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Influence of humic acids of different origins on oxidation of phenol and chlorophenols by permanganate

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ABSTRACT

The influences of humic acids (HAs) of different origins, including two commercial HAs, three soil HAs and one aquatic HA, on phenols oxidation by permanganate were studied. The apparent second-order rate constants of 2-chlorophenol (2-CP)/phenol oxidation by permanganate in the presence of HAs at pH 7 followed the order of commercial HA (Shanghai) > soil HAs > commercial HA (Fluka) > aquatic HA. Moreover, the commercial HA (Shanghai) could accelerate the oxidation of different chlorophenols (CP) significantly under neutral condition. The FTIR analysis demonstrated greater content of C=C moieties and less amount of carboxylate, aliphatic groups and polysaccharide-like substances in soil HAs than in aqueous HA, suggesting that the increase of aromaticity in HA was beneficial to the oxidation of phenols by permanganate. The apparent second-order rate constants of 2-CP/phenol oxidation by permanganate in the presence of HAs correlated well with specific visible absorption (SVA) at 665 nm of HAs. High positive correlation coefficients ($R^2 > 0.75$) implied that π-electrons of HA strongly influenced the reactivity of 2-CP/phenol towards permanganate oxidation, which agreed well with positive correlation between Fluorescence Regional Integration (FRI) and the apparent second-order rate constants. The π–π interaction between HAs and phenols, the steric hindrance effect and the dissociation of phenols may affect the oxidation of phenols by permanganate in the presence of HA at pH = 7.0.

1. Introduction

Phenolic compounds including chlorinated phenols, which are generated by petroleum and petrochemical, coal conversion, phenol producing industries, biocides, and other chemical processes, are common contaminants in wastewater [1]. The discharge of phenols containing domestic and industrial wastewater has caused the environmental contamination by phenols. Many surface waters [2,3], groundwater [4] and soils [5] have been reported to be contaminated by phenol and chlorophenols. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. Because of their toxicity, the US Environmental Protection Agency (EPA) has designated phenols as priority pollutants [6]. Therefore, the removal of phenols in drinking water treatment process and remediation of phenol-contaminated groundwater are necessary.

Various chemical oxidation processes can be applied to control phenols in water treatment processes and environmental remediation. Although rapid transformation of some phenols can occur during disinfection of wastewater and drinking water using free chlorine, primary products during chlorination could be considered as precursors of disinfectant by-products [7]. Ozonation is highly effective in treating phenols with electron-donating groups, such as hydroxyl, amine and alkyl groups [8]. Gimeno et al. reported that advanced oxidation processes, such as combining ozone and radiation, exerted good efficiencies in the elimination and mineralization of phenols [9]. However, in some cases when bromide coexists in water, ozonation suffers the potential formation of the potent carcinogenic brominated by-products [10]. Fenton reagent, consisting of H_2O_2 and ferrous iron, has been shown to be effective in the degradation of a wide spectrum of organic and inorganic pollutants. The pH optimum for Fenton oxidation is usually reported in the acidic range near pH 3. Therefore, the necessity to acidify the reaction medium limits the applicability of the Fenton process in the environmental technology [11]. Ferrate (Fe(VI); K_2FeO_4) as an environmentally friendly oxidant has recently been able to effectively remove some phenols containing electron-rich moieties [12]. However, the limits of field treatment application of Fe(VI) may be due to its instability in water and/or the difficulty in its preparation and storage. Compared to the above oxidants, permanganate

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is sometimes preferred for phenol oxidation because of its relatively low cost, ease of handling, effectiveness over a wide pH range and comparative stability in the subsurface [13]. More importantly, the oxidation of organic matters using permanganate does not lead to the formation of chlorinated or brominated by-products [14]. Permanganate as a green oxidant, has received more and more attention and been widely used in portable water treatment for enhancing coagulation and removing micropollutants [14–16] and in situ chemical oxidation in remediating phenols-contaminated groundwater and soil [17].

Humic acids (HAs) are ubiquitous organic material in terrestrial and aquatic ecosystems. They possess a highly complex and refractory character, and have the capacity for diverse chemical and physical interactions in the environmental remediation and drinking water treatment processes [18]. It was demonstrated that the presence of HA could enhance or inhibit the removal of organic pollutants in the oxidation reactions such as ozonation, photocatalytic oxidation, Fenton reaction, biomimetic catalytic system and oxidation with manganese oxides [11,19–24]. For the permanganate oxidation process, He et al. recently reported that the presence of a small amount of commercial HA could accelerate phenol oxidation by permanganate and higher molecular weight fractions of HA enhanced phenol removal more significantly than the lower molecular weight fractions under neutral conditions [25]. Jiang et al. found that the presence of HA can improve the oxidation of triclosan by permanganate at pH 5–7 [26]. However, in both studies the authors employed a commercial HA purchased from Shanghai Reagent Co. Ltd., China, which may not be appropriate as analogues of true soil or aqueous humic substances. It is well known that HAs are heterogeneous polyelectrolytes, whose chemical characteristics vary significantly with HA sources [27]. Accordingly, HAs from different sources may produce different effects on oxidation of phenols by permanganate. To identify the influences of HAs on the application of permanganate in water treatment and environmental remediation, it is critical to employ the HAs extracted from corresponding environments, i.e. from aquatic and soil sources. Therefore, the objective of this study is to investigate the influences of three different types of HAs (commercial, soil and aquatic HAs) on the oxidation of phenols with permanganate. Moreover, spectroscopic techniques, including Fourier transform infrared (FTIR), ultraviolet-visible (UV–vis) and fluorescence spectroscopies were employed to characterize HAs. Correlations between the removal of phenols and the chemical properties of HAs were investigated as well.

