Research Article

Spectroscopic Investigations of the Oxidative Polymerization of Hydroquinone in the Presence of Hexavalent Chromium

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Polyphenol polymerization receives much scientific attentions because it is an important reaction of humification processes. Through an oxidative polymerization reaction (OPR), hydroquinone (H_2Q), a naturally occurring compound, has been found to be a vital precursor of humic substances in soils. Chromate (Cr(VI)), a strong oxidant, is widely distributed in the environment due to the inappropriate disposal of Cr-containing wastes. The OPR of H_2Q in the presence of Cr(VI) may occur naturally. In the study, it was found that $400\,mg\,L^{-1}$ H_2Q could be polymerized at pH 3.0 with $105\,mg\,L^{-1}$ Cr(VI). The results of FT-IR revealed the presence of both hydroquinone and benzoquinone nuclei in the polymer. The spectra of X-ray absorption near edge structure (XANES) demonstrated a decrease in Cr(VI) content during the OPR of H_2Q. Based on the results of linear combination fitting (LCF) for the spectra of XANES, the proportions of Cr species in the precipitates mainly consisted of $Cr(OH)_3$, and Cr-carboxylate contents increased gradually from 15.3 to 25.5% over the reaction time. After acidizing the supernatants at pH 1.0 for 1 d, Cr(III)-HA dominated Cr(III) species. This suggested that humic-like substances were formed during OPR of H_2Q, possibly through the formation of Cr(III)-organic complex.

1. Introduction

Polyphenols exist in both terrestrial and aquatic environments and are an important precursor of humic substances (HSs)—the crucial components of soil organic matter [1–6]. Oxidative polymerization of polyphenols involving soil minerals has been considered as one of the important abiotic humification processes in soils, leading to the formation of HSs [3, 6–8]. The HS, a heterogeneous and complicated macromolecule with active oxygen-containing functional groups, such as hydroxyl, carboxyl, and carbonyl groups, exhibits a variety of colloidal behaviors (e.g., adsorption, ion-exchange, chelation, and soil-buffering capacity) and chemical/physical activities [9–12]. Their presences in the environment can regulate numerous biological and physical-chemical reactions involving nutrients and pollutants. HSs are classified into three major fractions of humic acid, fulvic acid, and humin depending on their solubility in acidic or alkaline solutions. Humic acid is soluble in a basic solution and fulvic acid is soluble at all pH ranges, but humin

is basically an insoluble molecule enriched with aliphatic domains [13, 14]. Because oxidative polymerization reactions can convert simple organic compounds to humic-like macromolecules/polymers with chemical properties similar to that of humic acid [7, 15–17], exposure of an alternative process of contributing to HS formations is required to fully understand the humification process in soils.

Hydroquinone (H_2Q), a metabolic product of plant materials in soils, is an isomer of polyphenolic compounds [18]. H_2Q is widely distributed in the ecological environments because it is a natural occurring compound and is commonly used in tanning, flavoring agents, medicine, cosmetics, photography, and pesticide productions [18, 19]. Due to its high toxicity and low degradability, H_2Q is considered as an organic pollutant by the US Environmental Protection Agency (EPA) [19–21]. The H_2Q could be catalytically transformed to organic polymers by soil minerals, such as metal oxides, including Fe, Al, Mn oxides, and layer silicates [22]. Among these metal oxides, birnessite (δ-MnO_2) had been confirmed as an efficient material capable of accelerating the

conversion of phenolic compounds, such as H_2Q, to humic-like polymers with a relatively high degree of humification [1, 16, 17, 23].

