

JES

JOURNAL OF
ENVIRONMENTAL
SCIENCES

ISSN 1001-0742
CN 11-2629/X

March 1, 2013 Volume 25 Number 3
www.jesc.ac.cn

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CONTENTS

Aquatic environment

Applicable models for multi-component adsorption of dyes: A review Babak Noroozi, George A. Sorial	419
Effects of sludge dredging on the prevention and control of algae-caused black bloom in Taihu Lake, China Wei He, Jingge Shang, Xin Lu, Chengxin Fan	430
Distribution characteristics and source identification of polychlorinated dibenzo- <i>p</i> -dioxin and dibenzofurans, and dioxin-like polychlorinated biphenyls in the waters from River Kanzaki, running through Osaka urban area, Japan Masao Kishida	441
Pre-oxidation with $KMnO_4$ changes extra-cellular organic matter's secretion characteristics to improve algal removal by coagulation with a low dosage of polyaluminium chloride Lei Wang (female), Junlian Qiao, Yinghui Hu, Lei Wang (male), Long Zhang, Qiaoli Zhou, Naiyun Gao	452
Identification of causative compounds and microorganisms for musty odor occurrence in the Huangpu River, China Daolin Sun, Jianwei Yu, Wei An, Min Yang, Guoguang Chen, Shujun Zhang	460
Influences of perfluorooctanoic acid on the aggregation of multi-walled carbon nanotubes Chengliang Li, Andreas Schäffer, Harry Vereecken, Marc Heggen, Rong Ji, Erwin Klumpp	466
Rapid degradation of hexachlorobenzene by micron Ag/Fe bimetal particles Xiaoqin Nie, Jianguo Liu, Xianwei Zeng, Dongbei Yue	473
Removal of Pb(II) from aqueous solution by hydrous manganese dioxide: Adsorption behavior and mechanism Meng Xu, Hongjie Wang, Di Lei, Dan Qu, Yujia Zhai, Yili Wang	479
Cr(VI) reduction capability of humic acid extracted from the organic component of municipal solid waste Barbara Scaglia, Fulvia Tambone, Fabrizio Adani	487
Off-flavor compounds from decaying cyanobacterial blooms of Lake Taihu Zhimei Ma, Yuan Niu, Ping Xie, Jun Chen, Min Tao, Xuwei Deng	495
Pollutant concentrations and pollution loads in stormwater runoff from different land uses in Chongqing Shumin Wang, Qiang He, Hainan Ai, Zhentao Wang, Qianqian Zhang	502

Atmospheric environment

Influence of fuel mass load, oxygen supply and burning rate on emission factor and size distribution of carbonaceous particulate matter from indoor corn straw burning (Cover story) Guofeng Shen, Miao Xue, Siye Wei, Yuanchen Chen, Bin Wang, Rong Wang, Huizhong Shen, Wei Li, Yanyan Zhang, Ye Huang, Han Chen, Wen Wei, Quyu Zhao, Bin Li, Haisuo Wu, Shu Tao	511
Synergistic impacts of anthropogenic and biogenic emissions on summer surface O_3 in East Asia Yu Qu, Junling An, Jian Li	520
Effect of central ventilation and air conditioner system on the concentration and health risk from airborne polycyclic aromatic hydrocarbons Jinze Lv, Lizhong Zhu	531
Emission inventory evaluation using observations of regional atmospheric background stations of China Xingqin An, Zhaobin Sun, Weili Lin, Min Jin, Nan Li	537
An improved GC-ECD method for measuring atmospheric N_2O Yuan Yuan Zhang, Yujing Mu, Shuangxi Fang, Junfeng Liu	547
Adsorption of carbon dioxide on amine-modified TiO_2 nanotubes Fujiao Song, Yunxia Zhao, Qin Zhong	554

Terrestrial environment

Factors influencing the contents of metals and As in soils around the watershed of Guanting Reservoir, China Li Xu, Tiejun Wang, Wei Luo, Kun Ni, Shijie Liu, Lin Wang, Qiushuang Li, Yonglong Lu	561
Photolysis of polycyclic aromatic hydrocarbons on soil surfaces under UV irradiation Chengbin Xu, Dianbo Dong, Xuelian Meng, Xin Su, Xu Zheng, Yaoyao Li	569
Sorption and transport studies of cetyl trimethylammonium bromide (CTAB) and Triton X-100 in clayey soil Sivaram Harendra, Kumaraswamy Vipulanandan	576

Environmental biology

Effects of soil water and nitrogen availability on photosynthesis and water use efficiency of <i>Robinia pseudoacacia</i> seedlings Xiping Liu, Yangyang Fan, Junxia Long, Ruifeng Wei, Roger Kjellgren, Chunmei Gong, Jun Zhao	585
Phytoremediation potential of charophytes: Bioaccumulation and toxicity studies of cadmium, lead and zinc Najjapak Sooksawat, Metha Meetam, Maleeya Kruatrachue, Prayad Pokethitiyook, Koravid Nathalang	596
Sulfur speciation and bioaccumulation in camphor tree leaves as atmospheric sulfur indicator analyzed by synchrotron radiation XRF and XANES Jianrong Zeng, Guilin Zhang, Liangman Bao, Shilei Long, Mingguang Tan, Yan Li, Chenyan Ma, Yidong Zhao	605
Hydrocarbon biodegradation and dynamic laser speckle for detecting chemotactic responses at low bacterial concentration Melina Nisenbaum, Gonzalo Hernán Sendra, Gastón Alfredo Cerdá Gilbert, Marcelo Scagliola, Jorge Froilán González, Silvia Elena Murialdo	613

Environmental health and toxicology

Biogeochemical reductive release of soil embedded arsenate around a crater area (Guandu) in northern Taiwan using X-ray absorption near-edge spectroscopy Kai-Ying Chiang, Tsan-Yao Chen, Chih-Hao Lee, Tsang-Lang Lin, Ming-Kuang Wang, Ling-Yun Jang, Jyh-Fu Lee	626
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Cr(VI) reduction capability of humic acid extracted from the organic component of municipal solid waste

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Received 11 June 2012; revised 14 August 2012; accepted 16 August 2012

Abstract

The capacity of humic acid extracted from organic waste (HAW) to reduce Cr(VI) was tested at pH 2.5, 4 and 6 and compared with coal-derived humic acid (HAc). HAW was more effective than HAc in reducing Cr(VI). The kinetics of Cr(VI) reductions depended strongly on pH. The calculation of the apparent rate coefficients indicated that HAW was more efficient at reducing Cr(VI) than HAc, but was also more efficient than HAs from soil and peat. The reduction capability of HAs depends on the type of functional groups (i.e., thiols and phenols) present, rather than the free radicals. HAW was more efficient at reducing Cr(VI) than HAc because more reactive phenols were present, i.e., methoxy- and methyl-phenols.

