Comparative characterization of two natural humic acids in the Pearl River Basin, China and their environmental implications

Juan Liu[1,2], Jin Wang[1], Yongheng Chen[1,*], Holger Lippold[2], Johanna Lippmann-Pipke[2]

*1. Key Laboratory of Water Safety and Protection in the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou 510006, China.
E-mail: liujuan858585@163.com
2. Forschungzentrum Dresden Rossendorf, Institute of Radiochemistry, Research Site Leipzig, Leipzig, 04318, Germany*

Abstract

Two humic acids (HAs) were isolated from contaminated river sediments present under comparative conditions in the Pearl River Basin, China. YFHA (the HA extracted at an open pyrite mining area in Yunfu) exhibited a lower absorption intensity for certain bands in the Fourier transform infrared spectra, a lower E_4/E_6 value (the UV absorbances at 465 nm (E_4) and 665 nm (E_6)), a lower apparent molecular weight, a lower polarity and a lower oxygen functionality in comparison with GZHA (the HA isolated at an urban living area in Guangzhou). All these differences indicated a higher degree of humification of YFHA than GZHA. Overall, the enrichment patterns of permanent heavy metals in the studied HAs were similar to those in corresponding sediments. In particular, YFHA exhibited high enrichment of trace element Tl, a characteristic concomitant from the mining of the pyrite minerals. The adsorption isotherms of two HAs for goethite and pyrolusite, two representative geological materials, conformed to the Langmuir equation. Based on the qualitative relationships between the Langmuir constants of the adsorption isotherms and the chemical characteristics of HAs, the main mechanism of HA adsorption on these materials was suggested to be hydrophobic interaction. This study highlighted the promising use of HA as a peculiar bio-indicator of uncommon trace metal contaminations. The HA adsorption mechanism on representative geological materials further provided a theoretical basis for the study on the unusual metal behavior in complex environmental settings.

Key words: humic acid; permanent metal load; adsorption; goethite; pyrolusite

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Introduction

As a predominant fraction of humic substances, humic acids (HAs) are ubiquitous organic materials in terrestrial and aquatic ecosystems. They have a significant influence on the transport and fate of organic and inorganic contaminants (e.g., Stevenson, 1994). For instance, the adsorption of metal ions and organic compounds to both HAs and mineral (hydr)oxides will be altered when the HAs are adsorbed onto the mineral (hydr)oxides. These influences are well-known to depend on the chemical properties of humic macromolecules (Chiou et al., 2000; Saito et al., 2005).

Pertinent studies have been carried out to characterize HAs from soils, waters and sediments (Chen et al., 1978; He et al., 2008; Kim et al., 1990; Fong and Mohamed, 2007). But limited studies are concerned with HAs isolated from sediments of the Pearl River Basin (PRB), China, which is subcoastal in location and influenced by a hot and humid climate. To our knowledge, only three of soil/sediment HAs from Guangzhou suburban areas in the PRB were investigated incidentally with the main focus

on the soil/sediment organic matter (e.g., black carbon, kerogen) (Song et al., 2002, 2005). There are major differences in the genesis, evolution and vegetation cover of the sediments in the PRB and elsewhere. Thus, information derived for HAs from elsewhere will not be entirely applicable to those from the PRB. The characteristics (size, chemical composition and functional groups) may differ considerably, depending on the origin and age of the material (Stevenson, 1994; Fong and Mohamed et al., 2007). As the most stable fraction of organic matter in soils, HA arise by the microbial degradation of plant (and possibly animal) biomolecules dispersed in the environment after the death of living cells. Since these biomolecules have functional groups with the ability to chelate positively charged metal ions, and might still possess the inorganic metals (such as K^+, Mg^{2+}, Fe^{3+}) that once participated in the organism's growth, it is not surprising that HA itself would carry some metals during its formation process. However, an area of persistent metal loads in the HA characterization is largely ignored by previous studies.

The aim of the present article was to determine and compare the key chemical features of two HAs from river sediments under typical comparative conditions (a mining site and a living area) in the PRB; to study and compare

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* Corresponding author. E-mail: chenyheng@eyou.com

the adsorption behavior of the two HAs onto representative geological materials; and to clarify the main mechanism that could control the adsorption of the HAs onto these materials. The HAs were characterized in the terms of the Fourier transform infrared (FT-IR) spectra, the UV absorbances at specific wavelength, the average molecular weight, the elemental composition (C, H, N, S and O) and in particular the permanent metal loads (Al, K, Ca, Mg, Fe, Mn, Zn, Pb, Cu, Cd and Tl). Batch equilibration techniques were also employed to investigate the adsorption of the HAs onto selected geological materials.