Although several soil minerals can convert polyphenol to humic-like substances via oxidative polymerization reactions, the effects of other powerful oxidants, for example, Cr(VI), on polyphenol polymerization of H_2Q remain unclear. Chromium is extensively used in industries, such as stainless steeling, plate processing, leather tanning, wood treatment, and pigments [24–26]. It has multiple oxidation states, but only Cr(III) and Cr(VI) are stable in the environments [27–29]. Cr(VI) is toxic to humans, animals, and plants and is highly soluble and mobile. In contrast, Cr(III) is less toxic and an essential trace element in human daily nutrition and is insoluble with the form of $Cr(OH)_3$ or soluble Cr(III)-organic complexes [27, 28, 30]. Cr(VI) is a widely distributed contaminant in the environments due to the inappropriate handling and disposal of Cr-containing wastes from various industrial processes [31, 32]. Because Cr(VI) is a potential hazardous element and a major environmental contaminant [30, 33], the conversion of Cr(VI) to Cr(III) in the Cr-contaminated media is a relatively important issue to minimize the threat of Cr(VI) to ecosystems [27, 34]. Cr(VI) can be reduced to Cr(III) by various reductants, such as Fe(0), Fe(II), and sulfide [34–36]. In addition, it is well known that the soil organic matter with various activated functional groups, such as phenolic and carboxylic groups, can reduce Cr(VI) to Cr(III) [26, 37–39]. However, the structural changes of the organic reductants involved in Cr(VI) reduction receive less scientific concerns. Thus, the objective of this study was to investigate the abiotic polymerization processes/products of H_2Q in the presence of Cr(VI). Several spectroscopic analyses, including UV-VIS spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, and X-ray absorption spectroscopy (XAS), were applied to examine the products of oxidative polymerization reaction of H_2Q in the presence of Cr(VI). We expect that the organic molecules of H_2Q with phenolic groups can be oxidized and converted subsequently to humic-like substances by Cr(VI) via the oxidative polymerization reactions.

2. Materials and Methods

2.1. Observations of the Interactions between H_2Q and Cr(VI) Using UV-VIS Spectroscopy.

The stock solutions of $1050 \, mg \, L^{-1}$ Cr(VI) and $5000 \, mg \, L^{-1}$ H_2Q were prepared by dissolving $K_2Cr_2O_7$ (predried at $120°C$ for 2 h, Merck) [28] and hydroquinone (Sigma-Aldrich), respectively, in the deionized water (DIW). The pHs of the Cr(VI) and H_2Q solutions were adjusted to 3.0 with 1 M HCl or NaOH. The $105 \, mg \, L^{-1}$ Cr(VI) and 200 or $400 \, mg \, L^{-1}$ H_2Q were then added in a reaction flask wrapped with aluminium foil at $25°C$. The 10 mL samples were periodically extracted at 10, 45, and 75 min and 24 h and passed through a membrane filter ($0.22 \, \mu m$). The filtrate was diluted 20-fold with DIW, and the time-dependent absorbance changes of the filtrates in the reaction were measured in a scanning model using an UV-VIS spectrophotometer (VARIAN CARY 50). The

spectra were recorded in the wavelength range from 200 to 600 nm (scan step 1 nm per 0.1 s). The wet pastes on the filter were collected in a plastic bag and stored at $4°C$ for X-ray absorption spectroscopy (XAS) analyses.

In another set of experiments, H_2Q and Cr(VI) were reacted for 24 h, followed by passing the suspension through a $0.22 \, \mu m$ pore-sized filter membrane (Advantec). The supernatants were then acidized to pH 1.0 using 6 M HCl. The acidized samples were stood overnight, and the filtrates and black precipitates on the filter, denoted as 1 d (pH 1), were collected and analyzed as mentioned previously. The remaining precipitates in the acidized solution were also collected after centrifuging (Hitachi, CR21) at $18,800 \times g$ for 20 min. The collected black precipitates were washed using DIW to remove excessive salts and then freeze-dried (Kingmech, FD4.5-12P) prior to the spectroscopic analyses.