Key words: hexavalent chromium; humic acid; reduction kinetic; organic fraction municipal solid waste; phenol molecules

DOI: 10.1016/S1001-0742(12)60078-3

Introduction

Chromium is a redox reactive element with oxidation states ranging from -2 to $+6$ (Park et al., 2005); the $+3$ and $+6$ states are prevalent in the environment. The oxidized Cr(VI) form is toxic, carcinogenic and teratogenic and is commonly present in the environment as relatively soluble oxyanions (i.e., CrO_4^{2-} , HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$) (Park et al., 2005). These anions have a high mobility in water and in soil because soil particles are predominately negatively charged and electrostatic repulsions prevent these anions from adsorption to the soil particles (Fendorf, 1995). In contrast, the reduced Cr(III) form is nontoxic and essential for maintaining the normal physiological functions of living organisms. The reduced Cr(III) form is found predominantly in its insoluble form in water and soil (Fendorf, 1995) as $\text{Cr}(\text{OH})_3$ (Pakzadeh and Batista, 2011) and/or as an organo-metal complex adsorbed on mineral surfaces in soils (Bartlett and James, 1998).

Cr(VI) is a strong oxidant that can be reduced to its trivalent form in water and soils by redox reactions with aqueous ions, electron transfers at mineral surfaces and simple organic molecules. Conventional technologies for Cr(VI) removal/reduction from aqueous solutions include

chemical reduction/precipitation, ion exchange, membrane separation and surface adsorption (Gao et al., 2008). Recently, researchers have increasingly focused their attention toward the use of eco-friendly options, such as bacteria, fungi, algae, industrial and agricultural wastes and humic acid (HA) for Cr(VI) removal from wastewater (Espinoza-Quiñones et al., 2009; Park et al., 2005; Pakzadeh and Batista, 2011; Liu et al., 2008).

HAs are natural organic substances ubiquitous in water and soil and composed of a complex mixture of low MW biogenic molecules that form colloidal suspensions, self-assembled in supramolecular structures in water solutions (Quadri et al., 2008). This structural ability is influenced by the experimental conditions adopted; i.e., pH, temperature, reagent concentrations, and HA properties (Wittbrodt and Palmer, 1995, 1996a, 1996b; Quadri et al., 2008).

All previous studies and technological applications of Cr(VI) reduction by HAs have used commercial HAs or HAs extracted from soil, coal and organic matter from water (Sanjay et al., 2000). However, the cost of the commercial products and the relatively low yields (mg of HA extracted per g of parent material dry matter) of HAs extracted from natural sources limited their potential use in the remediation of contaminated sites, including water. HAs can also be extracted from agro-industrial and municipal organic wastes (Quadri et al., 2008; Salati et al.,

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2010). The potential for using these wastes is attractive, as organic wastes are no-cost, are widely available, and the HA yield may be 10-fold greater than the yield from natural sources (Salati et al., 2010). Additionally, the widespread use of organic matrices with different compositions and the availability of simple biotechnologies (e.g., composting, anaerobic digestion, etc.) used to transform these matrices into other products provides the possibility of obtaining countless HAs with various chemical characteristics and redox properties at a reasonable yield and low cost.

The objective of this study is to assess the capability of waste-derived HA to reduce Cr(VI) in comparison with commercial-HA. Additionally, a tentative plan for understanding how waste-HA characteristics affect the reduction capability of HA is discussed.

1 Experimental

1.1 Isolation of HA

Humic substances used in this study consisted of waste HA (HA_w) extracted from garden-lignocelluloses and kitchen food wastes (60:40 wet weight/wet weight), and commercial humic substances from leonardite (HA_c) (53680-technical; Sigma-Aldrich). HA_w and HA_c were extracted from raw materials using an aqueous solution of 0.1 mol/L NaOH and 0.1 mol/L Na₄PO₂O₇, resulting in a 1:50 biomass/solution (W/V) ratio and successive flocculation with acid (pH < 1.5) of part of the alkali extract as previously described (Quadri et al., 2008). The HA fraction was separated from the liquid fraction by centrifugation and successively washed with deionized water until a neutral pH was obtained (Quadri et al., 2008).

1.2 Chemical characterization of HA substances

Micro-analytical data (C, H, N, and S contents; g/kg dry matter (dm)) were obtained by the C. Erba NA-2100 elemental analyzer (Carlo Erba, Italy). The oxygen content (g/kg dm) was calculated as the difference from 1000 g/kg dm. The reducing sugars content of HAs were determined by the Fehling reaction (Quisumbing, 1921).

CP MAS ¹³C-NMR spectra were acquired at 10 MHz on a Bruker AMX 600 spectrometer (Bruker Corporation, Germany). The pulse repetition rate was set at 0.5 sec and the contact time at 1 msec. Peak assignments and integrations were applied to the following chemical shift ranges (Yabuta et al., 2008): (1) alkyl carbon (alkyl-C; 0–45 ppm), (2) alkyl carbon attached to heteroatoms (N,O-alkyl C; 45–60 ppm), (3) alkyl carbon attached to oxygen atoms derived from polysaccharides (polysaccharide-C; 60–110 ppm), (4) aromatic and/or olefinic carbons attached to hydrogen or carbon atoms (aromatic-C-H, C-C, 110–150 ppm), (5) phenol carbons (phenol-C, 150–165 ppm) and (6) carboxyl and ketone carbons (carbonyl-C; 165–185 ppm). Area integrations were performed by using Bruker

Biospin software (Bruker Corporation, Germany).

