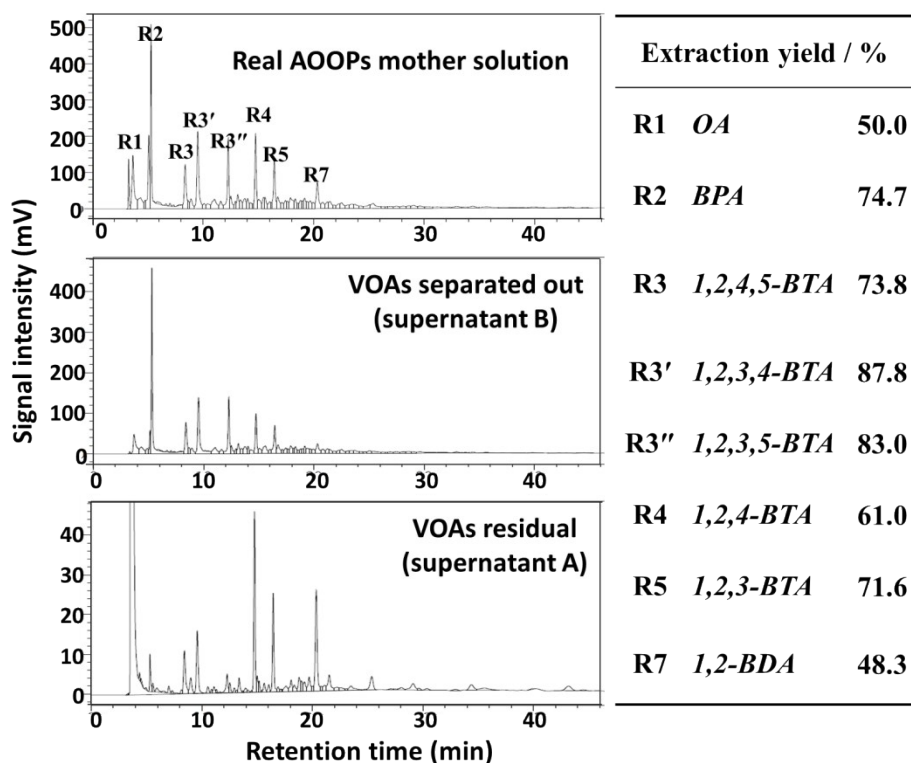
**Fig. S16** Separation results of the real AOOPs from lignite using  $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  as transfer molecules. Separation conditions:  $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  0.2 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=6.



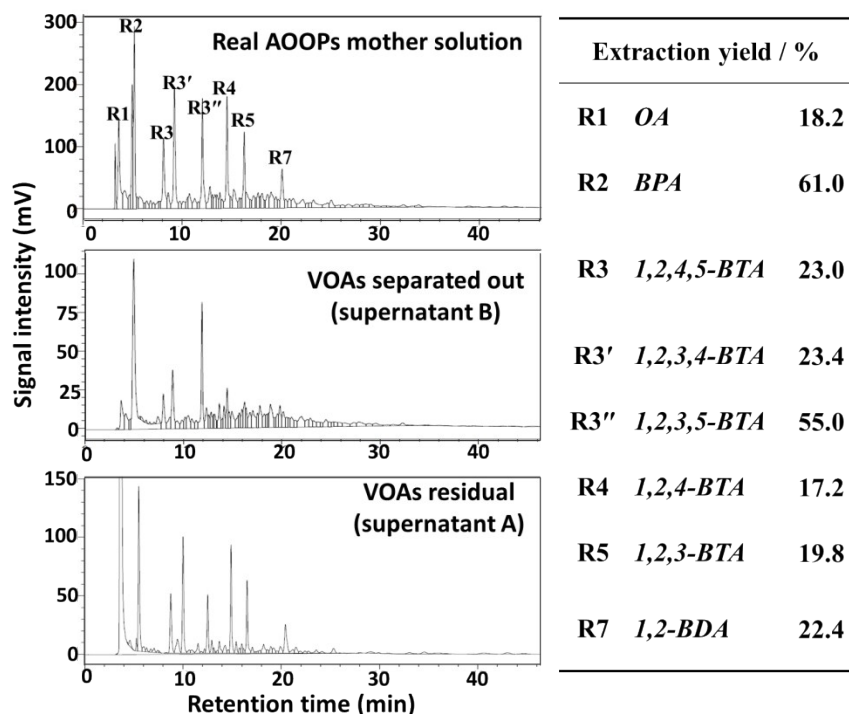
**Fig. S17** Separation results of the real AOOPs from lignite using  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  as transfer molecules. Separation conditions:  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  0.2 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=6.