1 Materials and methods

1.1 Sediment samples and extraction of humic acids

Two sediments were collected in April 2007 in Guangdong Province, China, an area with typical subtropical monsoon climate. One sediment sample was sampled from a river flowing through an open pyrite mining area, Yunfu (YF sediment). Tl, a rare element with low abundance in the common environment, is distinctively enriched in the pyrite minerals (10–98 μg Tl/g mineral) (Chen et al., 2001). The other sediment sample was sampled from a river in an urban living area, flowing through Guangzhou (GZ sediment). Samples were immediately put in plastic bags to prevent oxidation reactions, and then stored at –4°C. Prior to laboratory analysis, samples were air-dried at room temperature and sieved with nylon sieve to an adequate size (< 80 μm). The physico-chemical characteristics of the sediment samples were analyzed using a procedure reported previously (Yang et al., 2005). The results are listed in Table 1. The extraction and purification of humic acids were performed according to the recommendations of the International Humic Substance Society (Swift, 1996). The isolated quantities of humic acids from sediment samples are also specified in Table 1. The purified HAs were freeze-dried, and ground to fine powders for chemical analysis and adsorption experiments. High-purity water (Ultra Clear, Germany) was used in all experiments. All chemicals were of analytical grade (Sigma-Aldrich, Germany).

Table 1   Basic chemical characteristic of the sediment samples

Sample	pH	TOC (g/kg)	CEC (cmol/kg)	Extraction yield HA (g/kg)
GZ sediment	6.7	26.2	4.4	4.3
YF sediment	3.5	8.4	18.4	3.8

TOC: total organic matter, CEC: cation exchange capacity: HA: humic acid.

1.2 Sorbents

The sorbents used in this study were goethite (α-FeOOH, Fluka, Germany) and pyrolusite (β-MnO$_2$, Fluka, Germany). Specific surface areas of these samples were determined by the BET method, using a Surface Area Analyzer (QSurf S1, Thermo Scientific, USA). The specific surface area was found to be 45 m^2/g for goethite and 0.4

m^2/g for pyrolusite. The point of zero charge of goethite is 7.0 (Gaboriaud and Ehrhardt, 2003) and pyrolusite is 7.3 (Prélot et al., 2003).

1.3 Characterization of humic acids

The FT-IR spectra of KBr pellets prepared by mixing 1 mg of HA material with 100 mg of dry KBr were measured using an FT-IR spectrometer (Tensor 27, Bruker, Germany). A UV/Vis spectrometer (Lambda 25, PerkinElmer, USA) was used to measure the absorbances at 465 nm (E_4) and 665 nm (E_6) to determine the E_4/E_6 ratio. For this purpose, HA solutions (300 mg/L) in 0.05 mol/L NaHCO$_3$ solution (pH 8.34) were prepared.

A size exclusion chromatography (SEC) system equipped with a UV detector (Smartline 2500, Knauer, Germany) was used to determine the average molecular weight of HAs (Gottschalch et al., 2007). Separations were carried out with Fractogel TSK-HW 50F (Supecol, Germany) in a 40 × 16 cm glass column (Pharmacia, Germany) at a flow rate of 40 mL/hr. For analysis, 1 mL of 0.15 g/L solution of HA was injected by means of a Rheodyne valve (IDEX Health and Science, USA). Acetate buffer (pH 6.0) was used as eluent, and sodium perchlorate was added to yield an ionic strength of 0.01. The wavelength for detection was set to 254 nm. Molecular weight calibration was preformed using globular proteins: blue dextran (700 kDa), α-chymotrypsin from bovine pancreas (25 kDa) and vitamin B12 (1352 kDa).

The contents of C, H, N and S were determined with an elemental analyzer (Vario EL III, Elementar, Germany). The oxygen content was estimated as the remaining percentage of the total weight. The total acidity (oxygen functionality) was determined using the barium hydroxide method, and the content of carboxyl groups was measured using the barium acetate method (Ortiz De Serra and Schnitzer, 1973). The content of phenolic hydroxyl groups was calculated by subtracting the content of carboxyl groups from the total content of acidic groups.