2. Experimental

2.1. Materials

Potassium permanganate (primary standard reagent grade) and phenols of 99% purity, including phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP), were purchased from Sigma–Aldrich (St. Louis, USA) and used without further purification. All solutions were prepared with Milli-Q water. The $KMnO_4$ crystals were dissolved in Milli-Q water to make a 10 mM stock solution, which were stored in the dark until use (1–3 days). The stock solutions of phenols (2 mM) were freshly prepared for each set of experiments by dissolving a measured quantity of phenols in Milli-Q water to avoid its oxidation by air and its volatilization. The stock solution of sodium thiosulfate (0.1 M) as a scavenger of oxidants was prepared by dissolving a certain quantity of $Na_2S_2O_3$ crystals in Milli-Q water. The ionic strength of all the solutions was kept at 30 mM with KCl.

2.2. Extraction and purification of HAs

Three types of soil HAs (peat soil, leonardite and loam soil), purchased from the International Humic Substances Society, were extracted and purified according to the protocol of International Humic Substances Society (IHSS) [28]. The standard HA from Suwannee River was purchased from IHSS and used without further purification. Two commercial HAs purchased from Shanghai Reagent Co. Ltd., China and Sigma–Aldrich, USA, respectively, were purified by repeated pH adjustment, precipitation, and centrifugation to remove ash, humin, and fulvic acid, completely following the procedure described by Kilduff and Weber [29]. Before the analysis, the powdered HA samples were dehydrated by vacuum drying and stored in a desiccators over silica gel.

2.3. Characterization of HAs

The UV–vis absorbance spectra of HAs of different origins were recorded with a UV–vis spectrophotometer (UV-2550, Shimadzu). All samples were diluted to 5.0 mg L^{-1} as DOC. The measurements were carried out in a 300 mM KCl solution, which was also used as the blank. Specific ultraviolet absorbance (SUVA) and specific visible absorbance (SVA) were calculated by normalizing ultraviolet absorbance and visible absorbance to the DOC concentration, respectively ((mg C $L^{-1})^{-1}$ cm^{-1}). The E_4/E_6 ratios were calculated as the ratio of absorbance at 465 nm and 665 nm [30].

For the collection of fluorescence spectra, a spectrofluorometer (FP-6500, Jasco) was used. The spectrometer used a xenon excitation source, and slits were set to 3 nm for both excitation and emission. To obtain the fluorescence excitation–emission matrix (EEMs), excitation wavelengths were incremented from 250 to 500 nm at 5 nm steps for each excitation wavelength, and the emission was detected from 380 to 600 nm at 1 nm steps. All samples were adjusted to pH 7 and diluted to a final concentration of 2.0 mg L^{-1}. To partially account for Raleigh scattering, the fluorometer's response to a blank solution was subtracted from the fluorescence spectra recorded for samples containing DOC. The blank solution was prepared from Milli-Q water and contained <0.2 mg L^{-1} DOC [31].

Infrared spectra of different types of HAs were collected in transmission mode with a FTIR spectrophotometer (Spectrum One, Perkin Elimer). The freeze-dried HAs were diluted to a concentration of 2% with IR-grade KBr. The FTIR was set to scan from 4000 to 400 cm^{-1} at 1.0 cm^{-1} interval. All spectra of each sample were obtained by subtraction of the background spectra (pure KBr) from the spectra of KBr-mixed sample and normalized after acquisition to a maximum of 1.0 for comparative purpose.

2.4. Chemical analysis

A high performance pH meter with a saturated KCl solution as electrolyte (Corning 350) was used to measure solution pH. Daily calibration with proper buffer solutions (pH 4.00, 6.86 and 9.18) was performed to ensure its accuracy. DOC (mg L^{-1}) of HA was measured by high temperature combustion analysis (Analytik jena, Multi N/C 3100). A high performance liquid chromatography (HPLC) with a UV detector was used for analysis of phenols. The system consisted of a Waters 1525 pump, a Water 717 plus autosampler and 2784 dual λ UV-vis detector. Separation was accomplished with Atlantic C18 column (4.6 nm × 150 nm, 3 μm; Waters) and a mobile phase of methanol:water (between 45:55 and 65:35). The flow rate was 1 mL min^{-1}. Concentrations of phenols were determined by comparing peak area at 270–305 nm with that of standards of phenols, respectively.

2.5. Batch experiments

The experiments on the kinetics of phenol oxidation by $KMnO_4$ were conducted in brown glass bottles with stopple. The headspace of glass bottles to aqueous phase ratio was 1:10 by volume. All the experiments were carried out at 19 °C (±1.0 °C). In a typical experiment, a 200 mL of phenol solution containing pre-determined concentration of HA was prepared in a batch reactor. The experiments were initiated after addition of an aliquot of the oxidant stock solution into the reactor while stirring and the reaction time was 45 min. For the kinetic study, at fixed time intervals, 10 mL of sample was rapidly transferred with a syringe, terminated with 100 μL of sodium thiosulfate (100 mM) immediately and filtered with membrane (pore size: 0.2 μm). The concentration of residual phenol was analyzed directly by HPLC. No phosphate buffer was used to control pH value in the experiments, mainly because the phosphate buffer could prevent flocculation of colloidal particles of manganese dioxide (MnO_2) produced during the oxidations with $KMnO_4$, which resulted in the colloidal MnO_2 not removed by filtration efficiently [13,32]. The residual MnO_2 could still oxidize a small fraction of phenol, which may affect the analysis of phenol with HPLC [33]. Thus, all the experiments were carried out to control initial pH (7.0 ± 0.1) for consistency.