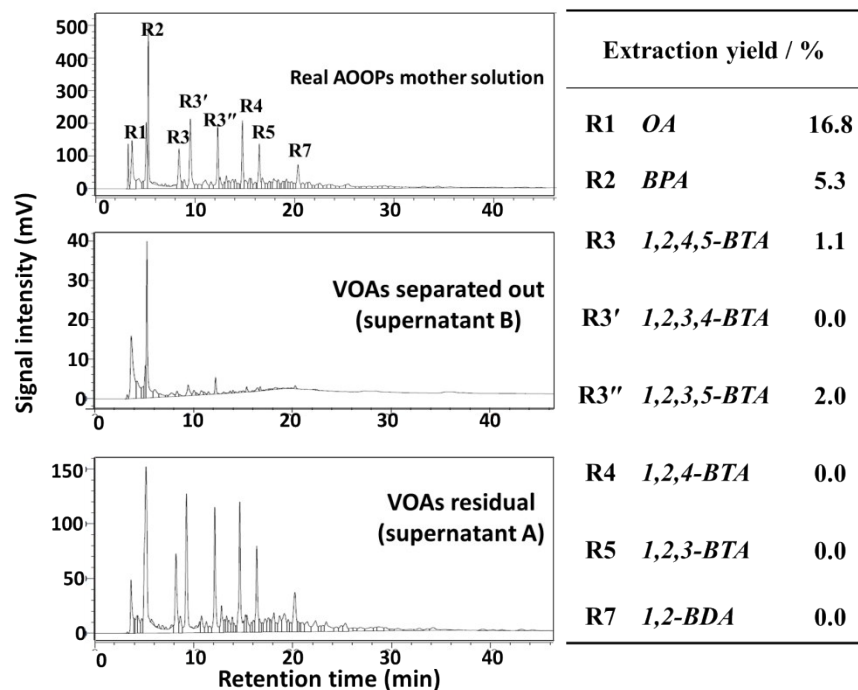
**Fig. S18** Separation results of the real AOOPs from lignite using  $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  as transfer molecules. Separation conditions:  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  0.2 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=6.



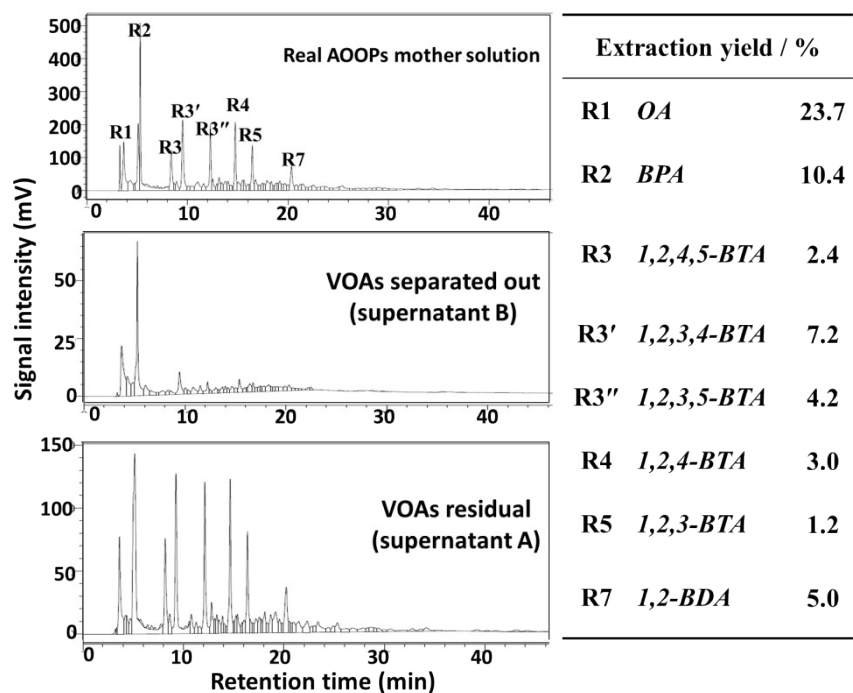
**Fig. S19** Separation results of the real AOOPs from lignite using  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  as transfer molecules. Separation conditions:  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  0.2 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=8.



