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# The role of different functional groups in a novel adsorption-complexation-reduction multi-step kinetic model for hexavalent chromium retention by undissolved humic acid<sup>☆</sup>

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## ABSTRACT

Undissolved humic acid (HA) has a great retention effect on the migration of hexavalent chromium [Cr(VI)] in soil, and HA functional groups play a predominant role in this process. However, the coupled mode between Cr(VI) retention and HA functional groups reaction is still unclear. In this study, it was found that a fair amount of Cr on HA existed in the forms of ion exchangeable and binding Cr(VI) during the reaction resulting from the ion exchange adsorption and complexation of Cr(VI). According to the results of two-dimensional correlation spectroscopic analysis (2DCOS), HA functional groups participated in the reaction with Cr(VI) in the order of carboxyl  $\approx$  chelated carboxyl > phenol > polysaccharide > methyl, and all the functional groups were more likely to be located at aromatic domains. Based on the results of XPS spectra, rather than to be oxidized by Cr(VI), carboxyl more tended to be complexed by chromium, which is regarded as the precondition for Cr(VI) reduction. Phenol, polysaccharide and methyl with distinct reaction activities successively acted as major electron donors for Cr(VI) reduction in different reaction stages. Consequently, it was determined that the retention of Cr(VI) by undissolved HA followed an adsorption-complexation-reduction mechanism, and based on this, a multi-step kinetic model with multiple types of complexation/reduction sites was developed to simulate the retention processes resulting in a much better fitting effect ( $R^2 > 0.99$ ) compared with traditional first-order and second-order kinetic models ( $R^2 < 0.95$ ). This demonstrated that the multi-step kinetic model is of great potential in accurately simulating the migration and transformation of Cr(VI) in soil environment.

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## 1. Introduction

Hexavalent chromium [Cr(VI)] is one of the most common heavy metal pollutants in groundwater, which is of great scientific concern due to its high mobility and acute toxicity to human (Brose and James, 2013). Rather than natural occurrence of Cr(VI) in the stratum (Landrot et al., 2012a,b; Rajapaksha et al., 2013), the main source of Cr(VI) in groundwater is the infiltration of Cr(VI) containing sewages from the anthropogenic activities on the ground, such as electroplating, leather tanning, dyeing, and metallurgy (Dhal et al., 2013). The soil layer located at the top of vadose zone has significant retention effect on Cr(VI) migration, and the soil

organic matter (SOM), Fe(II), and S(II) are considered as the main electron donors for Cr(VI) reduction to its trivalent form [Cr(III)] that is of much lower mobility and toxicity (Hsu et al., 2009). As known, Fe(II) and S(II) are more readily oxidized to higher valent form compared with SOM under oxic condition of surface soil, and therefore, SOM is considered to be of great importance for Cr(VI) reduction and immobilization (Jardine et al., 2013; Leita et al., 2009).

Humic acid (HA), one of the most abundant SOM constituents, has been widely studied in the reaction with Cr(VI), but the majority of related studies were focused on the HA in the form of dissolved organic matter (DOM) (Chen et al., 2011; Wittbrodt and Palmer, 1996, 1997). It has been reported elsewhere that HA in soil mainly exist in the undissolved form (Klučáková and Kolajová, 2014), the mass content of which is generally about two orders of magnitude greater than that of dissolved HA (DOM) in soil water (Xiao et al., 2012), and the environmental implications of them can

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be quite different from each other. Weng et al. has reported that the existence of HA (DOM) can even increase the concentration of dissolved metals by more than two orders of magnitude to facilitate the transport of heavy metals in soil (Weng et al., 2002). Undissolved HA, on the other hand, has been taken as a good adsorbent for Cr(VI) removal from water (Arslan et al., 2010; Kyziol et al., 2006; Li et al., 2008), which is considered to be in favor of Cr(VI) immobilization. Compared with dissolved HA, undissolved HA therefore tends to play a predominant role for Cr(VI) retention in soil, either from the perspective of quantity or property.

The pathway for Cr(VI) retention by undissolved HA is complicated involving the processes of adsorption, reduction, and complexation (Janos et al., 2009), the understanding of which is of great significance both for the prediction of Cr(VI) fate in the environment and the assessment of Cr(VI) risk for humans. However, the detailed mechanism is still unclear at present. HA functional groups are widely considered to be of vital importance in reaction processes with Cr(VI) by acting as both electron donors and complexation sites (Ohta et al., 2012). Among all the processes, the reduction of Cr(VI) by functional groups get the most scientific concerns, because it will reduce the toxicity and mobility of chromium. Carboxyl and phenol have been reported to be mainly responsible for the reduction of Cr(VI) according to infrared spectroscopy evidence (Huang et al., 2012; Zhao et al., 2016). From the point of view of classical organic chemistry, however, carboxyl is not a representative reducing functional group, and it can only be oxidized though decarboxylation producing carbon dioxide (Brose and James, 2013), which is much more difficult to happen than the oxidation of phenol, hydroxyl, and even methyl groups. Since multi process being involved in the reaction, will there be a possibility that instead of oxidation by Cr(VI) the decreasing infrared absorbance of carboxyl is induced by another process, such as complexation of chromium? In other words, what will be the coupled mode between Cr(VI) retention processes and HA functional groups reaction? This question is of vital importance for the interpretation and prediction of the mechanism and processes for Cr(VI) retention by HA functional groups, however, it has not been fully resolved.