2.2. Data Collection and Analysis of the Samples by Cr K-Edge XAS.

The analysis of the precipitates was performed by Cr K-edge XAS, conducted at Wiggler 20 beamline BL-17C1 in the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The storage ring was operated at 1.5 GeV with a beam current of 360 mA. The samples collected from the interactions of Cr(VI) with H_2Q were characterized using XAS technique, that is, XANES spectroscopy. The energy of the Si(111) monochromator was calibrated to 5989 eV at the first inflection point in the first derivative spectra of elemental Cr metal foil [33]. The spectrum of the Cr foil that was placed between the transmission ion chamber (It) and the reference ion chamber (Ir) detectors was monitored during data collection [40]. Samples and reference materials were analyzed in fluorescence mode using an $Ar_{(g)}$-filled Lytle detector between -200 and $+800$ eV relative to 5989 eV, using a step size of 0.3 eV in the near edge region (-20 to $+40$ eV) and a step size of $k = 0.06 \, Å^{-1}$ at higher energies. Multiple XAS scans on each sample were aligned, merged, and processed using the Athena program—an interface to IFEFFIT (version 1.2.10) [41, 42]. Spectra were baseline corrected using a linear pre-edge function between -200 and -50 eV for Cr-XAS. The spectral normalization was conducted using a linear or quadratic function between $+50$ and $+780$ eV for Cr-XAS, including a flattening function in the post-edge region [33, 43]. To determine the Cr species in the samples, the XAS data was analyzed using linear combination fitting (LCF) across the region between -20 and $+35$ eV of the Cr-XAS. The reference materials used in the LCF method included potassium dichromate ($K_2Cr_2O_7$), chromium hydroxide ($Cr(OH)_3 \cdot nH_2O$), chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$), chromium acetate hydroxide (Cr-acetate, $Cr_3(OH)_2(CH_3COO)_7$), and Cr(III) complexed with humic acid (Cr(III)-HA) synthesized according to the method of Elzinga and Cirmo [44].

2.3. The FT-IR Spectra.

The FT-IR spectra of the standard H_2Q, 1,4-benzoquinone (BQ, Sigma-Aldrich), and 1 d (pH 1) precipitates were obtained using a Thermo-Nicolet Nexus FT-IR spectrometer with an optical resolution of $4 \, cm^{-1}$. FT-IR pellets were prepared by mixing oven-dried ($110°C$)

(a) 105 mg L^{-1} Cr(VI) + 200 mg L^{-1} H$_2$Q
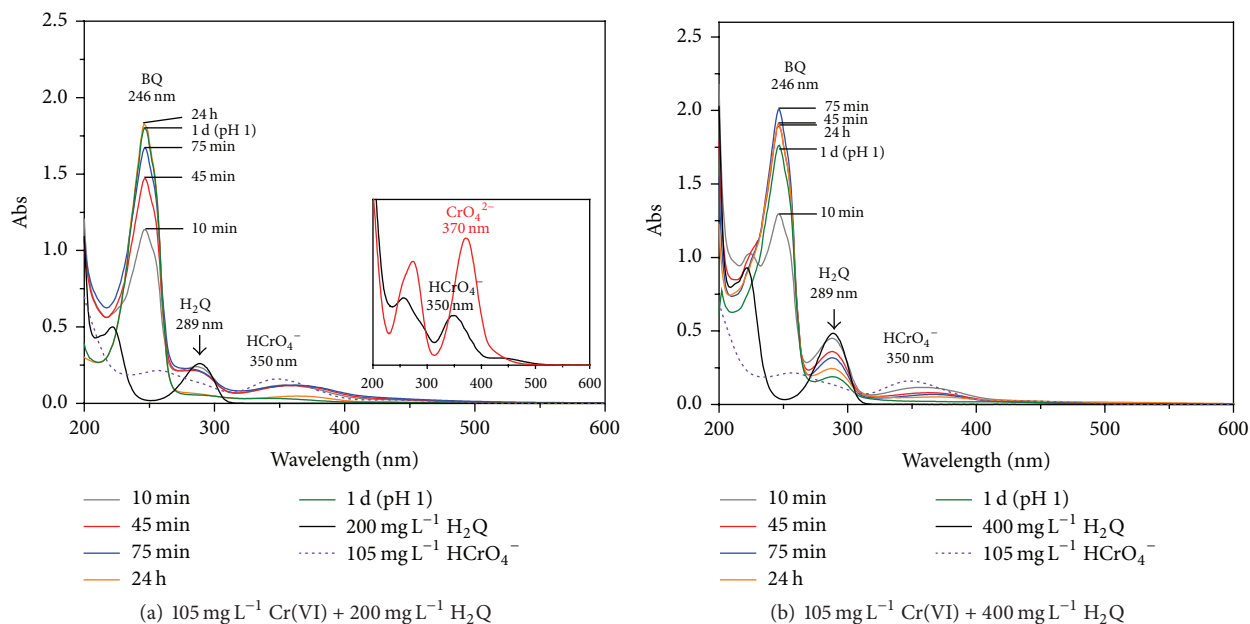
(b) 105 mg L^{-1} Cr(VI) + 400 mg L^{-1} H$_2$Q