For metal analysis, HAs were digested with a mixture of 65% HNO$_3$ and 31% H$_2$O$_2$ in a microwave system (Ethos Plus II, MLS GmbH, Germany) and the digestion solution was then filtered by 0.45 μm membranes (Satorius AG, Germany). Analyses were conducted by ICP-OES (Al, K, Ca, Mg and Fe) with a spectrometer (Spectroflame P/M, Spectro, Germany) and by ICP-MS (Mn, Zn, Pb, Cu, Cd and Tl) using a PQ Excell spectrometer (VG Elemental, UK).

Enrichments of heavy metals in HAs and sediments were assessed on the basis of specifying metal contents as indices of geoaccumulation I_{geo}. The I_{geo} determines the enrichments by comparing current metal contents with a background level. The calculation is expressed as Eq. (1):

$$I_{geo} = \log_2 \frac{C_n}{1.5 B_n} \tag{1}$$

where, C_n is the measured content of a certain heavy metal in the tested sample, and B_n is the geochemical background value in the continental crust (Wedepohl, 1995).

1.4 Adsorption of humic acids onto geological materials

Adsorption experiments were conducted using the batch equilibration technique as follows: 10 mL of HA solution (20 mg/L) in 0.1 mol/L NaClO$_4$ was added to an appropriate amount of solid (pyrolusite 20 mg; goethite:10 mg) in 20 mL plastic vials. For equilibration, the systems were horizontally shaken for 48 hr at 25°C, which was ascertained to be sufficient in time-dependent measurements of HA adsorption. After sedimentation, aliquots were taken for analysis.

Adsorption onto pyrolusite and goethite was determined by a UV/Vis spectrometer (Lambda 25, PerkinElmer, USA), set at a wavelength of 254 nm. Wall adsorption of HAs by plastic vials was found to be negligible. The amount of adsorption at equilibrium, q_e (g/kg), was calculated by Eq. (2):

$$q_e = \frac{C_e(C_0 - C_e)V}{W} \qquad (2)$$

where, C_0 (g/L) and C_e (g/L) are the initial and equilibrium liquid concentrations, respectively, V (L) is the liquid volumes and W (kg) is the weight of dried adsorbent used.

2 Results and discussion

2.1 FT-IR spectra and UV-Vis absorption ratios

The FT-IR spectra of the HAs studied are shown in Fig. 1. The bands at 3400, 2800–3000, 2400, 1715 and 1229 cm^{-1} and shoulders at 1600, 1410 and 1042 cm^{-1} are typical peaks for HAs (Fong and Mohamed, 2007; He et al., 2008). Notably, the bands at 2800–3000 cm^{-1} are stronger for GZHA than for YFHA, indicating that GZHA have higher contents of aliphatic structures. In addition, the bands at 1715 and 1229 cm^{-1} present obviously higher
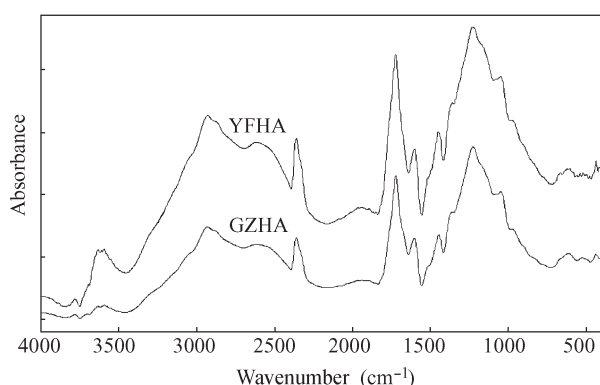

Fig. 1   FT-IR spectra of the studied humic acids.

absorption intensity in GZHA than in YFHA. It may be inferred that the carboxyl groups and phenolic OH groups are as well more abundant in GZHA than that in YFHA.

The E_4/E_6 ratio is inversely related to the degree of condensation of the aromatic network in humic substances (Senesi et al., 1989). The E_4/E_6 value of GZHA (5.20) is slightly higher than that of YFHA (4.85), indicating a lower aromaticity and humification.

2.2 Apparent molecular weight and elemental compositions

As shown in Table 2, the weight-average molecular weight of GZHA (27 kDa) is higher than that of YFHA (16 kDa). This suggests that YFHA has a smaller molecular size. HA, as it is known, is a system of closely related but not completely identical high molecular weight polymers with complex structures. As the humification proceeds, the molecular size of HA becomes smaller (Buffle et al., 1990). Furthermore, the difference in the molecular weight and size of HAs may be attributable to the different conditions under which the HAs were formed. For example, the YF sediment is characterized by low pH values (3.5) and is constantly covered by some sulfide minerals (FeS$_2$) discharged from the pyrite mining sites upstream (Chen et al., 2001). Under these conditions, aerobic degradation by some microbials (*Acidithiobacillus ferrooxidans*) may become important and occur at a significantly accelerated rate (Fong and Mohamed, 2007; Jiang et al., 2006; Tomikawa and Oba, 1991). This degradation might lead to the comparatively low molecular weight of YFHA.