HAs pyrolysis was performed to obtain qualitative information on the studied HAs. Pyrolysis was performed using a Pyroprobe 5100 instrument (SRA Instrument, Italy) directly connected to an Agilent 5792 CG/MS system equipped with a fused silica capillary column (5MS 30 m × 250 μm × 0.25 μm). The detector consisted of an Agilent 5975C mass selective detector (EI at 70 eV). Analyses were performed by applying methods reported in a previous study (Adani et al., 2007) that was partially modified i.e., approximately 0.2 mg of HA sample was loaded in a quartz tube in the pyrolysis unit before pyrolysis analysis was performed at 600°C for 50 sec. The pyrolysis products were then transferred to the GC system through a split/splitless injector operated in split mode (10:1) using He as the carrier gas. The GC oven was initially set at 40°C for 1 min, then heated at a rate of 7°C/min from 40°C to 320°C and finally maintained at this temperature for 15 min. Compounds were identified based on their mass spectra, GC retention time and comparison with library mass spectra (NIST). Area integrations were performed by using Agilent Chemstation software (Agilent Technologies, USA).

The free radical content of HAs was measured by applying electron spin resonance spectrometry (EPR). The EPR spectra were obtained with a Bruker Biospin GmbH using the conventional approximation, intensity line width squared (Wertz and Bolton, 1986). EPR analyses were conducted on dry HAs at a neutral pH. The EPR instrument was operated with the following parameters: a microwave frequency of 9.84 GHz, a conversion time of 20.48 msec, and a time constant of 2.56 msec. The spins (spin/g C) were evaluated via the peak height, and the *g*-value was estimated using a Mn²⁺/MnO marker.

1.3 Reduction property characterization of humic acids

The maximum quantity of reduction equivalents per gram of HA (mmol_e/g) was determined by a modified Walkley-Black method (Walkley and Black, 1934; Wittbrodt and Palmer, 1995). A mixture of 0.4 mL of 1000 mg/L HA and 0.2 mL of 20 mmol/L Cr(VI) solution was added to 2.0 mL of concentrated H₂SO₄ in a glass centrifuge tube. The reaction vessel was kept in a water bath at 90°C, and Cr(VI) concentrations were monitored over time. The number of HA reduction equivalents was calculated as three times the difference between initial and final Cr(VI) concentrations (mmol/L) divided by the initial concentration of HA (mg/L).

1.4 Cr(VI) reduction experiments

HA and K₂Cr₂O₇ solutions were prepared separately and successively combined in 300 mL conical flasks to obtain a mixed solution of HA/K₂Cr₂O₇ at a ratio of 25:1, with a HA concentration of 0.1 g/L and Cr(VI) concentration of 20 μmol/L (Wittbrodt and Palmer, 1996b). Experiments

of Cr(VI) reduction were conducted at a pH of 2.5, 4 and 6. To adjust the pH, the solutions were equilibrated for 15 min using 0.2 mol/L H₂SO₄. Additionally, sodium azide was added to avoid any biological activity. All Cr(VI) reduction experiments were performed in triplicate and carried out at (25 ± 2)°C in the dark under agitation and oxic conditions. Reduction experiments were performed until the concentration of Cr(VI) reached a plateau i.e., significant Cr(VI) reduction no longer occurred. A total of 3 mL of solution was sampled daily to measure the Cr(VI) concentration using the diphenylcarbazide colorimetric method (APHA, 1985). The calibration was performed using standard solutions containing 0.1 g/L HA and K₂Cr₂O₇ (0, 2, 10, 20, 25 μmol/L). Standard samples were freshly prepared prior to the application of the diphenylcarbazide method. All Cr(VI) measurements were performed at pH 2.5 after addition of H₂SO₄ 0.2 mol/L to the samples.

2 Results

2.1 Characterization of HA substances

After alkaline extraction, the HAc yielded 820 ± 2.1 g/kg dm of commercial-HA. Unfortunately, the total yield referred to the raw material was not available. The yield of HAw from waste, however, was 87.5 ± 2.1 g/kg dm, similar to the yield reported for different biomasses, e.g., 90 ± 38 g/kg dm, but much higher than the yield reported for soils e.g., 4 ± 3 g/kg dm (Salati et al., 2010). The elemental composition and ratios of the HAs are listed in **Table 1**.

The composition of the HAw differed from the HAc because the HAw had a higher N and H content and a

lower S and C/N ratio than the HAc; the H/C ratio of the HAc was nearly half of the HAw. In contrast, the C and O content and the O/C ratio were similar for the two HAs studied. The carbon distribution among different chemical groups was determined by applying CP MAS ¹³C-NMR spectroscopy (**Table 1**; **Figs. S1** and **S2**). Aromatic-C and phenol contents were greater in the HAc than in the HAw, reflecting the long evolutionary process of the humification of coal (leonardite) from which HAc was extracted (Zhilin et al., 2004). Other carbon types e.g., alkyl-C and primarily the O/N-alkyl-C and polysaccharides, which typically indicate poorly humified substances, were higher for HAw than HAc (**Table 1**; **Figs. S1** and **S2**). Organic compounds detected by pyrolysis for the two HAs studied were grouped on the basis of their chemical characteristics (**Table 2**; **Figs. S3** and **S4**).

Lipid, nitrogen and phenol compounds were present in HAw more than in HAc because of the HAw derivation from fresh organic matter (lignocelluloses and kitchen waste). On the other hand, the high percentage of the aromatic fraction (mono and polyaromatic fractions) in the HAc confirmed its derivation from well-humified organic matter. Elemental analysis, CP MAS ¹³C-NMR and Pyrolysis GC-MS analyses described the various origins of HAs (**Table 2**; **Figs. S1, S2, S3** and **S4**).

EPR results (**Table 1**; **Figs. S5** and **S6**) for both HAs showed a single inflection attributable to semiquinone free radicals associated with an extended aromatic network that delocalizes free electrons (Scott et al., 1998; Struyk and Sposito, 2001). These results are consistent with the assertions by previous studies that semiquinone is the primary organic radical in humic substances (Perminova et al., 2005). The abundance of free radicals in HAw was two orders of magnitude (4.1 × 10¹⁶ spins/mol C) lower than that for HAc (5.4 × 10¹⁸ spins/mol C) (**Table 1**; **Figs. S5** and **S6**). The reduction capacity of the HAs was greater for HAw than HAc (**Table 1**). Although this method does not support an absolute measurement of the potential reduction capacity of HAs, it allowed for the comparison of the reduction capacity of the two HAs studied with those reported in literature for soil and peat HAs (Wittbrodt and Palmer, 1995) and applied to the HAs studied in the previously proposed Cr(VI) reduction model (Wittbrodt and Palmer, 1995, 1996).