3. Results and discussion

3.1. Oxidation of phenol and 2-chlorophenol

The effects of HAs (2.0 mg L^{-1} as DOC) of different origins on phenol oxidation by permanganate were investigated, as illustrated in Fig. 1. In the absence of HAs, the residual concentration of phenol was 5.35 μM at the end of the reaction. In the case where Shanghai commercial HA (HA_{SH}) and Fluka HA (HA_F) were present, the residual concentrations were 1.13 μM and 4.76 μM, respectively. The remarkable differences in phenol removal could result from the quite different properties of commercial HAs. On the other hand, the influences of HAs extracted from soil on the oxidation of phenol with permanganate were similar. The residual concentrations of phenol were 3.33 μM, 3.01 μM and 2.96 μM in the presence of peat soil HA (HA_{PS}), leonardite HA (HA_L) and loam soil HA (HA_{LS}), respectively. However, phenol oxidation by permanganate was slightly inhibited by the presence of aquatic HA and the residual phenol concentration was 5.83 μM in the presence of Suwannee River HA (HA_{SR}).

The influence of different types of HAs (2.0 mg L^{-1} as DOC) on the 2-CP oxidation by permanganate were also examined and shown in Fig. 2. The presence of chlorine substituent can influence the reactivity of chlorophenols (CPs) towards permanganate oxidation by resonance and inductive effects [7]. The resonance effects enhance the density of electron cloud of the aromatic ring, which can increase the oxidation rate of CPs by electronphilic agent, while inductive effects decrease the density of electron cloud. For chlorine substituent, the resonance effects are stronger than inductive effects, and thus 2-CP is more easily oxidized by permanganate compared to phenol, as revealed by Fig. 2. Fig. 2 also showed that the presence of HAs except HA_{SR} could accelerate the oxidation of 2-CP by permanganate to different extents.

Previous studies drew the conclusion that the reaction of permanganate with phenol was second-order and first order with respect to phenol and permanganate in the presence of HA_{SH} [25]. Therefore, it can be assumed that the reaction of phenol with permanganate in the presence of HA of different origins also follows a second-order reaction and first order in each reactant. When the concentration of permanganate is present in excess, the rate of phenol oxidation can be simplified to Eqs. (1) and (2).

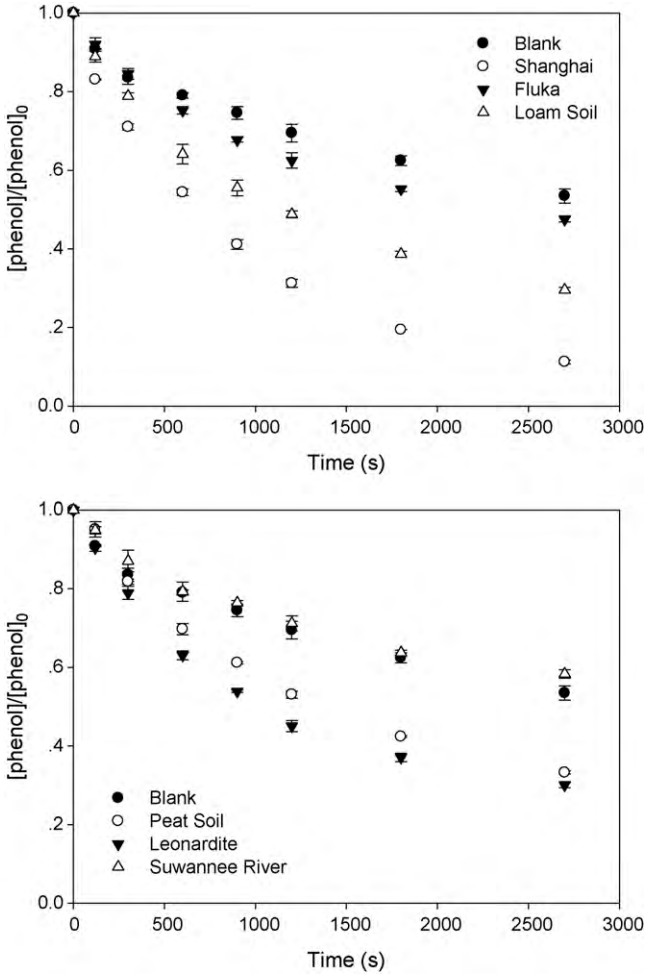

Fig. 1. The kinetics of phenol oxidation by permanganate in the presence of HAs from different origins. Experimental conditions: $[KMnO_4]_0$ = 50 μM, $[phenol]_0$ = 10 μM, $[HAs]_0$ = 2 mg L^{-1} as DOC, initial pH = 7.0 ± 0.1.

$$-\frac{d[\text{phenol}]}{dt} = k_{app}[MnO_4^-][\text{phenol}] = k_{obs}[\text{phenol}] \quad (1)$$

$$k_{obs} = k_{app}[MnO_4^-]_0 \quad (2)$$

where k_{obs} is the pseudo-first-order rate constant (s^{-1}) at pH 7 and $[MnO_4^-]_0$ is the initial permanganate concentration, which can be considered constant; k_{app} is the apparent second-order rate constant (M^{-1} s^{-1}). The values of k_{app} in these experiments were calculated by non-linear regression analysis ($R^2 > 0.95$) and summarized in Table 1. Table 1 shows that the apparent second-order rate constants of phenol oxidation by permanganate in the presence of HAs follow the order of $HA_{SH} > HA_L > HA_{LS} > HA_{PS} > HA_F > HA_{SR}$ under neutral condition. In the presence of HAs, the apparent second-order rate constants of 2-CP oxidation by permanganate follow the order of $HA_{SH} > HA_{LS} > HA_L > HA_{PS} > HA_F > HA_{SR}$, which is quite similar to the order of phenol oxidation in the presence of various HAs. The enhancement of phenol/2-CP oxidation due to the presence of HAs was quantified by the ratio of k_{app} of phenol/2-CP oxidation in the presence of HA to that of its counterpart (r_{HA}), as summarized in Table 1. Obviously, the improvement of phenol/2-CP oxidation induced by HAs followed the order of HA_{SH} > Soil HAs > HA_F > HA_{SR}.