Table 2 shows the elemental compositions of HAs isolated from the sediment samples. The contents of carbon and sulfur of GZHA are lower than those of YFHA. This may be due to a higher degree of humification for YFHA than for GZHA, for the carbon contents of HA is related to the degree of humification (Chen et al., 1978; Kim et al., 1990). Moreover, the high abundance of pyrite (FeS$_2$) in the depositional sediment, from which YFHA were extracted may explain the high sulfur contents of YFHA. The contents of hydrogen, oxygen and nitrogen of GZHA is little higher than that of YFHA.

In order to allow a better comparative characterization of HAs, the C/N, the O/C and H/C atomic ratios of HAs have been calculated. Considering the higher C/N ratio of YFHA than GZHA, the nutrients of YFHA might be poorer and the vegetation might be less degradable than GZHA. The O/C and H/C atomic ratios of GZHA (0.68 and 1.43) are a little higher than those of YFHA (0.62 and 1.07). It can be concluded that the polarity of GZHA is higher than YFHA. Besides, the O/C atomic ratio reflects

Table 2   Apparent molecular weight (MW), elemental compositions and atomic ratios of the studied HAs

Source	MW (KDa)	Elemental composition (wt.%)					Atomic ratio			Reference
		C	H	O	N	S	C/N	O/C	H/C	
GZHA	27	45.6	5.4	41.5	5.3	2.2	10.1	0.68	1.43	This study
YFHA	16	48.1	4.3	40.0	4.8	2.8	11.7	0.62	1.07	This study
Sediment (China)	NG	43.7–51.7	4.1–5.8	31.2–35.7	3.5–6.2	NG	8.1–14	0.62–0.78	0.77–1.2	He et al., 2008
Aldrich company	7.9	57.0	4.4	33.8	1.3	3.5	51.2	0.44	0.93	Gottschalch et al., 2007

NG: not given.

the content of O-containing groups (or the degree of the oxygen functionality), and the H/C atomic ratio inversely corresponds to the content of the aromatic structures and the degree of humification. This is in agreement with the FT-IR spectra and the E_4/E_6 values reported in Section 2.1. Additionally, since the H/C atomic ratios of both the studied HAs are above 1, the aliphatic structures prevail in both of the HAs.

2.3 Total acidity, carboxyl and phenolic hydroxyl group contents

The results of acid-base titrations of the studied HAs as well as purified standard HA from the Aldrich Company are summarized in Table 3. The total acidity of Aldrich HA (6.03 ± 0.45 milli-equivalent per gram (meq)/g) and the content of its carboxyl groups (5.23 ± 0.13 meq/g) in this study were found to be within the range reported elsewhere (Kim et al., 1990; Pompe et al., 1996).

YFHA (COOH (1.05 ± 0.06) meq/g; phenolic OH (0.12 ± 0.19) meq/g) was found to contain much less COOH and phenolic OH compared with GZHA (COOH (3.14 ± 0.09) meq/g; phenolic OH (2.42 ± 0.17) meq/g). Again, these results generally agree with the spectroscopic characteristics in Section 2.1 and the elemental compositions described in Section 2.2. The high acidity of HA from GZ sediment suggest that it has a greater ability of metal complexation than HA from YF sediment. As shown in Table 3, the respective carboxyl and phenolic hydroxyl group contents of YFHA are also much lower than those reported elsewhere (e.g., Chen et al., 1978; ElSayed et al., 1996; Fong and Mohamed, 2007). It could be explained by that large amounts of the carboxyl and phenolic hydroxyl groups of YFHA originally available have been already complexed with the excessive heavy metals released from the mining activity. In addition, as indicated by Saito and Hayano (1980), the phenolic OH content in HAs is related to their origins. The relatively low phenolic OH content in YFHA suggests that it originates from phytoplankton.