2.2 Cr(VI) reduction experimental results

Preliminary Cr(VI) reduction experiments without HA were performed. None Cr(VI) reduction was measured, therefore experimental conditions were considered adequate to measure HA reducing activity. When HAs were added, the results obtained indicated their capability to reduce Cr(VI). The Cr(VI) reduction was different for the two HAs in terms of both the percentage of Cr(VI) reduced and the time taken to reach the reduction plateau (**Fig. 1**). The most efficient Cr(VI) reduction for both HAs

Table 1 Chemical characterization of the humic acids

	HAw	HAc
Elemental composition		
N (g/kg dm ash free)	46.1 ± 0.0	16.2 ± 0.0
C (g/kg dm ash free)	598 ± 0.0	591 ± 1.0
S (g/kg dm ash free)	4.2 ± 0.0	15.8 ± 0.0
H (g/kg dm ash free)	68.7 ± 0.0	48.4 ± 0.1
O (g/kg dm ash free)	283	280
O/C	0.47	0.47
H/C	0.11	0.08
C/N	12.97	36.37
¹³CPMAS-NMR integrated area		
Alkyl C ^a (%C-NMR)	47.56	32.83
N,O-alkyl C ^b (%C-NMR)	11.17	8.46
Polysaccharide-C ^c (%C-NMR)	21.5	12.95
Aromatic-C ^d (%C-NMR)	9.75	33.78
Phenol ^e (%C-NMR)	3.5	5.16
Carbonyl-C ^f (%C-NMR)	6.62	6.83
Reduced sugar (mg/g dm)	0.68 ± 0.02	0.76 ± 0.07
Fe (mg/g dm)	0.54 ± 0.09	10.9 ± 0.2 ^g
Free radical content (Spins/mol C)	4.1 × 10 ¹⁶	5.4 × 10 ¹⁸
Reduction capacity (mmol _e /g dm)	77.7 ± 1.1	71.5 ± 0.9

^a band δ range (0–45 ppm); ^b band δ range (45–60 ppm); ^c band δ range (60–110 ppm); ^d band δ range (110–150); ^e band δ range (150–165); ^f band δ range (165–185); ^gPerämäki et al., 2000.

HAw: humic acid from waste; HAc: commercial humic acid.

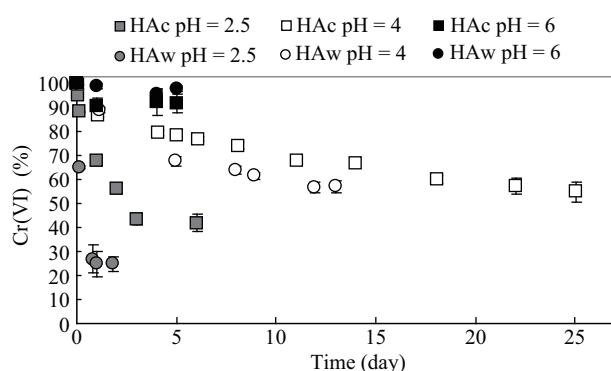
Table 2 Macromolecular characterization of HA based on the pyrolysis results

	HAW	HAc	Parent molecules
Fatty acid (%Pyrogram)	6.98	–	Lipid
Alkane (%Pyrogram)	3.2	2.4	Lipid
Cycloalkane (%Pyrogram)	8.66	2.2	Lipid
Alkene (%Pyrogram)	11.88	7.1	Lipid
Cycloalkene (%Pyrogram)	–	0.9	Lipid
Ketone (%Pyrogram)	–	0.8	Lignin
Furan derivatives (%Pyrogram)	4.6	3.6	Polysaccharides
Nitrogen compounds (%Pyrogram)	7.01	0.74	Protein
Benzene (%Pyrogram)	26.75	49.2	Protein, lignin
Polyaromatic (%Pyrogram)	0.1	4.7	Coal, humified organic matter
Isoprenoid (%Pyrogram)	1.7	–	Tannin
S-compounds (%Pyrogram)	4.9	16.4	Protein, S-oxidized compounds
Aldheyde (%Pyrogram)	3.9	–	Protein
Phenol (%Pyrogram)	17.84	10.1	Protein, lignin, humified organic matter
Sulfur dioxide (% of total S-compounds)	–	72.69	
Methanethiol (% of total S-compounds)	100	27.3	
Monomethoxy phenol (% of total phenol)	64.59	–	
Dimethoxy phenol (% of total phenol)	6.67	–	
Trimethoxy phenol (% of total phenol)	2.13	–	
Methyl phenol (% of total phenol)	22.14	51.8	
Unsubstituted phenol (% of total phenol)	4.47	48.2	

occurred at pH 2.5: 75% and 60% of Cr(VI) was reduced after 2 day and 6 day using HAW and HAc, respectively (Fig. 1). When the experiments were conducted at pH 4, HAW and HAc performed similarly in reducing Cr(VI): 43% and 45% of the Cr(VI) was reduced, respectively, although HAW reduced Cr(VI) in approximately half the time of HAc. Finally, for the experiments performed at pH 6, no Cr(VI) reduction was observed for either of the HAs studied.

3 Discussion

The presence of free radicals in the HA molecules have always been considered responsible for the reduction capability of HAs (Scott et al., 1998). Analytical investigations by EPR analysis identified the semiquinone free radicals, the probable electron-transfer agent of HA (Scott et al., 1998). Because HAc showed a higher free radical content than HAW (Table 1), a higher Cr(VI) reduction efficiency was expected for the HAc compared with the HAW, which was contrary to the results obtained in this study (Fig. 1).

**Fig. 1** Trend of the Cr(VI) reduction experiments at different pH values.

To better understand the role of free radicals in the reduction process occurring in this study, the theoretical amount of reduced Cr(VI) (mol Cr(VI)/g HA) by HAs radicals during the reduction experiments was calculated as previously reported (Struyk and Sposito, 2001). The results obtained (Table 3) indicated that free radicals accounted for only a fraction (0.02%–0.03% and 1.8%–2.3%) of the total reduced Cr(VI) by HAW and HAc

Table 3 Reduced Cr(VI) attributed to various HA compounds

Experiment	Total reduced Cr(VI) (μmol Cr(VI)/g HA)	HA radical ^a (μmol Cr(VI)/g HA)	S _{thiol} ^b (μmol Cr(VI)/g HA)	Reduced sugar ^c (μmol Cr(VI)/g HA)	Phenol ^d (μmol Cr(VI)/g HA)	Fe ^e (μmol Cr(VI)/g HA)
HAW, pH = 2.5	150 ± 6	0.029	43	1.3	48.4–96.8	3.2
HAc, pH = 2.5	116 ± 7	2.1	43.5	1.4	70.5–141.1	59.7
HAW, pH = 4	86 ± 8	0.029	43	1.3	48.4–96.8	3.2
HAc, pH = 4	90 ± 5	2.1	43.5	1.4	70.5–141.1	59.7
HAW, pH = 6	0	0	0	0	0	0
HAc, pH = 6	0	0	0	0	0	0

^aValue calculated using EPR data.

