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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.