2.4 Permanent metal loads of HAs

After acidification during the extraction of HA from samples, the metals which are loosely bound by electrostatic interaction are exchanged by protons, while those which are stably complexed with chelating ligands of

HA are resistant to the conditional changes (Gottschalch et al., 2007). As shown in Table 4, both YFHA and GZHA are mainly loaded with the lithophile elements Al, K, Ca and Mg as well as siderophile Fe. Also, the lithophile metals Cr, Mn and the chalcophile Cu and Zn are bound permanently. It is noteworthy that the contents of almost all analyzed metals are considerably higher in YFHA compared to GZHA. This as well indicates a higher degree of humification for YFHA than GZHA, since the compounds of metals (such as, Al, Fe and Mn) were confirmed to have contributions to the acceleration of the humification process (Bulosan-Atendido et al., 2005).

In order to present a clear regional influence, the elemental distributions of both the HA and the corresponding sediments were normalized to the natural abundances (Wedepohl, 1995) and plotted as I_{geo} in Fig. 2a, b, respectively. The elements were arranged according to the Goldschmidt classification (Goldschmidt, 1937). Both YFHA and GZHA are characterized by a relative enrichment of chalcophile metals. The loading patterns, however, are different. Tl and Pb are enriched in YFHA relative to GZHA, Cu and Cd are depleted. As a rare element, Tl is usually of very low abundant in the natural environments
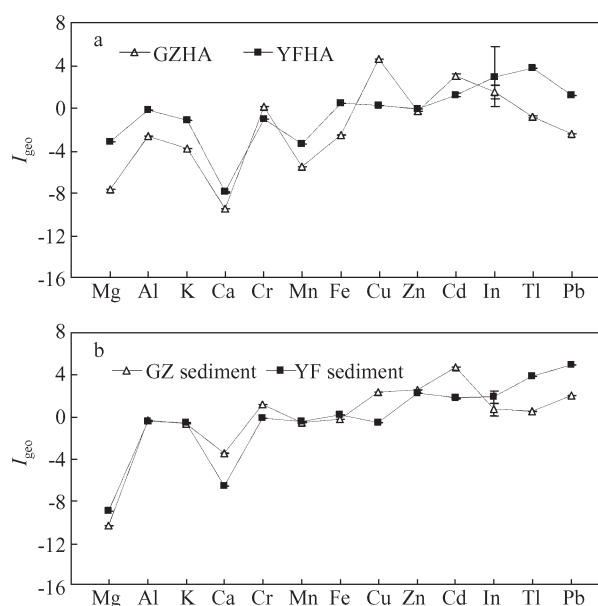

Fig. 2 I_{geo} for the studied humic acids (a) and sediments (b).

Table 3 Acidic functional groups of the humic acids

Source	Total acidity (meq/g)	COOH (meq/g)	Phenolic OH (meq/g)	Reference
GZ sediment	5.56 ± 0.08	3.14 ± 0.09	2.42 ± 0.17	This study
YF sediment	1.17 ± 0.18	1.05 ± 0.06	0.12 ± 0.19	This study
Aldrich company	6.03 ± 0.45	5.23 ± 0.13	0.80 ± 0.47	This study
	7.06 ± 0.67	4.80 ± 0.21	2.26 ± 0.72	Kim et al., 1990
	6.90 ± 0.70	4.74 ± 0.05	3.20 ± 0.70	Pompe et al., 1996
Marine sediment (Japan)	5.80 ± 0.22	3.27 ± 0.13	2.53 ± 0.25	Saito and Hayano, 1980
Sediment (Egypt)	4.20 ± 0.51	2.80 ± 0.51	1.40 ± 0.08	ElSayed et al., 1996
Sediment (Latvia)	NG	2.26 ± 0.54	NG	Klavins and Alpsite, 1997
Soil (Malaysia)	5.84 ± 0.44	3.34 ± 0.19	2.50 ± 0.40	Fong and Mohamed, 2007
Temperate soil	5.70–8.90	1.50–5.70	2.10–5.70	Fong and Mohamed, 2007
Tropical soil	6.20–7.80	2.50–4.50	0.99–3.00	Fong and Mohamed, 2007
Soil (Mediterranean)	6.50–8.03	3.13–4.09	2.41–4.42	Chen et al., 1978

meq/g: milli-equivalent per gram; NG: data are not available.

