

Supplementary Information:

1. Preliminary experiment

To investigate the reduction of Cr (VI) by the HAS_{cm} at different reaction time, three 250 mL flasks as reactors were conducted. The flasks were wrapped and placed in the shaking table (DKY-II) to maintain the temperature and agitation, the temperature was set at 25 °C and the shaking speed was 150 rpm. The reaction vessels were prepared in an anaerobic glove box (Thermo 1029 Forma) during the experiment, and the initial pH of the reaction solution was controlled at 2.5. A stock solution of HAS_{cm} (0.1 g L^{-1}) used in the experiment was made by dissolving 50 mg of the HAS_{cm} in 495 ml Milli-Q water added with 5 ml of 1 M NaOH solution. In each vessel, the initial Cr (VI) concentration was adjusted to 4 mg L^{-1} . We took samples in the anaerobic glove box at 2 h, 5 h, 10 h, 24 h, 48 h, 96 h, 144 h, 240 h, 360 h, and 600 h, respectively. Then we measured the concentration of Cr (VI), the result is plotted in Fig. S1.

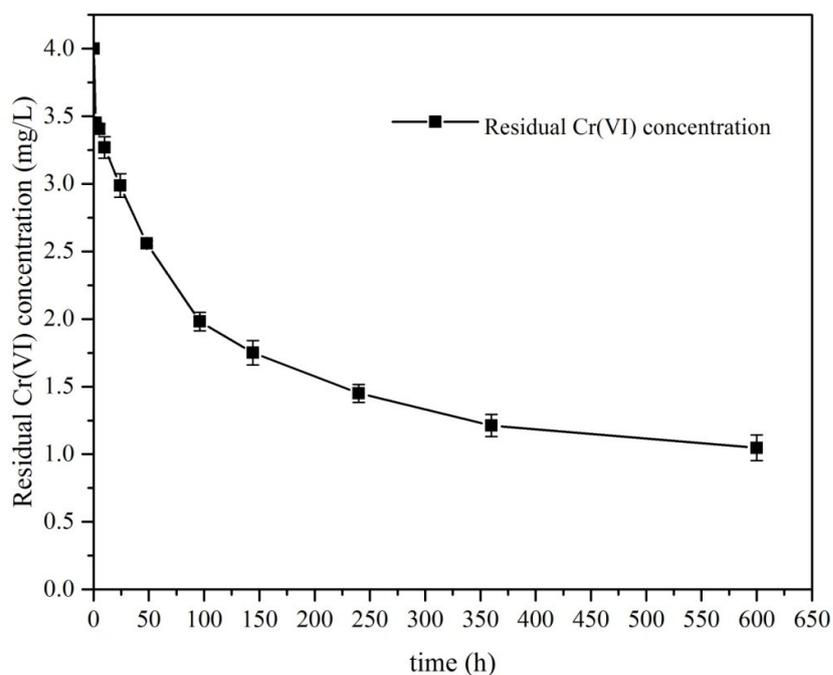


Fig. S1 The influence of reaction time on the reduction reaction of Cr(VI)

As in the literature most of the reaction rate tends to equilibrate after 96 hours of reaction on the reduction of Cr (VI) by HAs.¹⁻³ According to Wittbrodt, P. R. et al.'s¹ research on reduction of Cr(VI) by soil humic substances, the reaction rate tends to equilibrate after 96 hours (5760 minutes) in figure 2. (B). And in the preliminary Cr(VI) reduction experiments of B. Scaglia et al.,² it took 96 hours (4 days) to reach the reduction plateau (figure 1). Our preliminary experiment results show that at 96 h more than half of Cr (VI) was reduced, and after 96 h, the removal rate of Cr (VI) was only slightly increased. So in view of the time cost we chose 96 h for the rest experiment. And in subsequent study, we would increase the dosage of HAs to shorten the reaction time.