^bValue calculated taking into consideration HA-S and thiol contents (μmol), and a stoichiometric thiol/Cr(VI) ratio of 3.

^cValue calculated taking into consideration reduced sugar (glucose) content (μmol) a stoichiometric reduced sugars/Cr(VI) ratio of 3.

^dValue calculated taking into consideration phenol contents (μmol) and a stoichiometric phenol/Cr(VI) ratio of 1.5–3.

^eValue calculated taking into consideration Fe (μmol), and a stoichiometric Fe/Cr(VI) ratio of 3, for more information see the text.

at pH 2.5 and 4, respectively; therefore, although HAs redox activity has been primarily ascribed to quinone-semiquinone structural moieties (free radicals), this results diminish free radicals as the primary active agents, which is consistent with previous studies (Struyk and Sposito, 2001).

Organic compounds containing heteroatoms, such as aldehydes, thiols and phenols, have been previously described as Cr(VI) reduction agents (Elovitz and Fish, 1995). Because HA is composed of a heterogeneous mixture of organic compounds self-assembled into a pseudo-micellar structure, it contains different organic functional groups including those previously reported (Elovitz and Fish, 1995). Considering that the reduction of Cr(VI) to Cr(III) requires 3 electrons (e^-), the quantification of such organic functional groups and knowing the number of e^- transferred during the reaction could provide information about the role of each organic compound contained in the HA that is involved in the Cr(VI) reduction. This approach is important because it allows for the study of various performances of HA in Cr(VI) reduction with respect to HAs origin and chemical composition.

The involvement of the S-compounds contained in HAs in redox processes has been reported (Szulczewski et al., 2001). Although HAs contain several forms of S-compounds (sulfonates, sulfones, sulfoxides, thiols, sulfides and disulfides) with different valence states (from -2 to $+6$) (Xia et al., 1998; Szulczewski et al., 2001), only S in the reduced state (e.g., thio and thiol, valence = -1) is reactive in the electron transfer processes (Xia et al., 1998) and becomes the oxidized disulfide form (valence = 0). HAc contained four times more sulfur than HAw (Table 1); nevertheless, for coal-derived HA, i.e., HAc, a high number of S-oxidized molecules, e.g., sulfonates and sulfates (Olivella et al., 2002) was reported that do not have any reduction properties (Szulczewski et al., 2001). In contrast, HAw is primarily composed of reduced/reactive S-compounds, i.e., thiol group in proteins (e.g., methionine) and in glutathione molecules, derived from the biomass contained in food waste from which HAw was extracted (Table 2). Pyrolysis GC-MS analysis confirmed the presence of thiol for both HAw and HAc (100% and 27.3% of all S compounds detected with pyrolysis for HAw and HAc, respectively) but also a relatively large amount of oxidized S compounds for HAc (72.69% of all S compounds detected with pyrolysis) (Table 2). Moreover, by using the stoichiometric reaction reported in the literature (i.e., 3 mol of thiol for each mol of Cr(VI) reduced (Szulczewski et al., 2001), the S contained in HAw, and assuming that all S contained in the HAw was redox reactive (e.g., that of protein derivation) (Tables 1 and 2), the theoretical contribution of $-S$ active groups to the Cr(VI) reduction was 43 $\mu\text{mole Cr(VI) g/HA}$ (Table 3). For HAc, considering the total S content (Table 1) and its repartition into oxidized and thiol groups (see pyrolysis

data in Table 2), the contribution of the $-S$ group to Cr(VI) reduction was 43.5 $\mu\text{mol Cr(VI) g/HA}$ (Table 3). The results, although representing an approximation, indicated that thiols were not completely responsible for the Cr(VI) reduction (150 and 116 $\mu\text{mol of Cr(VI) g/HA}$ reduced for HAw and HAc at pH 2.5, respectively) (Table 3).

HA is largely composed of O-alkyl C, i.e., oligosaccharides or simple sugars, that have been reported in the literature to have reduction properties (Zhilin et al., 2004) (Table 1). For example, peat-HA was reported to be more active than leonardite-HA in the reduction of Cr(VI) because of the high concentration of polysaccharides (23% of the total carbon content) (Zhilin et al., 2004). HAw is composed of a greater oligosaccharide fraction than that observed in HAc (see CP MAS ^{13}C NMR) (Table 1), and it was expected that this fraction could play an important role in the Cr(VI) reduction process. Nevertheless, the reduction capability of saccharides is attributed to the reducing sugar group, i.e., mono and disaccharide molecules that have an open form with an accessible aldehyde group. The relatively low content of reducing sugars, as was detected for both HAs studied (Table 1), indicated that HA-oligosaccharides did not have a significant role in the Cr(VI) reduction.

Phenols have also been cited as responsible for Cr(VI) reduction (Elovitz and Fish, 1995; Hsu et al., 2009) because of the oxidation of the phenolic hydroxyl group to produce a phenoxy radical (Elovitz and Fish, 1995; Matthiessen, 1995). In particular, it has been shown that Cr(VI) is reduced through the formation of a Cr(VI)-phenol ester complex, followed by the transfer of one electron to Cr(VI) to produce Cr(V), and by the formation of numerous end-products, e.g., dimeric ketones, polymeric phenols (dimeric and trimeric coupled phenols), monomeric aldehyde, carboxylic acid and quinones. Depending on the experimental conditions (e.g., pH) and the phenol molecular characteristics (i.e., the type of substituents present and their position in the aromatic ring), 1 or 2 electrons are involved in the redox reaction (Elovitz and Fish, 1995).

Considering the two HAs studied, the phenol contents detected with the CP MAS ^{13}C -NMR analysis (Table 1), and a stoichiometric reaction of 1.5–3 mol of phenol for each mol of Cr(VI) reduced (Elovitz and Fish, 1995), a theoretical contribution of phenol to the total Cr(VI) reduction was calculated (48.4–96.8 $\mu\text{mol/g HAw}$ and 70.5–141.1 $\mu\text{mol/g HAc}$) (Table 3) for the two stoichiometric reactions considered.