Table 4 Metal contents of the studied humic acids (HAs) isolated from GZ sediment and YF sediment measured by means of ICP-OES and -MS

	Element	GZHA	YFHA	Aldrich HA[a]
Lithophile	Al (mg/g)	19.40 ± 0.04	102.0 ± 1.1	<0.5
Lithophile	Ca (mg/g)	0.08 ± 0.03	0.24 ± 0.90	0.6
Siderophile	Fe (mg/g)	10.7 ± 0.0	89.0 ± 0.8	3.3
Lithophile	K (mg/g)	2.18 ± 0.02	13.9 ± 0.1	<2
Lithophile	Mg (mg/g)	0.16 ± 0.02	3.71 ± 0.03	<0.1
Chalcophile	Zn (μg/g)	79.8 ± 3.4	90.0 ± 7.1	200
Siderophile	Mn (μg/g)	23.1 ± 0.4	102.0 ± 1.8	NG
Chalcophile	Pb (μg/g)	4.00 ± 2.00	50.4 ± 5.7	NG
Lithophile	Cr (μg/g)	210 ± 1	87.9 ± 1.6	NG
Chalcophile	Cu (μg/g)	927 ± 10	42.0 ± 1.6	<0.2
Chalcophile	Cd (μg/g)	1.15 ± 0.04	0.35 ± 0.01	NG
Chalcophile	Tl (μg/g)	0.44 ± 0.03	10.5 ± 0.2	NG

NG: not given; [a] Lippold et al., 2005.

(Yang et al., 2005). The relative enrichment of Tl in YFHA and the YF sediment may be due to the typical Tl contamination from the mining activities of Tl-bearing pyrite minerals. Pb contamination from mining may also explain its enrichment in YFHA and the YF sediment. Comparatively, Cu and Cd are apparently enriched in GZHA and the GZ sediment. It may due to the contamination of Cu and Cd from industrial and municipal

wastewater discharge. Another significant observation is that the enrichment pattern of heavy metals in the studied HAs is generally identical to that of heavy metals in the corresponding sediments (Fig. 2a, b). Altogether, these indicate that HA could be used as a preservation of distinctive rare elements and provide typical fingerprints of the heavy metal contamination.

2.5 Adsorption isotherm of humic acids onto geological materials

Figure 3 shows the adsorption isotherms of GZHA and YFHA on goethite and pyrolusite, respectively. All data are the average values of triplicate experiments. Two commonly used isotherm equations have been tested in the present study, namely, the two-parameter Langmuir (Eq. (3)) and Freundlich (Eq. (4)) equations.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_F C_e^{1/n} \tag{4}$$

where, q_e (g/kg) is the amount of HA adsorbed to the surface of the geological materials, C_e (g/L) is the equilibrium concentration of HA in solution, and q_{max} is the maximum amount adsorbed to the surface. K_L (L/g) is the Langmuir
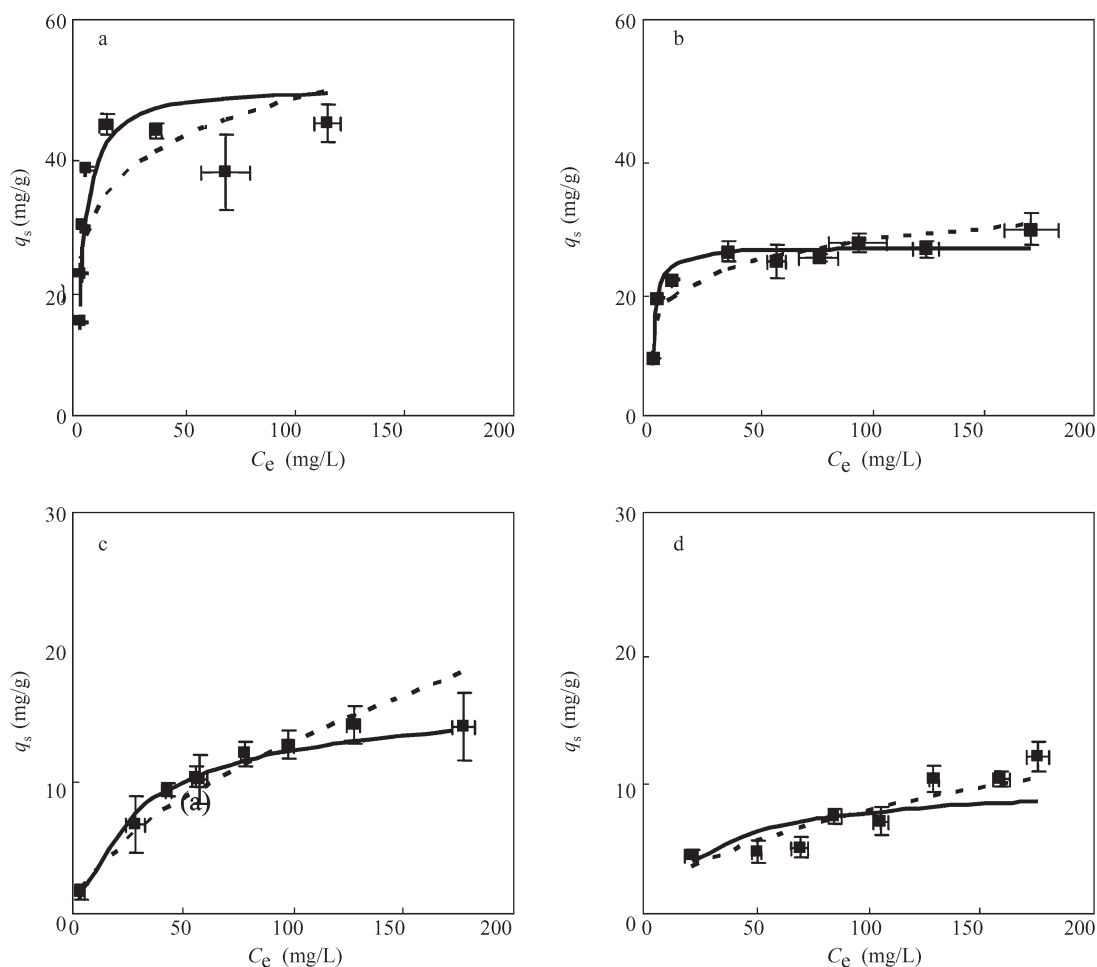