In this work, the retention process of Cr(VI) by undissolved HA was studied, and the variations of chromium concentration and valence state in both aqueous and solid phase with time were investigated. On the other hand, a series of spectroscopies were utilized to characterize the variations of functional groups in the meantime, and then two-dimensional spectroscopy correlation analysis (2DCOS) was employed to reveal the coupled mode between Cr(VI) retention processes and functional groups reaction, based on which a multi-step kinetic model for Cr(VI) retention by undissolved HA was developed.

## 2. Materials and methods

### 2.1. Cr(VI) sorption by HA

Commercial HA (Sinopharm Chemical Reagent Co., China) was sieved through a 74  $\mu\text{m}$  sieve to remove coarse particulates, and homogenized. The element composition, acidic groups content, ash content, water content, surface area, point of zero charge ( $\text{pH}_{\text{PZC}}$ ) can be found in our previous work (Zhang et al., 2017).

A series of 250 mL of Cr(VI) solutions with initial concentrations of 5 mM were added into 300 mL brown flasks containing  $125.0 \pm 0.5$  mg HA. The solution contained a background electrolyte of 0.01 M NaCl, and the initial pH was adjusted to 1 by adding 2.5 M HCl. Each solution was shaken at 25  $^{\circ}\text{C}$  using a horizontal shaker with an intensity of agitation of 200 rpm. A control experiment was conducted in the same procedure just without HA. All experiments

were performed in triplicate. At given time intervals, 10 mL of each supernatant was sampled by filtering through a 0.45  $\mu\text{m}$  membrane, and then the vacuum filtration was used to separate undissolved HA from the solutions. One of the three HA samples was freeze-dried for Fourier transform infrared spectroscopy (FTIR), solid-state cross-polarization magic angle spinning  $^{13}\text{C}$  nuclear magnetic resonance ( $^{13}\text{C}$  CP/MAS NMR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy/energy dispersive X-ray analysis (SEM-EDX) characterization. The other two samples were sequentially desorbed by 250 mL 0.1 M  $\text{Na}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$  and 0.1 M NaOH for 2 d and 1 d respectively, and 10 mL supernatant was filtered through 0.45  $\mu\text{m}$  membrane. The  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  with high concentration are considered to be able to desorb nearly all the ion exchangeable Cr(VI) on HA (Kozuh et al., 2000). The HA will be completely dissolved in the high concentration of NaOH, and the binding Cr(VI) that cannot be desorbed by phosphate solution will be released into aqueous phase. The concentration of Cr(VI) in the filtrate was determined using a UV/vis spectrophotometer (SHIMADZU UV-1800) at 540 nm after reacting with 1,5-diphenylcarbazide indicator (DPC). Total chromium was determined using ICP-AES (SPECBLUE) at 283.56 nm. The Cr(III) concentration in the filtrate was determined by the difference between total chromium and Cr(VI) concentration.

### 2.2. FTIR, $^{13}\text{C}$ CP/MAS NMR, XPS, and SEM-EDX characterization

FTIR spectra of samples were obtained on an IR spectrometer (Bruker LUMOS, Germany) at room temperature. All samples were fully ground to guarantee high homogeneity prior to tests. The samples were uniformly mixed with dried KBr powder at mass ratio of 1:200. Each spectrum was obtained after 64 scans with  $2\text{ cm}^{-1}$  resolution.

Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra of the samples were collected on a Bruker AVANCE III 400 NMR spectrometer with 4 mm NMR rotors with Kel-F caps. NMR spectra were obtained by applying the following parameters: rotor spin rate of 13 kHz, 1s recycle time, 2 ms contact time, 20 ms acquisition time, and 10000 scans. Chemical shifts were calibrated with adamantane.

XPS was measured with Thermo escalab 250XI. The X-ray excitation was provided by a monochromatic Al K $\alpha$  (excitation energy 1486.6 eV). The binding energies of the spectra were corrected using the hydrocarbon component of adventitious carbon at 284.8 eV.

### 2.3. 2DCOS analysis

The spectra of a series of HA samples from FTIR and  $^{13}\text{C}$  CP/MAS NMR under the perturbation of pH were analyzed by the method described by Noda and Ozaki (2005). The dynamic spectra that represents the variation of spectral intensity compared with the reference spectrum can be calculated from the following:

$$\tilde{x}(v) = \bar{x}(v, t_j) = x(v, t_j) - \bar{x}(v), j = 1, 2, \dots, m \quad (1)$$

where the variable  $v$  is the spectral index of FTIR, NMR or XPS.  $\bar{x}(v, t_j)$  is the dynamic spectra measured at  $m$  equally spaced points in perturbation  $t$  between  $t_1$  and  $t_m$ , and the average spectrum  $\bar{x}(v) = \sum_{j=1}^m x(v, t_j)/m$  has been subtracted from raw data  $x(v, t_j)$ . The synchronous correlation intensity of two spectral indices can be directly calculated from the following:

$$\Phi(v_1, v_2) = \frac{1}{m-1} \sum_{j=1}^m \tilde{x}_j(v_1) \cdot \tilde{x}_j(v_2) \quad (2)$$

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