Characterization of humic acids extracted from a lignite and interpretation for the mass spectra

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Single factor experiments

Humic acids yield (Y %) is defined as the weight percentage of the humic acids (W_{HA}) relative to the weight of raw coal sample (W_R) (Eq. (1)).

$$Y\% = W_{HA}/W_R\ (1-M_{ad}-A_d) \times 100\% \quad (1)$$

M_{ad} = moisture (air dried base); A_d = ash (dry base);

Single factor experiments were conducted to test the effects on humic acids yield via the following four factors, dosage of alkali (factor A), reaction time (factor B), dosage of water (factor C) and reaction temperature (factor D). A factor was regulated during the experiments while keeping other three factors constant. For example, the alkali consumption (factor A) dependence of humic acids yield was measured between 0.05 g and 0.25 g (Figure S1 a). The optimal amount of alkali with the highest yield of humic acids was around 0.20 g. Thus factor A can narrow to a optimized range (0.15 g to 0.25 g) to simplify calculation process of the following orthogonal array experiment.[1]

Orthogonal array experiment

According to the preliminary results from single factor experiments, the measurement range of each factor has been confirmed (Table S1) and will be optimized in orthogonal array experiment ($L_9 3^4$).

There are two important parameters in orthogonal array experiment: K_{ji} and R_j. K_{ji} is defined as the sum of humic acids yield at all of the levels (i = 1, 2, 3, Table S1) for each factor (j = A, B, C, D). The mean value of K_{ji} is used to determine both the optimal level and the optimal combination of factors. R_j is defined as the difference

between the maximum and minimum mean value of K_{ji} and used for evaluating the significance of factors.[2]

As shown in Table S2, the best reaction condition is A3B2C3D2 i.e. 5.0 g dried coal sample and sodium hydroxide solution (300 mL, 0.21 mol/L) are mixed to react for 120 min.

References

1 Y. Z. Liang, K. T. Fang and Q. S. Xu, *Chemometrics Intellig. Lab. Syst.*, 2001, **58**, 43-57.

2 X. Wu and D. Y. Leung, *Appl. Energ.*, 2011, **88**, 3615-3624.

Table S1 Factor level table

Factor level	Factor A (g)	Factor B (mL)	Factor C (min)	Factor D (°C)
1	0.15	10	90	50
2	0.20	20	120	60
3	0.25	30	150	70

Table S2 Orthogonal table

Level	Factors				
	A	B	C	D	Results (%)
1	1	1	1	1	3.94
2	1	2	2	2	4.46
3	1	3	3	3	4.22
4	2	1	2	3	4.58
5	2	2	3	1	5.46
6	2	3	1	2	4.44
7	3	1	3	2	7
8	3	2	1	3	6.22
9	3	3	2	1	4.88
Mean value K_1	4.21	4.91	4.87	4.76	
Mean value K_2	4.83	5.38	4.64	5.30	
Mean value K_3	6.03	4.51	5.56	5.01	
Range R	1.82	0.87	0.92	0.54	

Table S3 Ultimate analysis of humic acids (wt.%)

Ultimate analysis (daf)				
C	H	N	S	O_{diff}
72.93	5.05	1.28	1.34	19.41

daf = dry and ash - free base; diff: by difference.