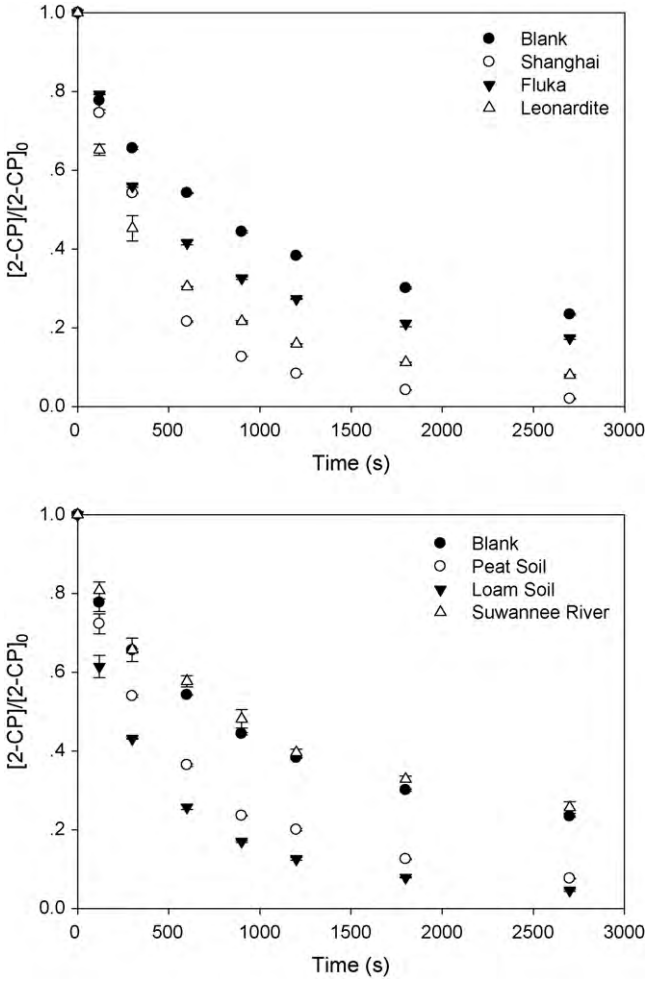

Fig. 2. The kinetics of 2-CP oxidation by permanganate in the presence of HAs from different origins. Experimental conditions: $[KMnO_4]_0 = 50\ \mu M$, $[2\text{-CP}]_0 = 10\ \mu M$, $[HAs]_0 = 2\ mg\ L^{-1}$ as DOC, initial pH = 7.0 ± 0.1.

Table 1
Summary of kinetic rate constants of oxidation of phenol and 2-CP by permanganate in the presence of HAs from different origins[a].

Contaminants	Origins of HA	k_{obs} ($\times 1000\ s^{-1}$)	k_{app} ($M^{-1}\ s^{-1}$)	R^2	r_{HA}
Phenol	–	0.23	4.60	0.952	–
	Fluka	0.30	6.00	0.953	1.30
	Peat soil	0.47	9.40	0.98	2.04
	Leonardite	0.56	11.20	0.963	2.43
	Loam soil	0.52	10.40	0.972	2.26
	Shanghai	0.81	16.20	0.99	3.52
	Suwannee River	0.21	4.20	0.941	0.91
2-CP	–	0.68	13.58	0.939	–
	Fluka	1.08	21.59	0.995	1.59
	Peat soil	1.50	30.02	0.927	2.21
	Leonardite	1.81	36.22	0.971	2.67
	Loam soil	2.22	44.33	0.948	3.26
	Shanghai	2.27	45.44	0.962	3.35
	Suwannee River	0.62	12.40	0.927	0.91

[a] Experimental conditions: $[KMnO_4]_0 = 50\ \mu M$, $[phenols]_0 = 10\ \mu M$, $[HAs]_0 = 2\ mg\ L^{-1}$ as DOC, initial pH = 7.0 ± 0.1.