2. The result of FTIR

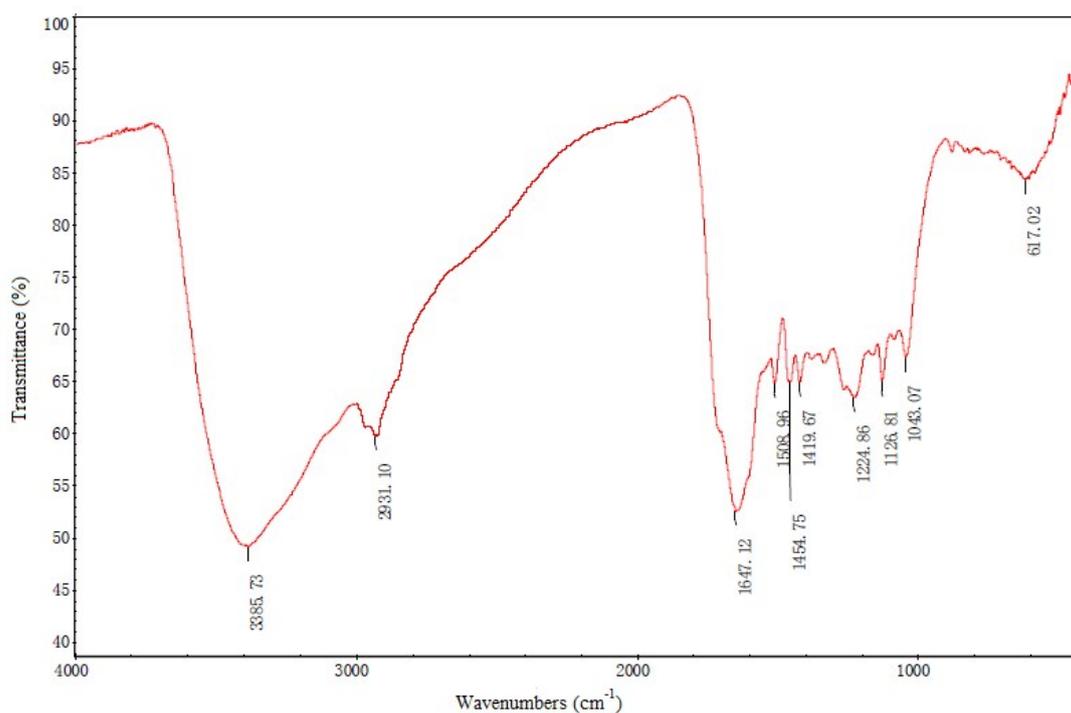


Fig. S2 FTIR spectra of humic acids composted from cattle manure

3. The result of Elemental Analysis

Table S1 Elemental Analysis of HAS_{cm}

Test	N%	C%	H%	S%	O%
1	6.25	53.49	5.26	2.17	32.83
2	6.23	53.60	5.34	2.12	32.71
Average	6.24	53.55	5.30	2.15	32.76
Variance	0.01	0.08	0.06	0.04	0.04

4. The results of ¹³CP-MAS NMR

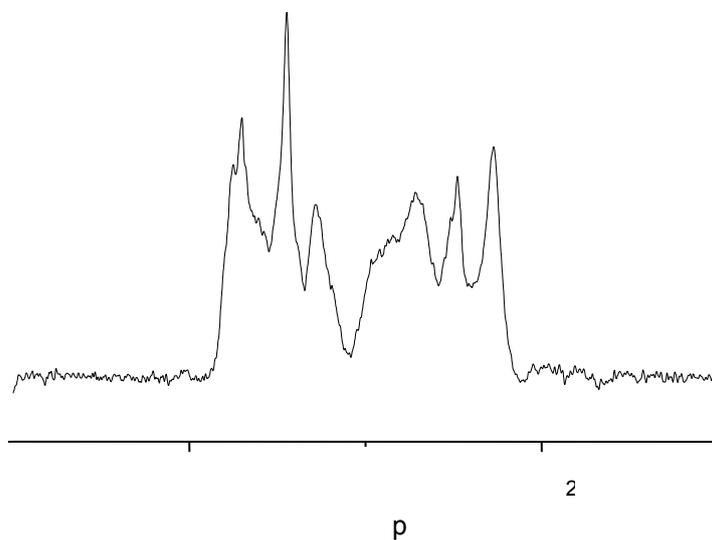


Fig. S3 ¹³CP-MAS NMR spectra of humic acids composted from cattle manure

Table S2 Integration values for the different regions of the ¹³CP-MAS NMR spectra of HAS_{cm}

C type	Carbonyl C	Carboxyl C	O,N-aromatic C	H,C- aromatic	O- alkylC	OCH ₃	alkylC
Shift ppm	220-190	190-160	160-145	145-110	110-65	65-45	45-0
weight	8.57%	16.26%	7.61%	17.03%	13.40%	11.06%	26.08%

5. Table S3 Representatives of each region in the three dimensional fluorescence

Em/Ex	Representatives ⁴
310-330/200-250	aromatic protein I; tyrosine
330-380/200-250	aromatic protein II; Biochemical Oxygen Demand (BOD ₅)
380-580/200-250	fulvic acid; hydrophobic acid
310-380/250-520	soluble microbial byproducts
380-580/250-520	humic-like substances