FIGURE 1: The UV-VIS spectra of the reaction products of 105 mg L^{-1} Cr(VI) with (a) 200 mg L^{-1} and (b) 400 mg L^{-1} H$_2$Q at pH 3.0 and 25°C for 10, 45, and 75 min and 24 h, respectively. 1 d (pH 1) indicated that the sample was obtained by mixing 200/400 mg L^{-1} H$_2$Q and 105 mg L^{-1} Cr(VI) at pH 3.0 for 24 h, followed by the acidification treatment at pH 1.0 for 1 d. The insert in (a) indicated that the absorption peak of HCrO$_4^-$ at 350 nm was shifted to CrO$_4^{2-}$ at 370 nm with an increase in pH.

KBr (Merck) with powder samples to obtain a concentration of 5 mg g^{-1} for the standard samples and 3 mg g^{-1} for the acidized samples. FT-IR spectra in the range of 2000 to 400 cm^{-1} were obtained by coaddition of 64 individual scans with an optical resolution of 4 cm^{-1}.

3. Results and Discussion

3.1. The Polymerization of H$_2$Q in the Presence of Cr(VI). The UV-VIS spectra of the interactions of 105 mg L^{-1} Cr(VI) with 200 or 400 mg L^{-1} H$_2$Q for 10, 45, and 75 min and 24 h at pH 3.0 and 25°C were shown in Figure 1. The supernatants (1 d (pH 1)), which were obtained from acidification of the reactive products of Cr(VI) and H$_2$Q, were also analyzed by the UV-VIS spectrometer and shown in Figure 1. The original absorption peaks of H$_2$Q and Cr(VI), mainly HCrO$_4^-$, appeared in the UV-VIS spectra at the wavelengths of 289 and 350 nm, respectively. Upon interactions of Cr(VI) with H$_2$Q, the absorption intensities of Cr(VI) and H$_2$Q decreased significantly with an increase in reaction time for both 200 and 400 mg L^{-1} H$_2$Q systems. The results indicated that H$_2$Q was oxidized accompanied with Cr(VI) reduction. The redox reactions consumed protons, and thus the absorption peak of HCrO$_4^-$ at 350 nm was shifted to 370 nm (CrO$_4^{2-}$) with a prolonged reaction time (Figure 1, inserted) due to an increase in the solution pH from pH 3.0 to 7.2. In addition, a new absorption peak at 246 nm was observed and its intensity increased with an increasing reaction time from 10 min to 24 h (Figure 1(a)), attributed to the oxidation of H$_2$Q to BQ with the loss of 2 H$^+$ and 2 electrons (Figure 2) [45–47].
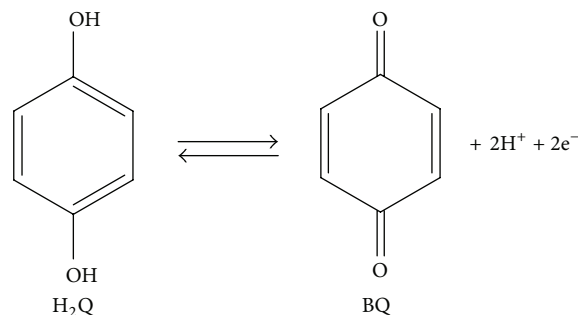

FIGURE 2: The redox reaction between H$_2$Q and BQ.

However, the characteristic absorption peak of BQ increased gradually while the reaction of 105 mg L^{-1} Cr(VI) with 400 mg L^{-1} H$_2$Q was less than 75 min, followed by a decrease in the absorption peak at 24 h (Figure 1(b)). The results indicated that within 75 min reaction, the oxidation of H$_2$Q to BQ overwhelmed the subsequent polymerization of BQ, leading to an accumulation of BQ in the solution. After the rapid production of BQ, a polymerization reaction involving BQ occurred, and thus BQ concentration gradually decreased (Figure 1). Based on the current results, we presumed that BQ was probably the primary intermediate of the oxidative polymerization of H$_2$Q.