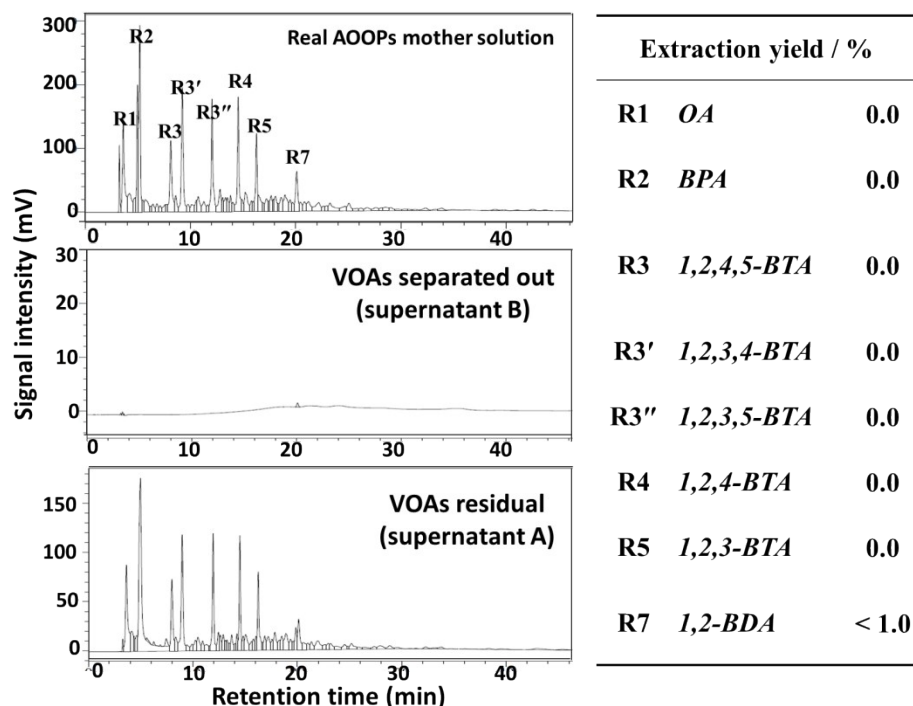
**Fig. S20** Separation results of the real AOOPs from lignite using  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  as transfer molecules. Separation conditions:  $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  0.2 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=6.



**Fig. S21** Separation results of the real AOOPs from lignite using  $\text{CaCl}_2$  as transfer molecules. Separation conditions:  $\text{CaCl}_2$  0.05 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=8.



**Fig. S22** Separation results of the real AOOPs from lignite using  $\text{MnCl}_2$  as transfer molecules. Separation conditions:  $\text{MnCl}_2$  0.2 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=8.



**Fig. S23** Separation results of the real AOOPs from lignite using  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  as transfer molecules. Separation conditions:  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  0.05 g. Temperature: 50 °C. time: 2h. AOOPs: 5 mL. pH=6.

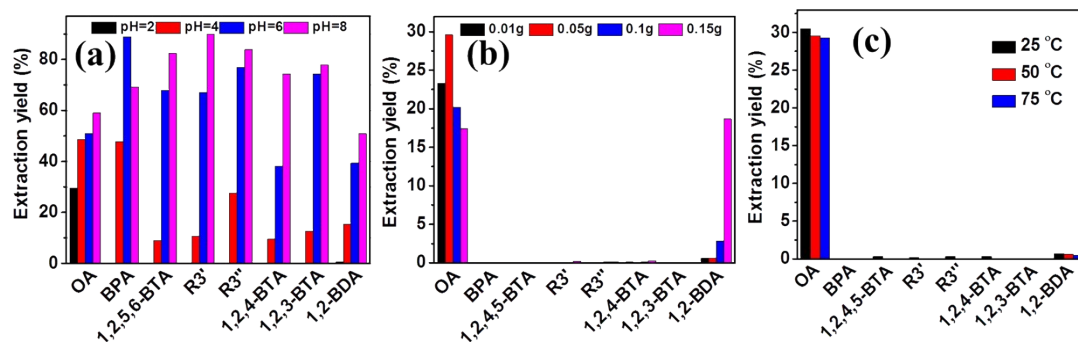
**Table S2** Classification of the metal ions based on the performances of separating different VOAs from real AOOPs system<sup>a</sup>.

Group	Metal ions ( $\text{M}^{n+}$ )	VOAs combined with $\text{M}^{n+}$
1 <sup>b</sup>	$\text{Fe}^{3+}$ , $\text{Al}^{3+}$	<b>Mainly:</b> BPA, OA, 1,2,4,5-BTA, 1,2,4-BTA, 1,2,3-BTA, 1,2 BDA
2	$\text{Cu}^{2+}$	<b>Mainly:</b> OA <b>Much less:</b> BPA, 1,2,4-BTA, 1,2,3-BTA, 1,2-BDA
3	$\text{La}^{3+}$ , $\text{Ce}^{3+}$ , $\text{Pr}^{3+}$ , $\text{Nd}^{3+}$ , $\text{Yb}^{3+}$	<b>Mainly:</b> OA, BPA, 1,2,4,5-BTA, 1,2,4-BTA, 1,2,3-BTA, 1,2-BDA
4	$\text{Ca}^{2+}$ , $\text{Mn}^{2+}$	<b>Mainly:</b> OA, BPA <b>Much less:</b> 1,2,4,5-BTA, 1,2,4-BTA, 1,2,3-BTA, 1,2-BDA
5	$\text{Co}^{2+}$	No VOAs were detected in the intermediate precipitate

<sup>a</sup> Separation condition:

<sup>b</sup> For  $\text{Fe}^{3+}$ , the detected VOAs was mainly OA.





**Fig. S24** Effects of pH of the mother solution (a), dosage of the metal salts (b), and temperature (c) on the separation results using  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  as transfer molecule. Separation conditions: for (a), 5 mL AOOs, 0.05g  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 50 °C, 2h. for (b), 5 mL AOOs, pH=2, 50 °C, 2h. for (c), 5 mL AOOs, pH=2, 0.05g  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 2h.