The reduced form of iron (Fe(II)) has also been reported capable of reducing Cr(VI) at a low pH (Wittbroadt and Palmer, 1996a); therefore the possible contribution of Fe to the Cr(VI) reduction has been considered. HAw showed a relatively low Fe content (0.54 ± 0.09 mg/g dm) in the HAs, and assuming all Fe was considered to be present in the reduced form (Fe(II)), its contribution to the total

Cr(VI) reduction would be 3.2 $\mu\text{mol Cr(VI)/g HA}$, i.e., 2% and 4% of the total Cr(VI) reduced at pH 2.5 and pH 4, respectively (**Table 3**). The HAc, however, showed a high Fe content ($10.9 \pm 0.2 \text{ mg/g HA}$). Considering the literature data, approximately 92% of the total Fe in leonardite was Fe(II) (Perämäki et al., 2000), and it was possible to calculate a theoretical contribution of Fe(II) to the Cr(VI) reduction of 59.7 $\mu\text{mol Cr(VI)/g HAc}$, i.e., 51.5% and 66.3% of the total Cr(VI) reduced at pH 2.5 and 4, respectively (**Table 3**). Nevertheless, no previously published studies indicated that Fe(II)-HAs were directly involved in the redox reactions, unless it was involved as an electron-shuttle (Gu and Chen, 2003).

The reduction of Cr(VI) by the HAs studied was strongly pH-dependent (**Fig. 1**). Previous studies indicated that there was a considerable reduction in the system's efficiency with an increasing pH (Wittbrodt and Palmer, 1995, 1996a; Zhilin et al., 2004; Hsu et al., 2009). In our study, the pH shift from 2.5 to 4 caused a significant decrease in Cr(VI) reduction, and at pH 6, no Cr(VI) reduction occurred (**Fig. 1**). A previous study (Hsu et al., 2009) suggested two mechanisms for the pH effect: (1) decreasing the pH resulted in an increase in the redox potential of the Cr(VI)/Cr(III) couple; and (2) the formation of an inner- or outer-sphere complex between the electron donor and acceptor is a prerequisite for the successive reduction reaction. For the organic molecules aforementioned, the formation of a chromate ester was suggested to play a role in Cr(VI) reduction. Elovitz and Fish (1995) suggested that ester formation is instantaneous and is not a limiting step in the reduction of Cr(VI) and that it is independent on the pH conditions. Nevertheless, lower pH than point of zero charge of functional groups could result in the formation of positive charges associated with the enhancement of electrostatic interactions of the chromate anions compared with a high pH that can result in repulsion because of the prevalence of negative charges (Hsu et al., 2009). Thus, it is not possible to provide a simple mechanistic understanding of the pH effect on Cr(VI) reduction.

The rate of Cr(VI) reduction ($\frac{dC_{Cr}}{dt}$) by HA was described by an empirical rate equation based on a continuum model (Eq. (1)) that accounts for the proton concentration (pH) (Wittbrodt and Palmer, 1996a).

$$\frac{dC_{Cr}}{dt} = \frac{-(k_0 + kC_{H^+}) \times C_{Cr0}^{0.5}}{X_e} \quad (1)$$

where, $(k_0 + kC_{H^+})$ represents the apparent rate coefficient (k') that explains the dependence of the reaction on proton concentration, C_{Cr0} is the initial concentration of Cr(VI) and X_e is the equivalent fraction of oxidized HA (Eq. (2)):

$$X_e = \frac{C_{Cr t} - C_{Cr 0}}{C_{HA 0}} \quad (2)$$

where, $C_{Cr t}$ is the concentration of Cr(VI) at time t , and $C_{HA 0}$ is the initial concentration of HA in $\text{g/L} \times$ the reduction equivalents (mmol_e/g , **Table 1**) referred to the HAc content (mmol_C/g) $\times 3$ (Wittbrodt and Palmer, 1996).

Considering the general integrated form of Eq. (1) (Eq. (3)):

$$z = \varepsilon t \quad (3)$$

where,

$$z = \left(\frac{C_{Cr 0} + C_{HA 0}}{C_{HA 0}} \right) \times \ln \left[\frac{(C_{HA 0} - C_{Cr 0} + C_{Cr t}^{0.5} - C_{Cr 0}^{0.5})}{C_{HA 0} + C_{Cr 0}^{0.5}} \right] + \frac{(C_{Cr t} \times (C_{HA 0} - C_{Cr 0} + C_{Cr t})^{0.5})}{C_{HA 0}} + \left(\frac{C_{Cr 0}}{C_{HA 0}} \right)^{0.5} \quad (4)$$

the z values were calculated for each sampling time; thus, there is a linear relationship between variables z and t , in which the slope is ε (i.e., angular coefficient) ($R^2=0.97$ and $R^2=0.99$ for HAw at pH 2.5 and pH 4, respectively; $R^2=0.97$ and $R^2=0.93$ for HAc pH 2.5 and pH 4, respectively).

The ε values calculated for the four experiments performed (HAw at pH 2.5 and pH 4; HAc pH 2.5 and pH 4) were validated through the quantification of the fitting indices (**Table S1**).

Fitting tests were performed by evaluating the consistency between the measured and estimated ε values, through the quantification of the fitting indices. The experimental ε values were calculated as $z_{\text{experimental}}/t$. The theoretical ε values were calculated as $z_{\text{theoretical}}/t$, where $z_{\text{theoretical}}$ were determined by using the z vs. t equation and the t values. Fitting indices consisted of the following: the coefficient of determination (R^2 ; range: -1 to $+1$; optimum: -1 , $+1$); the relative root mean squared error (range: 0 to $+1$; optimum: 0); the modeling efficiency (range: -1 to $+1$; optimum: $+1$); and the coefficient of residual mass (range: -1 to $+1$; optimum: 0) (Loague and Green, 1991).

Validation results were consistent between the theoretical and experimental ε (i.e., indices were all close to the best value) (**Table S1**), confirming that the experimental data in this study was well-represented by the kinetic model proposed by Wittbrodt and Palmer (1996).