The continuous changes in the solution colors were observed when 105 mg L^{-1} Cr(VI) reacted with 200 or 400 mg L^{-1} H$_2$Q at pH 3.0 and 25°C. Upon the oxidation of H$_2$Q by Cr(VI), the solution colors changed from light yellow-brown to dark reddish-brown over the reaction time,
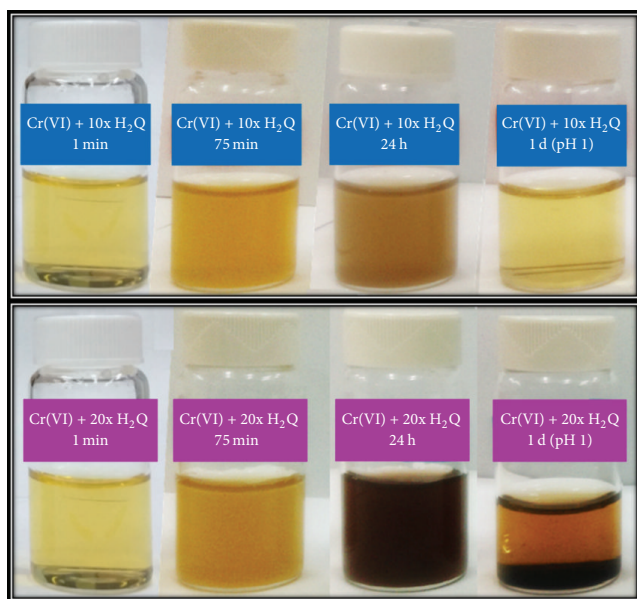
FIGURE 3: The changes in the solution colors of $105 \, mg \, L^{-1}$ Cr(VI) reacting with $200 \, mg \, L^{-1}$ and $400 \, mg \, L^{-1}$ H_2Q at pH 3.0 and 25°C, denoted as Cr(VI) + 10x H_2Q and Cr(VI) + 20x H_2Q, respectively, for 1 and 75 min and 24 h. 1 d (pH 1) indicated that the sample was obtained by mixing 200/400 $mg \, L^{-1}$ H_2Q and $105 \, mg \, L^{-1}$ Cr(VI) at pH 3.0 for 24 h, followed by the acidification treatment at pH 1.0 for 1 d.

particularly in the system with $400 \, mg \, L^{-1}$ H_2Q (Figure 3). After acidification treatments of the filtrates of the reactions of Cr(VI) with H_2Q for 24 h, the solutions exhibited a similar color change (Figure 3); however, the dark brown precipitates were only formed in the system with $400 \, mg \, L^{-1}$ H_2Q (Figure 3). This means that, after 24 h reaction, the oxidative polymerization of solution BQ only occurred in a system with initial $400 \, mg \, L^{-1}$ H_2Q which led to a decrease in the absorption peak at 246 nm (Figure 1(b)). Accordingly, upon interactions of H_2Q with Cr(VI), UV-VIS spectroscopic analyses found that the chemical structures of organic products in the solution and the bonding configurations between Cr and organic molecules changed continuously. The changes in spectroscopic analyses and solution colors were similar to the oxidative polymerization of H_2Q in the presence of MnO_2 within 24 h over a pH range of 4.0–7.8 [1]. In the study, the "browning phenomenon" and acid-induced (below pH 2) flocculation/precipitation of organic products were very similar to the properties of humic acid. We presumed that the oxidative polymerization of H_2Q through the formation of BQ may occur in the presence of Cr(VI), leading to the formation of humic-like polymers. To further characterize the structures and Cr species in the precipitated products, synchrotron technique was applied.