Fig. 3 Adsorption isotherm of the studied HAs onto goethite and pyrolusite at room temperature (25°C). (a) adsorption isotherm of GZHA onto goethite; (b) adsorption isotherm of GZHA onto goethite; (c) adsorption isotherm of GZHA onto pyrolusite; (d) adsorption isotherm of YFHA onto pyrolusite.

Table 5 Model parameters, coefficients of determination (r^2) and standard deviations (SD) for the adsorption of GZHA and YFHA onto goethite and pyrolusite

Adsorbate	Adsorbent	Langmuir				Freundlich			
		K_L (L/g)	q_{max} (mg/g)	SD (%)	r^2	K_L (L/g)	q_{max} (mg/g)	SD (%)	r^2
GZHA	Goethite	36.31	50.06	3.25	0.846	21.05	0.180	7.57	0.595
	Pyrolusite	3.06	16.31	0.33	0.998	0.915	0.577	1.93	0.961
YFHA	Goethite	83.47	25.88	0.36	0.987	12.76	0.163	7.57	0.836
	Pyrolusite	3.63	10.00	5.34	0.602	0.962	0.462	2.78	0.803
Rostherne Mere HA[a]	Goethite	620	16.8	NG	NG	NG	NG	NG	NG
Esthwaite Water HA[a]	Goethite	310	30.1	NG	NG	NG	NG	NG	NG
Aldrich HA[b]	Pyrolusite	0.9	2.1	NG	NG	0.6	0.4	NG	NG

NG: data are not available;
[a] Data are from reference (Tipping, 1981a); [b] data are from reference (Bernard et al., 1997).

equilibrium constant. K_F and n are the Freundlich parameters. The Langmuir and Freundlich parameters as well as the coefficient of determination (r^2) for the adsorption of GZHA and YFHA are listed in Table 5. The quality of the fits is characterized by the standard deviation (SD) between the measured the modeled results, which is calculated as

$$SD = \left(\frac{\sum_{1}^{N} (q_{e,exp} - q_{e,cal})^2}{N - 1} \right)^{1/2} \quad (5)$$

As can be seen in Table 5, the Langmuir equation is more suitable for the description of adsorption isotherms of GZHA on both goethite and pyrolusite and YFHA on goethite, which is also evident from the coefficients of determination and the SD values. The Freundlich equation provides a better description of the adsorption isotherm of YFHA on pyrolusite. The values of Langmuir constants or Freundlich constants are obviously different from those reported elsewhere (Bernard et al., 1997; Tipping, 1981a). The adsorbents used in this study and elsewhere are by and large the same (goethite and pyrolusite), thus this difference might be explained by the dissimilarity of the HAs' characteristics. Furthermore, as shown in Fig. 3, almost all adsorption isotherms exhibited an initial steep "knee", followed by a plateau, indicating a decrease in surface sites participating in adsorption. This behavior is commonly observed for the adsorption of HAs on metal (hydr)oxides (Gu et al., 1994; Polubesova et al., 2008; Saito et al., 2004; Tipping, 1981a, 1981b).