The ε values, calculated as the slope of the straight line obtained by plotting z vs. t , were then used to calculate the apparent reaction rate, k' (Eq. (5))

$$k' = \frac{\varepsilon}{\left(\frac{\{H^+\}}{K_2 * (\gamma_1/\gamma_2) + \{H^+\}} \right)^{0.5}} \quad (5)$$

where, the $\{ \}$ denotes the activities, K_2 is the acid dissociation constant for HCrO_4^- and γ_1 and γ_2 are the activity coefficients (Davies equation) for dichromate and chromate, respectively (Wittbrodt and Palmer, 1996).

Table 4 Apparent rate constants (k') calculated for HAs in this study and reported in the literature

	Experimental condition			$\log k'$ ($l^{0.5}/(\text{mol}^{0.5}\cdot\text{sec})$)
	pH	C_{Cr0} (μmol)	C_{HA0} (g/L)	
HAW	2.5	20	0.1	-8.45 ± 0.03
	4			-9.63 ± 0.05
HAc	2.5	20	0.1	-9.41 ± 0.04
	4			-10.41 ± 0.06
Soil humic acid ^a (IHSS IR102H)	2	20	0.1	-9.63 ± 0.03
	3			-10.07 ± 0.09
	4			-10.49 ± 0.08
Summit Hill ^a (IHSS IR106H)	3	20	0.1	-9.86 ± 0.08
Peat humic acid ^a (IHSS IR103H)	3	20	0.1	-9.61 ± 0.09
Soil Fulvic acid ^a (IHSS IR102F)	3	20	0.1	-9.46 ± 0.03

^a Wittbrodt and Palmer, 1996a.

The model above reported well described the kinetic of Cr(VI) reduction obtained in this work such as fitting indices indicated (Table S1). Therefore, the model was used to calculate the apparent reaction rates to be compared with literature data (Table 4). Apparent rate coefficients, $\log k'_{\text{HA}}$, were -8.45 and -9.63 for HAW, and -9.41 and -10.41 for HAc, at pH 2.5 and 4, respectively. These values indicated that Cr(VI) reduction occurred at a faster rate when HAW was the reducing agent. This trend was also evident when comparing the HAW k' data with those calculated from soil and peat HAs experiments under identical conditions (although pH 3 was used instead of 2.5) (Wittbrodt and Palmer, 1996a) (Table 4). Although the reduction capability of the two HAs had similar chemical origins, the reduction kinetics were quite different. These differences could be explained by the diverse reactivity of the electron donating groups of HAs. Considering that the theoretical contribution of the thiols to the Cr(VI) reduction were identical for both HAs studied (Table 4), it can be assumed that phenols played the main role in determining the reaction rate.

This assumption is more credible if the presence of a substituent could modify phenol reactivity (Elovitz and Fish, 1995). Phenols in HAW consisted of lignin-derived methoxy-phenol, (e.g., guaycol and syringol and their derivatives) and lignin-derived methyl-phenol (Table 2) that have both been reported to be reactive in electron donating reactions (Elovitz and Fish, 1995). HAc, however, contains less phenol (Table 2), which consisted of an equal amount of methyl-phenol and un-substituted-phenol; the latter was less reactive than methyl- and methoxy-phenols (Table 2).

4 Conclusions

HAs extracted from wastes were shown to have a good reduction capability, depending on the presence of thiols

and phenols in the HAs. Waste-HA was more efficient than HA extracted from leonardite because of the presence of more reactive phenols. The various HA compositions depends on the origin of the parent material from which HA were extracted, e.g., fresh organic matter and humified material.

These results suggest that fresh organic matter, i.e., wastes, can be an interesting source of HA containing reduction properties. Moreover, the high HA yield from wastes presents the potential for future industrial development by using HA to treat wastewater.

Acknowledgments

Cesare Cosentino and Giorgio Eisele of the Ronzoni Institute (Milan, Italy) are gratefully acknowledged for the use of the EPR instrument. Annalisa Gozzi is acknowledged for her experimental support.

Supporting materials

Supplementary data associate with this article can be found in the online version.

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Supporting materials

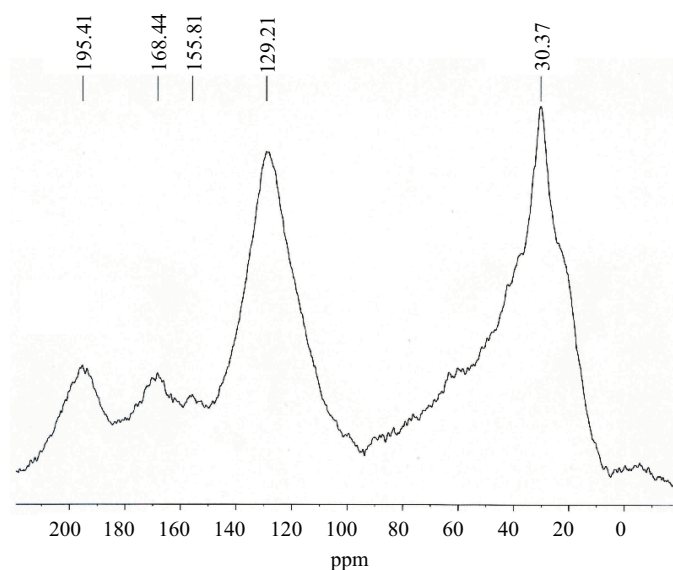
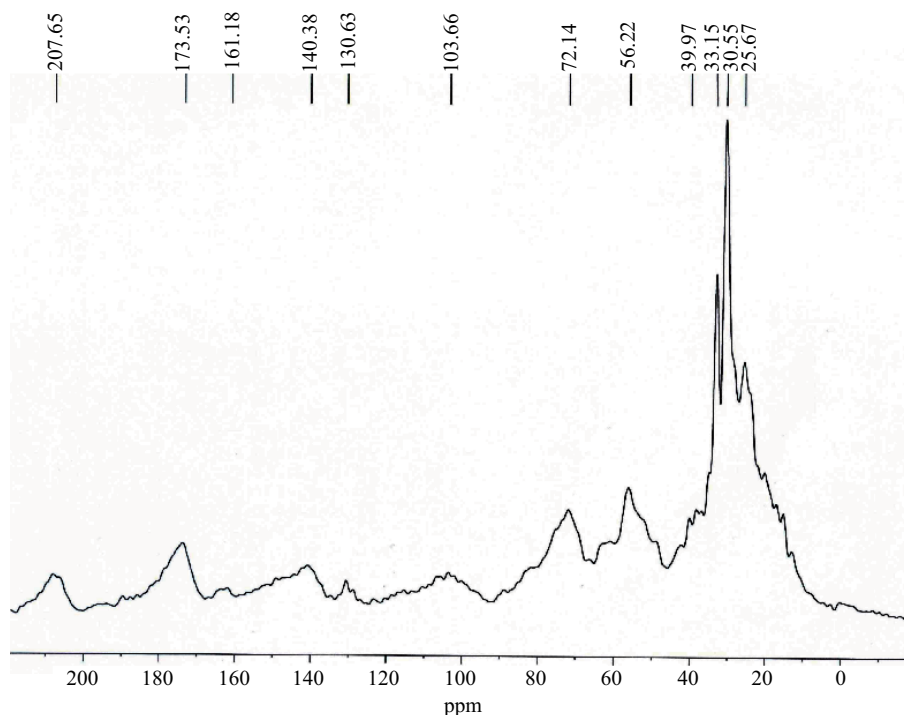
Fig. S1 CP MAS ^{13}C -NMR spectra of HAc.Fig. S2 CP MAS ^{13}C -NMR spectra of HA_w.