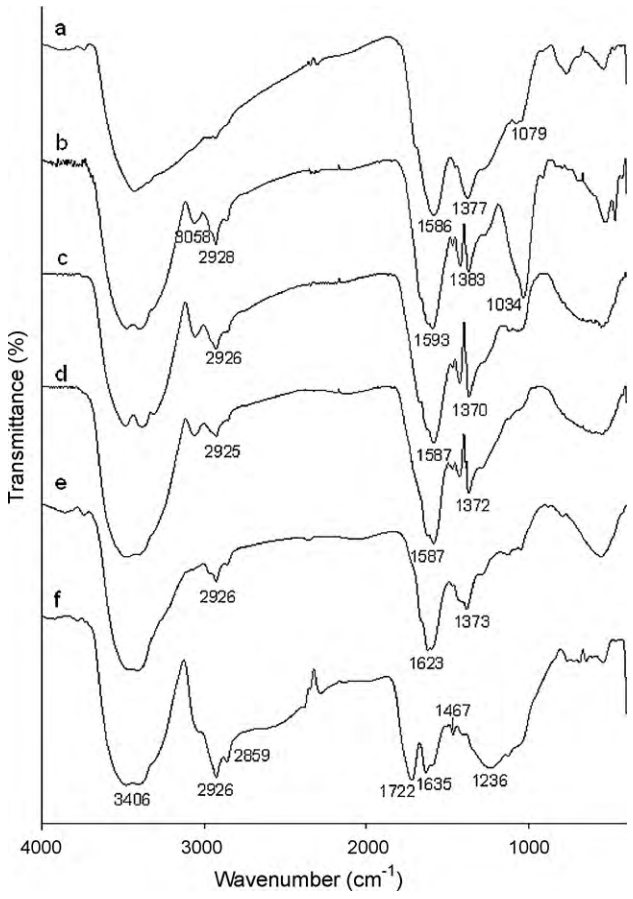

Fig. 3. FTIR spectra of HAs from different origins: (a) Shanghai commercial; (b) Fluka commercial; (c) Peat soil; (d) Leonardite; (e) Loam soil; and (f) Suwannee River.

3.2. FTIR spectroscopic analysis

The FTIR spectra of HAs of different origins were collected and shown in Fig. 3. All spectra had a broad band around 3400 cm^{-1}, which was generally attributed to the ν(O–H) vibration of carboxylic and alcoholic groups under different conditions [34]. On the other hand, the peaks at around 2930 and 2850 cm^{-1} were assigned to asymmetric and symmetric C–H stretching motions of aliphatic groups [34]. These bands in HA_{SR} were more intense than those in HA from other origins, indicating that the aliphatic nature of HA from Suwannee River was more remarkable than that of HAs from soils and commercial HAs.

In general, the profiles of all the spectra were dominated by two very prominent bands appearing at around 1600 and 1400 cm^{-1}. The band appearing at ~1600 cm^{-1} was attributed to vibrations corresponding to aromatic C=C stretching and olefinic carbon–carbon bands, together with the asymmetric COO^- stretching vibration [35,36]. The intensity of band at ~1600 cm^{-1} was lower in HA_{SR} than that in other types of HAs, which may be related to a decrease in C=C moieties in HA from aqueous environment. The band ~1400 cm^{-1} could be assigned to the symmetric COO^- stretching vibrations and to the bending vibrations of aliphatic groups. The band at ~1400 cm^{-1} in HA_{SR} was much less intense than that in HAs from other origins, while the band at approximately 1720 cm^{-1} in HA_{SR} was much more intense, which commonly assigned to ν(C=O) motion in carboxyl groups [37]. Thus, it was demonstrated that the content of carboxyl groups in aqueous HA still accounted for a large proportion. Furthermore, less intense bands appeared in these spectra at the following frequencies: one at approximately 1280 cm^{-1}, assigned to the C–O

Table 2
The UV–vis properties of HAs from different origins[a].

HAs	SUVA[b], 254 nm	SVA[c], 465 nm	SVA[c], 665 nm	E_4/E_6 [d]
Shanghai	9.04	1.60	0.34	4.71
Fluka	8.35	1.30	0.18	7.22
Peat soil	7.27	0.96	0.13	7.38
Leonardite	8.33	1.29	0.14	9.21
Loam soil	6.94	1.25	0.27	4.63
Suwannee River	6.30	0.45	0.08	5.63

[a] Experimental conditions: initial pH = 7.0 ± 0.1.
[b] Specific ultraviolet absorption [(mg C L^{-1})$^{-1}$ cm^{-1}].
[c] Specific visible absorption [(mg C L^{-1})$^{-1}$ cm^{-1}].
[d] Ratio of absorbance at 465 nm to absorbance at 665 nm.

stretching of phenolic group bands [35]; another at 1466 cm^{-1}, which could be attributed to $\delta(CH_2)$ and $\delta(CH_3)$ vibrations of aliphatic groups.

The bands in the 900–1200 cm^{-1} region were usually attributed to C–O stretching vibrations of polysaccharide or polysaccharide-like substances [38]. The aliphatic and polysaccharide-like character represented by bands at 2925 cm^{-1} and 1075 cm^{-1} became stronger in HA_{SR} and HA_F, respectively. In addition, the intensity of bands in the 900–1200 cm^{-1} region was more intensive in HA_{SR} than that in other types of HAs. In summary, the FTIR spectra of HAs of different origins showed that aqueous HA contained less C=C moieties but more carboxyl, aliphatic groups and polysaccharide-like substances than those in soil HAs. For the commercial HAs, the contents of polysaccharide-like substances were much higher in HA_F than those in HA_{SH}. Considering the effects of HAs of different origins on the oxidation of phenol and 2-CP by permanganate, it could be concluded that the increase in the contents of carboxyl, aliphatic groups and polysaccharide-like substances and decrease of C=C moieties in HAs resulted in little or no enhancement in the oxidation of phenol and 2-CP by permanganate under neutral conditions.