3.2. The Spectroscopic Analyses of the Precipitates Derived from the Reactions of H_2Q and Cr(VI). The Cr species in the precipitates were characterized using LCF of the XANES spectra obtained from the reference materials, including $K_2Cr_2O_7$, $Cr(OH)_3 \cdot nH_2O$, Cr-acetate, Cr $(NO_3)_3 \cdot 9H_2O$,
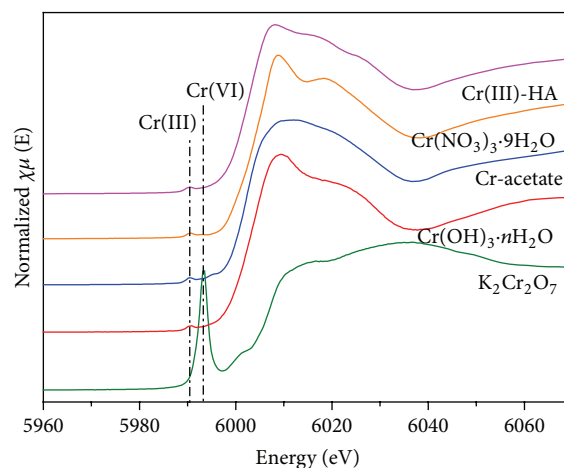
FIGURE 4: Normalized Cr K-edge XANES spectra for the Cr reference materials of $K_2Cr_2O_7$, $Cr(OH)_3 \cdot nH_2O$, Cr-acetate, $Cr(NO_3)_3 \cdot 9H_2O$, and Cr(III)-HA.

Cr(III)-HA, chromium acetylacetonate $(Cr(C_5H_8O_2)_3)$, CrO_3, and Cr_2O_3. It was found that five reference materials fitted well in the LCF results of samples. The reference materials of $Cr(OH)_3 \cdot nH_2O$, $K_2Cr_2O_7$, and Cr(III)-HA represent the species of Cr(III) hydroxide, Cr(VI), and Cr(III) bound to polymerized organic matters, respectively. The $Cr(NO_3)_3 \cdot 9H_2O$, a hydrated compound, is a model of pseudo-outer-sphere complexes between Cr(III) and organic substance [26, 48]. Cr-acetate is attributed to the Cr species bounded to the carboxyl groups of low molecular weight of organic acids. The XANES spectra of five reference materials were shown in Figure 4, and the LCF results of Cr K-edge XANES spectra for the precipitated products of Cr(VI) and H_2Q at different reaction time were shown in Figure 5. The normalized XANES spectra of the Cr(VI) species exhibit a sharp pre-edge feature at 5993 eV, attributed to the electric dipole transition of 1s electrons to an empty p-d hybridized orbital of Cr(VI) in a tetrahedral coordination [49]. In contrast, indiscernible pre-edge features were observed at 5990.5 eV due to a forbidden transition of Cr(III) electrons in an octahedral coordination. Hence, the diverse pre-edge feature can be used to identify the presence of Cr(VI) species [33]. The pre-edge peak characteristic of Cr(VI) at 5993 eV was observed for the Cr K-edge XANES spectra of the solid precipitates, obtained from the interactions of Cr(VI) with $400 \, mg \, L^{-1}$ H_2Q for 75 min and 24 h (Figure 5). The intensity of characteristic peak of Cr(VI) decreased over the reaction time, indicating that Cr(VI) reduction by H_2Q, Cr(VI) still existed in the system. However, the characteristic peak of Cr(VI) at 5993 eV disappeared for the 1 d (pH 1) precipitates (Figure 5), indicating that no Cr(VI) existed in the acidized samples. Because the conversion of Cr(VI) to Cr(III) would consume H^+ [50, 51], the system pH increased from 3.0 to 7.2 when Cr(VI) was reduced by H_2Q. The LCF results of the precipitates revealed that the proportions of Cr species in the precipitates at 75 min and 24 h consisted mainly of $Cr(OH)_3 \cdot nH_2O$ (64.8–65.2%), $K_2Cr_2O_7$ (9.3–19.9%), and Cr-acetate (15.3–25.5%) (Figure 5). On the other hand,
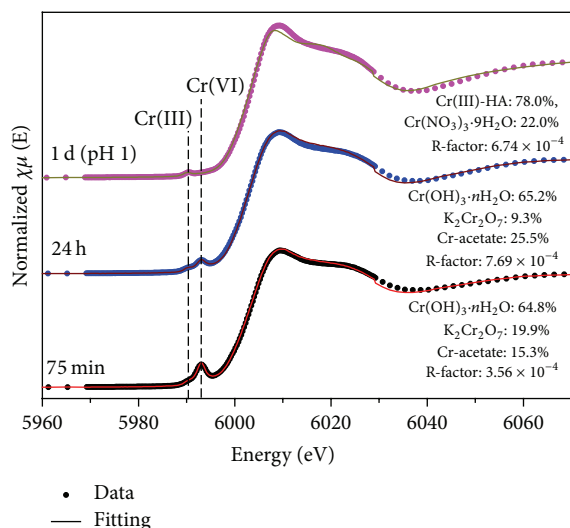
FIGURE 5: Cr K-edge XANES spectra (dashed lines) and the results of linear combination fitting (solid lines) for the precipitates collected from the reactive products of 105 mg L^{-1} Cr(VI) with 200 or 400 mg L^{-1} H$_2$Q at pH 3.0 and 25°C for 75 min and 24 h. The spectrum of the precipitates obtained from the 1 d (pH 1) sample was also shown. The spectra of the reference materials of K$_2$Cr$_2$O$_7$, Cr(OH)$_3$·nH$_2$O, Cr-acetate, Cr(NO$_3$)$_3$·9H$_2$O, and Cr(III)-HA were used for calculation during linear combination fitting.