Table S1 Validation indices calculated for the three proposed models

Parameter	Min	Max	Best	HA _w		HAc	
				pH = 2.5	pH = 4	pH = 2.5	pH = 4
R^{2a}	-1	+1	+1; -1	0.99	0.99	0.99	0.99
RRMSE ^b	0	$+\infty$	0	-0.57	-0.2	-0.11	-0.97
EF ^c	$-\infty$	1	1	0.99	0.99	0.99	0.99
CRM ^d	$-\infty$	$+\infty$	0	0	0	0	0
Slope ^e	$-\infty$	$+\infty$	1	1.01	1	1	1
Intercept ^f	$-\infty$	$+\infty$	0	0	0	0	0

^a coefficient of determination; ^b root mean squared error; ^c modeling efficiency; ^d coefficient of residual mass; ^e slope of the regression equation between the observed and predicted values; ^f intercept of the regression equation between the observed and predicted values

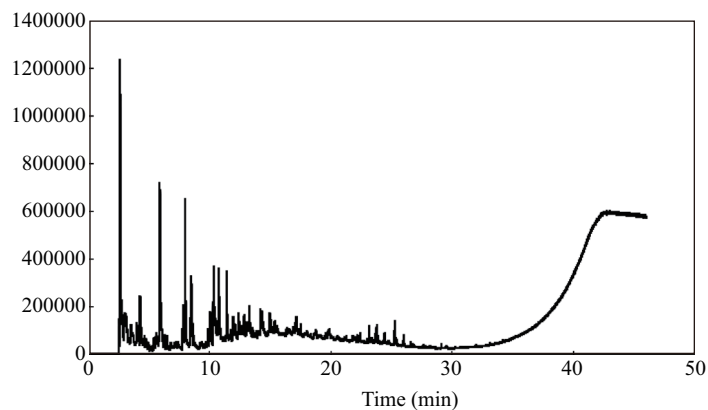


Fig. S3 Pyrogram of HAC.

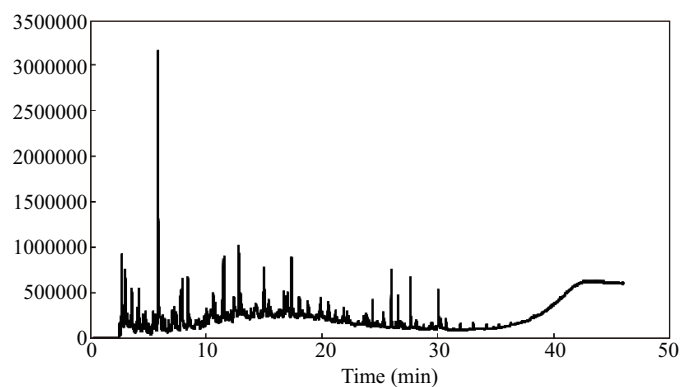


Fig. S4 Pyrogram of HAW.

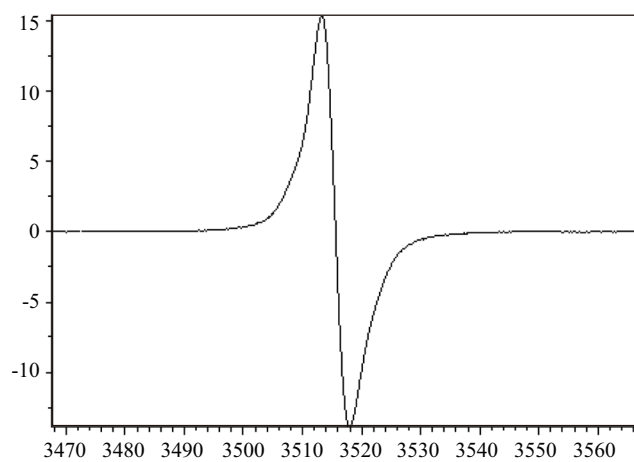


Fig. S5 EPR spectra of HAC.

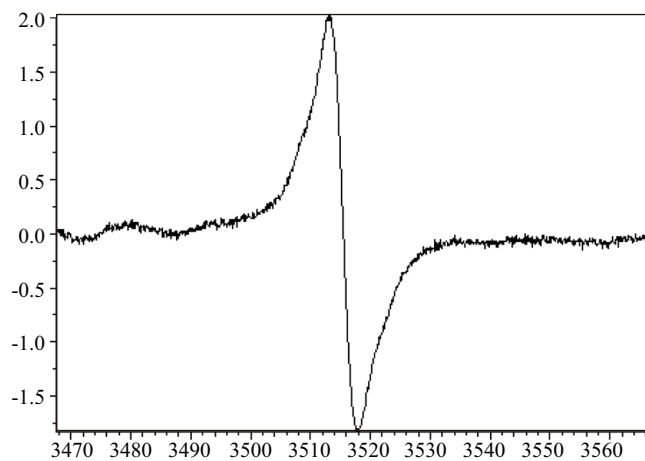


Fig. S6 EPR spectra of HAW.

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Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 3 2013

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Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Distributed by	Domestic Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
Editor-in-chief	Hongxiao Tang	Foreign	Elsevier Limited http://www.elsevier.com/locate/jes
CN 11-2629/X	Domestic postcode: 2-580	Printed by	Beijing Beilin Printing House, 100083, China
		Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742



www.jesc.ac.cn