3.3. UV-vis and fluorescence spectroscopic analysis

HA generally shows strong absorbance in the UV–vis range, particularly in the UV region, because of the presence of aromatic chromophores and/or other organic compounds [39,40]. The SUVA of HAs of different origins at 254 nm, SVA at 465 nm, SVA at 665 nm and E_4/E_6 ratios were calculated and summarized in Table 2. The UV absorbance at 254 nm is commonly used to determine the relative abundance of aromatic C=C content of natural organic matter (NOM) because π–π^* transitions in substituted benzenes or polyphenols occur in this wavelength region [39]. SVA at 465 nm or 665 nm can also be used to determine extent of π-electron, and high SVA correlates well with great number of aromatic rings or long conjugated bonds in aromatic structure. The ratios of absorbance at 465 nm to 665 nm, commonly referred to as the E_4/E_6 ratios, are characteristic of the extent of humification and molecular weight of humic substances (HSs) [41]. Correlation analysis revealed that the apparent second-order rate constants of phenol/2-CP oxidation by permanganate in the presence of HAs correlated poorly with the SUVA of various HAs at 254 nm or 465 nm, the E_4/E_6 ratios of various HAs. However, the apparent second-order rate constants of the oxidation of phenol and 2-CP by permanganate in the presence of HA correlated well with SVA at 665 nm of HAs of different origins, as demonstrated in Fig. 4a. It suggests that increase in the SVA at 665 nm of HAs results in enhancement in the reactivity between permanganate and 2-CP/phenol. The positive correlations between the reaction rates of 2-CP/phenol with permanganate and the UV–vis absorbance of HA at 665 nm indicate the importance of electron-rich carbon–carbon double bonds within HA for the oxidation of 2-CP/phenol by permanganate. It demonstrates that

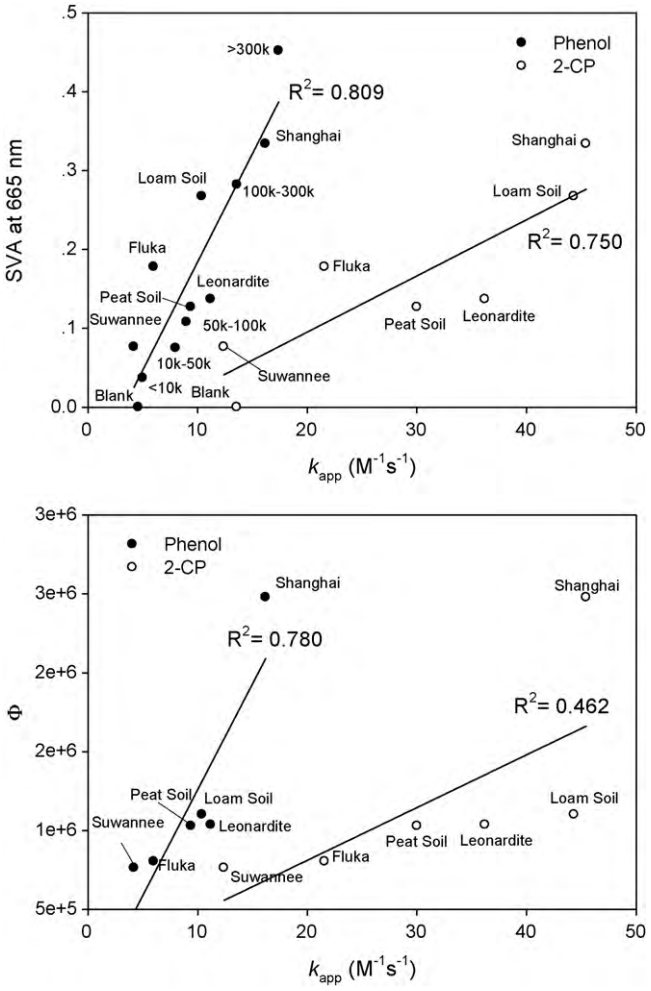

Fig. 4. Correlation between the apparent second-order rate constants of 2-CP/phenol oxidation by permanganate with (a) SVA at 665 nm and (b) FRI volume. Experimental conditions: pH = 7.0 ± 0.1.

the reactions between permanganate and 2-CP/phenol are greatly affected by HAs with large extent of π-electron, such as the great number of aromatic rings or long conjugated bonds in HA structure. In addition, it was observed that with increasing SVA of HAs, enhancement of reaction rates of 2-CP was more remarkable than that of phenol, which was attributed to the strong complexation between 2-CP and HAs. The substitution of chlorine atoms on aromatic ring increased phenol hydrophobicity and formed strong binding between HAs, which might be beneficial for electronphilic attack on the aromatic rings [42].

The fluorescence excitation–emission matrix spectra of HAs from different origins were collected and presented in Fig. 5. The fluorescence intensity of NOM appeared to be related with the molecular weight and polycondensation of aromatic compounds within NOM macromolecules [41]. However, NOM-related literature lacks analytical techniques capable of quantifying intensity of multiple broad-shaped EEM peaks. Fluorescence Regional Integration (FRI), a quantitative technique that integrates the volume beneath an EEM was developed to analyze EEMs quantitatively [31]. The volume (Φ) beneath region of the EEM can be calculated with

$$\Phi = \int_{ex}\int_{em} I(\lambda_{ex}\lambda_{em})\, d\lambda_{ex}\, d\lambda_{em} \quad (3)$$