the acidized precipitates (1 d (pH 1)) consisted of 78.0% Cr(III)-HA and 22.0% Cr(NO$_3$)$_3$·9H$_2$O. By combination of the XANES spectra and the LCF results, it was found that the Cr-acetate contents increased gradually from 15.3 to 25.5%, along with a decrease in Cr(VI) content from 19.9 to 9.3% during the 24 h reaction. For the acidification treatment, about 78.0% Cr(III)-HA and 22.0% Cr(NO$_3$)$_3$·9H$_2$O existed in the 1 d (pH 1) precipitates, suggesting that Cr(III) was partially bound with larger polymerized organic molecules derived from the oxidative polymerization of H$_2$Q/BQ. Park et al. [52] reported a similar result that Cr(III) was bound to the carboxyl groups of the brown seaweed (*Ecklonia* sp.) upon Cr(VI) reduction. Based on the current results, we presumed that the redox products of Cr(III) play an important role of forming a cationic bridge for the oxidative products of H$_2$Q/BQ, resulting in the formation of polymerized humic-like polymers.

The FT-IR spectra of H$_2$Q, BQ, and the 1 d (pH 1) precipitates were shown in Figure 6. The H$_2$Q exhibited several absorption peaks at 1515, 1472, 1208, 828, and 520 cm^{-1}, and the peak at 1653 cm^{-1} was the major absorption for BQ molecules (Figure 6(a)). The peaks at 1653, 1515/1472, 1208, 828, and 520 cm^{-1} were assigned to aromatic C=C vibration or quinone group, C=C stretching of aromatic ring, phenolic hydroxyl or carboxylic C-O-H deformation or C-O stretching, C-H out-of-plane bending, and C-C stretching, respectively [53, 54]. The bands that appeared at 1617, 1485, 1380, 1210, 820, and 520 cm^{-1} were only found for the acidized precipitates (1 d (pH 1)) (Figure 6(b)). The absorption band at 1617 cm^{-1} was assigned to the bands of quinonoid nuclei,

and the absorption peaks at 1485, 1210, and 820 cm^{-1} were attributed to the substituted benzenoid structures [55]. It suggested that both hydroquinone and benzoquinone moieties may coexist in the acidized precipitates/polymers. In addition, a new band at about 1380 cm^{-1} was observed, resulting from the asymmetric and symmetric stretching of the Cr(III) coordinated carboxylates [48, 53]. Based on the FT-IR spectra, H$_2$Q was first converted to BQ, resulting in the subsequent polymerization of low molecular weight organic molecules to humic-like polymers. During the oxidative polymerization of H$_2$Q in the presence of Cr(VI), XANES and FT-IR results indicated that Cr(III) could bind the carboxylic groups of organic molecules to facilitate the formation of organic polymers. However, the bonding configurations of Cr(III) with organic compounds are still unclear, because the analyses of bonding configurations of Cr through the diagnoses of EXAFS spectra, including coordination numbers, interatomic distances, and the Debye–Waller factors, for the precipitated products of H$_2$Q and Cr(VI) are rather complicated and challenging. The bonding configurations and the structures of Cr(III) in the organic polymers will be examined in our future works.