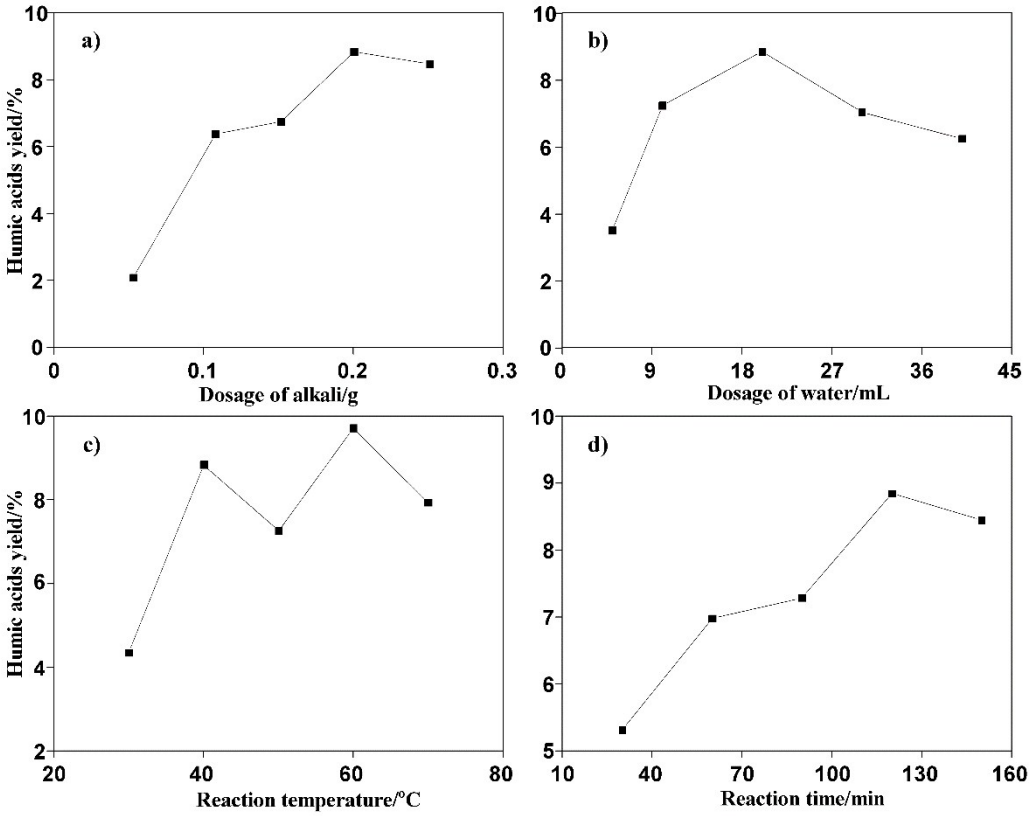

Figure S1 Influence of a) dosage of NaOH, b) dosage of water, c) reaction temperature and d) reaction time for yield of humic acids

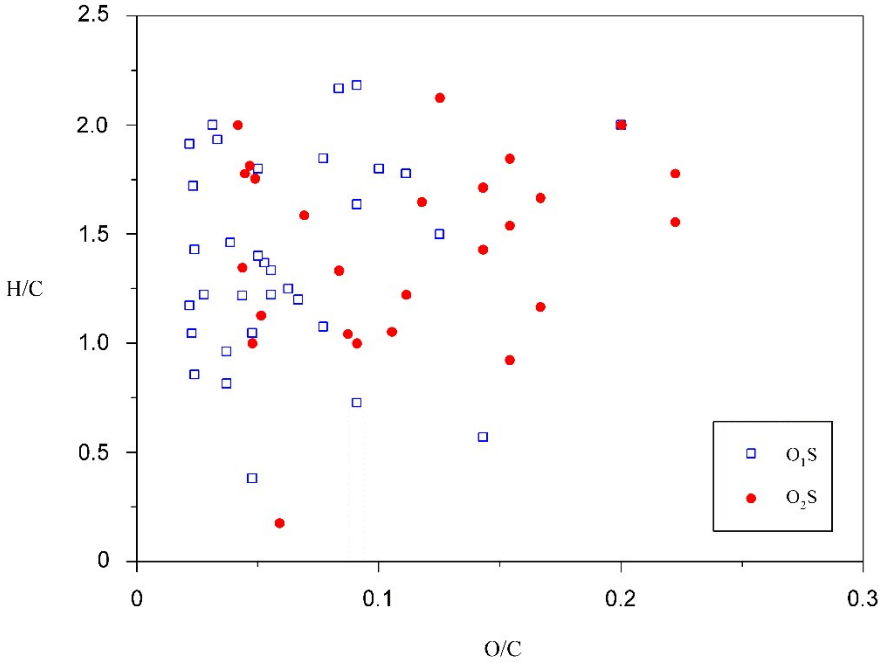

Figure S2 van Krevelen diagram for O_1S and O_2S species

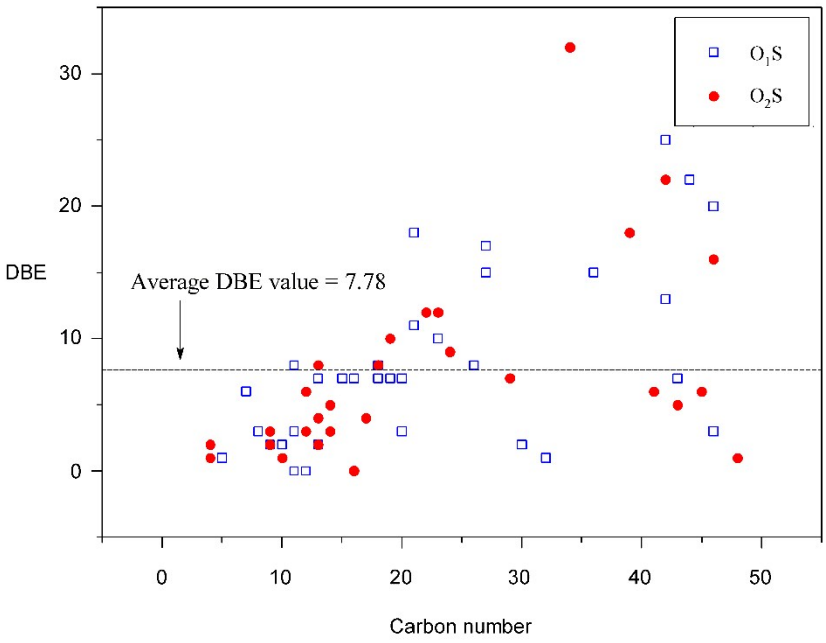

Figure S3 DBE vs. carbon number for O_1S and O_2S species