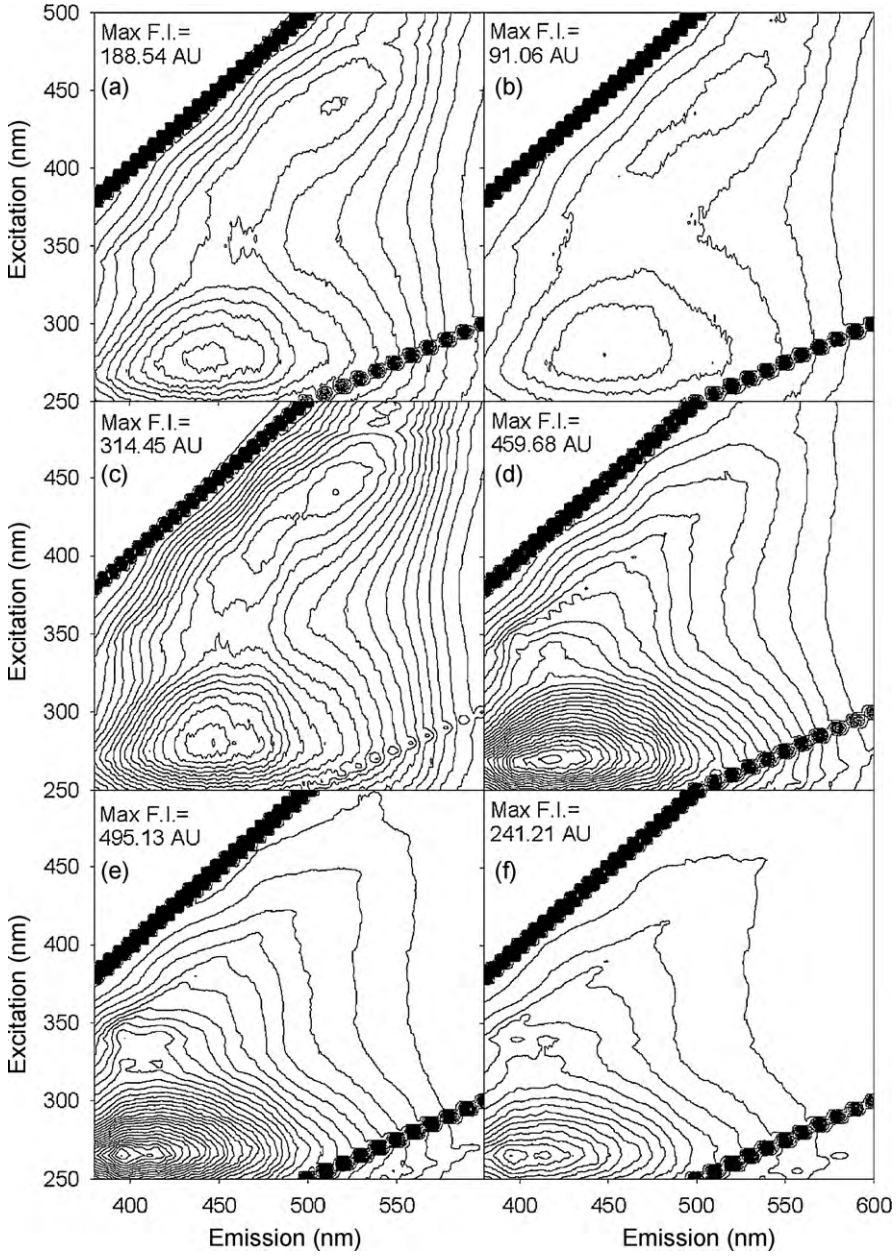

Fig. 5. Fluorescence excitation–emission matrix spectra of HAs from different origin: (a) Shanghai commercial; (b) Fluka commercial; (c) Peat soil; (d) Leonardite; (e) Loam soil; and (f) Suwannee River. Experimental conditions: $[HA]_0 = 1.0\,mg\,L^{-1}$ as DOC, pH = 7.0 ± 0.1.

For discrete data, the volume (Φ) was expressed by

$$\Phi = \sum_{ex}\sum_{em} I(\lambda_{ex}\lambda_{em})\ \Delta\lambda_{ex}\,\Delta\lambda_{em} \quad (4)$$

in which $\Delta\lambda_{ex}$ is the excitation wavelength interval (taken as 5 nm), $\Delta\lambda_{em}$ is the emission wavelength interval (taken as 1 nm), and $I(\lambda_{ex}\lambda_{em})$ is the fluorescence intensity at each excitation–emission wavelength pair. Within FRI regions, 11,000 wavelength-dependent fluorescence intensity data points are represented. All Φ values were normalized to a DOC concentration of $1\,mg\,L^{-1}$ for comparison of EEMs from different sources of HAs. The DOC-normalized FRI volumes of HAs of different origins have a unit of $AU\,nm^2\,(mg\,L^{-1}\,C)^{-1}$.

As reported by Chen et al. [41], low fluorescence intensity might be due to the depletion of its aromatic and/or polyphenolic contents, and also due to the enrichment of its carbohydrate materials, which do not give fluorescence. FTIR analysis showed that aqueous HA contained less C=C moieties but more carboxyl, aliphatic groups and polysaccharide-like substances, which resulted in the lower FRI volume of aquatic HA compared to that of soil HAs. Fluka HA also had low FRI volume, which could be attributed to high content in polysaccharide-like structure. The positive correlations between the reaction rates of phenol/2-CP with permanganate and FRI volume, as illustrated in Fig. 4b, indicated that HA which possess a greater degree of conjugation could be much more beneficial to the oxidation of phenol by permanganate, which corresponds well with the information offered by UV-vis spectroscopy. However, FRI volumes of HAs were less related to its reactivity between 2-CP/phenol and permanganate than SVA at 665 nm. One possible reason is that FRI technique does not pull out the fluorescence properties that are related to other functional groups (hydroxyl or carboxyl groups) or molecular weight [43]. In addition, the above results also imply that some easily measured parameters of HA, such as SVA at 665 nm or FRI volume, are powerful indicators for

Table 3
Summary of kinetic rate constants of oxidation of different CPs by permanganate in the presence of HA_{SH} [a].