The Langmuir equation is generally a suitable model for all the present systems. It can be seen in Table 5, the K_L (adsorption affinity) values of both GZHA and YFHA on goethite (36.31 L/g and 83.47 L/g, respectively) are comparatively larger than those of the two HAs on pyrolusite (3.06 L/g and 3.63 L/g, respectively). The q_{max} values of both GZHA and YFHA on goethite (50.06 g/kg and 16.31 g/kg, respectively) are generally higher those of the two HAs on pyrolusite (25.88 g/kg and 10.00 g/kg, respectively). This indicates that goethite has a higher adsorption ability for the studied HAs than pyrolusite. This can be explained by the fact that the specific surface area of goethite is larger than that of pyrolusite (45 m²/g for goethite and 0.4 m²/g for pyrolusite). Additionally, the weak-crystalline structure of goethite could promote a higher adsorption capacity of HAs, while the well-crystalline structure of pyrolusite could limit its adsorption

capacity.

The K_L values of GZHA for both goethite and pyrolusite (36.31 L/g and 3.06 L/g, respectively) are smaller than those of YFHA (83.47 L/g and 3.63 L/g, respectively). In contrast, the q_{max} values of GZHA for both of the adsorbents (50.06 g/kg and 25.88 g/kg, respectively) are larger than those of YFHA onto the corresponding adsorbents (16.31 g/kg and 10.00 g/kg, respectively). Factors which may influence adsorption of humic molecules onto metal (hydr)oxides include molecular weight, polarity (hydrophobicity) and acidity (Balcke et al., 2002; Marshall et al., 1998; Polubesova et al., 2008). As stated in Section 2.2, GZHA has a larger molecular weight than YFHA, and the O/C atomic ratio indicates that the polarity of GZHA is slightly higher than that of YFHA. The larger molecular weight of HAs explains the higher q_{max} while the lower polarity explains the higher K_L. The quantitative relationship obtained by Balcke et al. (2002) using 11 well characterized HAs onto kaolin clay also showed that the adsorption affinity (K_L) was inversely correlated with the polarity, and the maximum adsorption capacity (q_{max}) was positively related to the molecular weight. Hydrophobic interaction is the mostly possible adsorption mechanism that could explain these relationships between the Langmuir constants and the parameters of HA chemical characteristics (Balcke et al., 2002). The operating pH (7.0) of the adsorption HA is close to the point of zero charge (PZC) of the studied geological materials. The pH_{PZC} is 7.0 for goethite (Gaboriaud and Ehrhardt, 2003) and 7.3 for pyrolusite (Prélot et al., 2003). Under this condition, the positive surface charge is nearly neutralized, which limits the HA adsorption through ligand exchange but supports hydrophobic interaction.

3 Conclusions

As a result of anthropogenic influences, humic acids (HAs) isolated from river sediments under different contaminated conditions are of different chemical characteristics. YFHA from Yunfu (YF) pyrite mining site is characterized by a lower absorption intensity for specific bands in the FT-IR spectra, a lower E_4/E_6, a smaller size of structure, a lower content of O-containing functional groups, and a lower polarity, compared with GZHA from a typical urban living area in Guangzhou. Altogether, this indicates the higher humification degree of YFHA

than that of GZHA. In the respect of permanent metal loads, two isolated HAs are mainly carried with Al, K, Ca, Mg and Fe, and show an enrichment of chalcophile metals related to the elemental distribution in the continental crust. The enrichment modes of the metals in the studied HAs are generally similar to those in the respective sediment. YFHA are particularly enriched with the rare trace element Tl, a typical incidental contaminant from the mining of pyrite ore. In this way, HA could be used as distinctive fingerprints of the heavy metal contamination. The adsorption isotherms of the HAs for two representative geological materials (goethite and pyrolusite) were found to fit the Langmuir equation. The higher adsorption affinity is attributed to the lower polarity index, while the higher maximum adsorption capacity is related to the larger molecular weight. Hydrophobic interaction is then supposed to be the main mechanism of HA adsorption onto goethite and pyrolusite. This study points out the significance of HAs as a special preservation of characteristic rare metals from anthropogenic activities of regional particularities, and uncovers the possible main mechanism of HA adsorption on representative geological materials. All this lays a theoretical foundation to study the uncommon metal behavior in the complicated natural system.

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