4. Conclusions

The occurrence of oxidative polymerization of H$_2$Q in the presence of Cr(VI) and the changes in the structures of redox products were spectroscopically investigated. Results showed that Cr(VI) could oxidize H$_2$Q to BQ at pH 3.0, and the reaction led to a significant increase in the solution pH. BQ was rapidly accumulated at the beginning of the reactions; however, with a prolonged reaction time, BQ contents decreased due probably to the occurrences of polymerization reactions. Combination of the XANES spectra and the LCF results indicated that Cr(VI) was reduced to Cr(III), and the contents of Cr(III) associated with carboxylic groups increased gradually during 24 h reaction, consistent with the FT-IR results that the carboxylic groups of organic molecules were responsible for Cr(III) bonding. The chemical compositions of precipitates, obtained from the acidized treatments of the supernatants from the reactions of Cr(VI) and H$_2$Q for 24 h, were similar to that of Cr(III)-HA complex. The results suggested that, upon Cr(III) formation, Cr(III) could serve as a metal bridge to facilitate the formation of a larger polymerized organic molecule. Based on the current study, we presume that the metal cation plays an important role in oxidative polymerization of small organic molecules. However, the bonding configurations and the structures of Cr in the organic polymers require further study to examine comprehensively the contributions of heavy metals with redox properties to the humification processes in soils.

Competing Interests

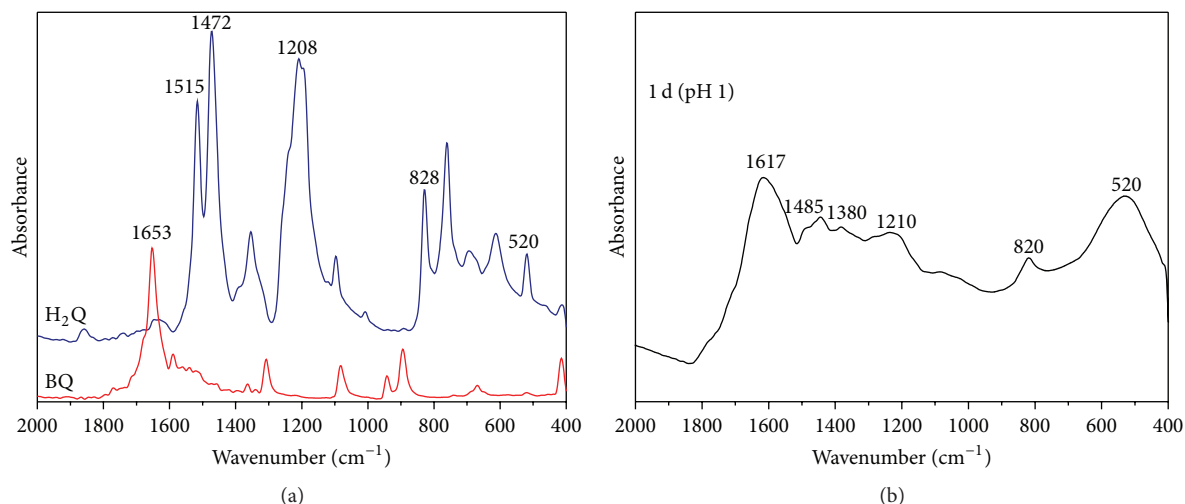The authors declare that there are no competing interests regarding the publication of this paper.

FIGURE 6: FT-IR spectra of (a) the standard H_2Q and BQ samples and (b) the acidized precipitates (1 d (pH 1)).
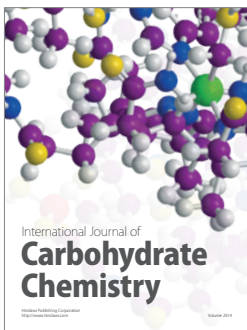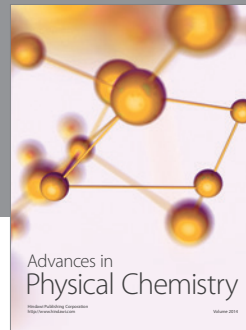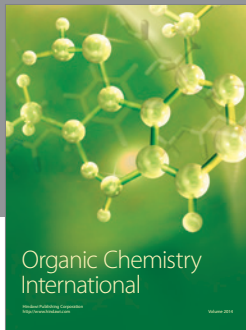
Acknowledgments

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