Contaminants	$[HA]_0$ (mg L^{-1}) as DOC	k_{obs} ($\times 1000\ s^{-1}$)	k_{app} ($M^{-1}\ s^{-1}$)	R^2	pK_a	r_{HA}
Phenol	0.0	0.23	4.60	0.952	9.89	–
	2.0	0.81	16.20	0.99		3.52
2-CP	0.0	0.68	13.58	0.939	8.56	–
	2.0	2.22	44.33	0.995		3.26
4-CP	0.0	0.42	8.38	0.955	9.2	–
	2.0	1.53	30.52	0.998		3.64
2,4-DCP	0.0	0.81	16.23	0.979	7.89	–
	2.0	3.04	60.84	0.986		3.75
2,6-DCP	0.0	0.98	19.63	0.998	6.8	–
	2.0	5.08	101.71	0.987		5.18
TCP	0.0	0.97	19.41	0.992	5.99	–
	2.0	4.60	91.92	0.951		4.74
PCP	0.0	0.03	0.60	0.976	4.7	–
	2.0	0.10	1.96	0.979		3.27

[a] Experimental conditions: $[KMnO_4]_0 = 50\ \mu M$, $[phenols]_0 = 10\ \mu M$, initial pH = 7.0 ± 0.1.

reaction rate between permanganate and 2-CP/phenol, although HA is heterogeneous in nature.

3.4. Oxidation of CPs

Considering the noted positive effects of HA_{SH} on 2-CP/phenol oxidation by permanganate, the influence of HA_{SH} on the oxidation of other chlorophenols was also studied. The kinetic parameters of phenol and chlorophenols oxidation by permanganate in the absence or presence of HAs were summarized in Table 3. In the absence of HA_{SH}, apparent second-rate reaction rate of permanganate with chlorophenols was increased from 4.6 to 19.63 $M^{-1}\ s^{-1}$ with increasing the number of chlorine substitutes on the aromatic ring from three to five; however, further increasing in the number of chlorine substitutes from three to five resulted in a dramatically decline in apparent second-rate reaction rates from 19.41 to 0.60 $M^{-1}\ s^{-1}$, which could be attributed to the fact that five chlorine substitutes on the ring exerted stereo-hindrance effect on the oxidation of PCP by permanganate. In the case where HA_{SH} was present, the enhancement (r_{HA}) of oxidation rate of CPs by permanganate were different, as illustrated in Table 3. As reported by Smejkalova et al. [42] and Nanny and Maza [44], phenols could interact with HAs via hydrophobic sorption besides π–π interactions. Sorption of phenols to HAs can be understood as a partitioning between water and the hydrophobic domains of HAs [45]. The Henry equation connects the loading q (in μg/kg DOC) of phenol to dissolved organic matter and the equilibrium concentration β (in μg/L) of the free phenol in the liquid phase [46].

$$q = K_{oc}\beta(\mathrm{Phe})_{eq}$$

where K_{OC} is the sorption coefficient of phenol to dissolved organic matter. The sorption of phenols to HA was evaluated based on the data presented by Ohlenbusch et al. [46] and the results indicated that the fraction of phenols sorbed to 2 mg/L humic acid was <0.01% of the total phenols. Although it is suspected that sorption of the phenols to HA is related with the observed rate enhancement of their oxidation by permanganate, it cannot be proven by experimental results so far. Besides hydrophobic sorption, there should be non-covalent interactions, such as π–π interactions between HA and phenols. π–π interactions are the interactions between the aromatic ring of phenols and aromatic components of HAs [44]. Although the presence of HAs could increase the van der Waals repulsion between phenols and permanganate [47], the π–π interaction between HAs and phenols could enhance the electron density of aromatic ring of phenols, which is beneficial to the eletrophilic attack by permanganate to phenols and can enhance the oxidation of phenols. According to the information offered in Table 3, there are other factors, including the steric hindrance effect (PCP) and the dissociation of phenols, affecting the oxidation of phenols by permanganate in the presence of HA at pH = 7.0. Compared to the case where HA_{SH} was absent, the apparent second-rate reaction rates of 2-CP, 4-CP, 2,4-DCP, 2,6-DCP, TCP and PCP in the presence of HA_{SH} were improved to 44.33, 30.52, 60.84, 101.71, 91.92 and 1.96 $M^{-1}\ s^{-1}$, respectively, suggesting that the performance of permanganate in remediating groundwater polluted by CPs could be enhanced by dosing HA_{SH} together with permanganate.

4. Conclusion

This study revealed that the influences of HA on oxidation of phenols by permanganate were strongly dependent on the resource of HAs. Although HA from Suwannee River (HA_{SR}) exerted slightly inhibitive effects on the oxidation of phenol/2-CP by permanganate, the soil HAs and two commercial HAs could enhance the oxidation of phenol/2-CP significantly. The FTIR analysis revealed greater content of C=C moieties and less amount of carboxylate, aliphatic groups and polysaccharide-like substances in soil HA than those in aqueous HA, suggesting that the increase in HA aromaticity was beneficial to the oxidation of phenols by permanganate. The apparent second-order rate constants of 2-CP/phenol oxidation by permanganate in the presence of HAs correlated well with SVA at 665 nm of HAs. High positive correlation coefficients ($R^2 > 0.75$) implied that π-electrons of HA strongly influenced the reactivity of 2-CP/phenol towards permanganate oxidation, which agreed well with positive correlation between FTIR and the apparent second-order rate constants. Moreover, the commercial HA_{SH} could accelerate the oxidation of different CPs by permanganate significantly. The oxidation of phenols by permanganate in the presence of HA could be affected by the π–π interaction between HAs and phenols, the steric hindrance effect and the dissociation of phenols. The results of oxidation of CPs indicated that the performance of permanganate in remediating groundwater, polluted by CPs, might be enhanced by dosing some commercial HAs (e.g. HA_{SH}).

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