6. Table S4 Main bands of the FTIR absorption spectra and the associated functional groups

Wavenumbers (cm ⁻¹)	Functional groups	References
3300-3500	O-H Str., vibr., (stretching vibration) of -OH group; N-H Str., vibr.,	5
2900-2940	C-H Str., vibr., of CH ₂ , CH ₃ in alkane	6
1700-1720	C=O Str., vibr., of carboxy group;	7
1600-1660	Secondary amine, NH bend; C=C Str., vibr., of aromatic; C=O Str., vibr.,	8
1500-1540	N-H in plane (amide II); proteinaceous origin	9
1450-1460	C-H Str., vibr., of aliphatic chain	5
1380-1400	COO- symmetric stretching of aromatic; C-O Str., vibr., of phenol	10
1215-1250	C-O Str., vibr., of carboxy groups; deformation vibration of O-H	11
1130-1160	O-H Str., vibr., and C-OH Str., vibr., of aliphatic	5
1030-1080	Combination of C-O Str., vibr., and O-H deformation; polysaccharides; Si-O Str., vibr.,	12

7. The schematic diagram of reduction and complexation of Cr(VI) by HAS

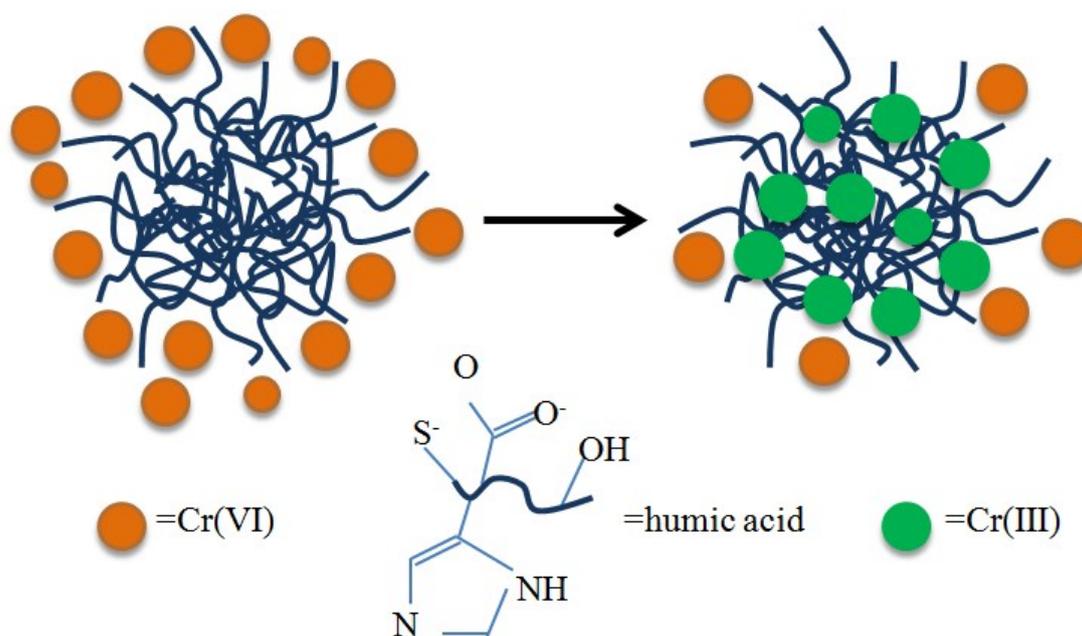


Fig. S4 The schematic diagram of reduction and complexation of Cr(VI) by HAS

References:

1. P. R. Wittbrodt and C. D. Palmer, *Environ. Sci. Technol.*, 1996, **30**, 2470-2477.
2. B. Scaglia, F. Tambone and F. Adani, *J. Environ. Sci-China*, 2013, **25**, 487-494.
3. P. R. Wittbrodt and C. D. Palmer, *Environ. Sci. Technol.*, 1995, **29**, 255-263.
4. W. Chen, P. Westerhoff, J. A. Leenheer, K. Booksh, *Environ. Sci. Technol.*, 2003, **37**, 5701-5710.
5. M. Perez-Rodriguez, I. Horak-Terra, L. Rodriguez-Lado, A. M. Cortizas, *Spectrochim. Acta A.*, 2016, **168**, 65-72.
6. A. Fakhry, O. Osman, H. Ezzat, M. Ibrahim, *Spectrochim. Acta A.*, 2016, **168**, 244-252.
7. M. Ibrahim, M. A. El-Aal, *Int. J. Environ. Pollut.*, 2008, **35**, 99-110.
8. M. Ibrahim, A. J. Hameed, A. Jalbout, *Appl. Spectrosc.*, 2008, **62**, 306-311.
9. J. V. Ibarra, E. Munoz, R. Moliner, *Org. Geochem.*, 1996, **24**, 725-735.

10. M. S. Packalen, S. T. Bagley, J. W. McLaughlin, *Ontario Canada. Wetlands*, 2011, **31**, 353-365.
11. P. Zaccheo, G. Cabassi, G. Ricca, L. Crippa, *Org. Geochem.*, 2002, **33**, 327-345.
12. J. A. Gonzalez, F. J. Gonzalez-Vila, G. Almendros, M. C. Zancada, O. Polvillo, F. Martin, *J. Anal. Appl. Pyrol.*, 2003, **68-9**, 287-298.