



# The influence of pH, co-existing ions, ionic strength, and temperature on the adsorption and reduction of hexavalent chromium by undissolved humic acid

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## HIGHLIGHTS

- Verified the adsorption-reduction mechanism under various conditions.
- Established the relationship between adsorption and reduction under varied conditions.
- The slope of the relationship suggested different reduction rate constants.
- $\text{Ca}^{2+}$  functioned as a cation bridge enhancing adsorption and indirectly reduction.
- Temperature enhanced adsorption (distribution coefficient) and reduction rate constant.

## ARTICLE INFO

### Article history:

Received 27 June 2018

Received in revised form

13 August 2018

Accepted 14 August 2018

Available online 15 August 2018

Handling Editor: Willie Peijnenburg

### Keywords:

Aqueous factors

Adsorption

Reduction

Hexavalent chromium

Undissolved humic acid

## ABSTRACT

The retention of Cr(VI) in subsurface environment is highly dependent on humic acid (HA), however, the undissolved form is poorly investigated, the amount of which can be of two magnitude higher compared with the dissolved one in soils and sediments. In this study, the effects of time, initial concentration, pH, ionic strength, ion species and temperature on the adsorption and reduction respective processes by undissolved self-extracted peat soil HA from Northeast China (EHA) and from Sigma Aldrich (CHA) were investigated by batch experiments. Cr(VI) removal rates by EHA were higher than CHA and the maximum Cr(VI) removal amount for EHA and CHA were 0.77 ( $\pm 0.01$ ) and 0.61 ( $\pm 0.02$ ) mmol/g. Of these, 98% and 54% were reduced to Cr(III) by EHA and CHA respectively, which were related to the phenolic group content of HA. With time, the adsorbed Cr(VI) on HA increased to a maximum level (equilibrium) beyond which Cr(VI) reduction dominated the removal process. Cr(VI) adsorption and reduction by undissolved HA increased as pH decreased. Co-existing ion species had varying effect on Cr(VI) adsorption and indirectly on reduction especially divalent cations which was suggestive of cation bridging between Cr anions and ionized carboxyl group of HA. The positive effect of ionic strength ( $\text{Ca}^{2+}$ ) on Cr(VI) adsorption through complexation corroborated the cation bridge effect of divalent cations. Temperature increased both Cr(VI) adsorption (complexation) and reduction with enhancing reduction rate constants and partitioning.  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  parameters showed that Cr(VI) adsorption and reduction processes were endothermic, irreversible and spontaneous.

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## 1. Introduction

Industrialization in recent times has led to the widely use of chromium in diverse areas such as electroplating, alloying (e.g. in

stainless steel), and leather tanning (Asgari et al., 2008; Akar et al., 2009; Giri and Patel, 2011; Hao et al., 2014) which tends to be a main source of Cr(VI) pollution in groundwater. The exposure of hexavalent chromium contaminated water and environment is known to potentially cause cancer, and its exposure by inhalation has already been declared as carcinogenic (Hao et al., 2014; Haney et al., 2012; Sharma et al., 2012; Tziritis et al., 2012) and hence the need to understand the processes that govern its migration and

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transformation in the subsurface environment (Wittbrodt and Palmer, 1996; Zhang et al., 2018a).

Soil humic substances (SHS) are known to be redox-active natural organic matter which is ubiquitous in the environment and can be extracted from nearly all types of soil, sediments and peat lands (Stevenson, 1994; Lovley et al., 1999; Miltner et al., 2012). They have been established to have great retention effect for Cr(VI) migration especially in the subsurface environment. SHS can be subdivided into three major fractions (1) humin (HM) (2) humic acid (HA), and (3) fulvic acid (FA). These sub divisions are arbitrarily based on the solubility of each fraction in water adjusted to different acid/alkaline (pH levels) conditions (Zhang et al., 2013; van Zomeren and Comans, 2007). In the past two decades, the use of HA as electron donors for Cr(VI) reduction to Cr(III) has been studied extensively with the focus especially on dissolved organic matter (DOM) (Wittbrodt and Palmer, 1996). This is because DOM has been reported to serve as a sink for chromium in the aquatic environment and also identified to be the most bioavailable fraction of SHS that facilitates Cr(VI) reduction to Cr(III) in soils and sediments (Jardine et al., 1999; Nakayasu et al., 1999). However, according to Klučáková and Kolajová (2014), within the humus layer (making up 65–75% of soil organic matter) of the vadose zone, HA virtually exists in the undissolved form, which is reported to function as electron donors and adsorption sites for both Cr(VI) and Cr(III). Weng et al. (2001) therefore argued that the retention capacity of the humus layer is virtually related to the undissolved HA content of SHS. Again, the physicochemical characteristics (molecular weight, carbon and oxygen contents) of DOM and undissolved HA are known to be quite different from each other, and may most likely have different environmental processes (Pettit, 2004). For example, while DOM has been reported by Weng et al. (2002) and Xiao et al. (2012) to increase the concentration of dissolved metals (liquid-liquid phase) by more than two orders of magnitude, undissolved HA has been established to be good sorbent for Cr(VI) removal from water (solid-liquid phase) (Arslan et al., 2010; Kyziol et al., 2006; Li et al., 2008).

In our previous study, the retention of Cr(VI) by undissolved HA in the subsurface environment was reported to follow an adsorption-reduction mechanism (Zhang et al., 2018b). We established under strongly acidic conditions that, there is an electrostatic and ion exchange adsorption of Cr(VI) on the HA surface after which the adsorbed Cr(VI) is reduced to a less toxic Cr(III) by the phenol and polysaccharide groups which serve as the main electron donors. The carboxylic group of the total acidic content of HA then complexes with the reduced Cr(III). Similar interaction mechanism has also been reported elsewhere (Janoš et al., 2009; Park et al., 2007). However, due to the strongly acidic conditions of our previous study, the use a single background electrolyte and ionic strength, it limits the results and conclusions. There is therefore the need to do further investigation under different pH, background electrolyte, and ionic strength conditions to established its influence and hence draw conclusions that are applicable under a wide variety of conditions. This is because based on the Stern electrical-double layer theory of the interaction between Cr(VI) and undissolved HA, the molecular diffusion layer is highly pH dependent as it determines the electrostatic force (attraction or repulsion) at play. This highly influences the binding of Cr(VI) on HA which is a prerequisite for Cr(VI) reduction. Again, different temperatures may influence activities within diffusion layer like ion exchange which may have varying implications on Cr(VI) adsorption and reduction processes that need further investigation.

Traditional physicochemical aqueous factors (example, pH, ionic strength, co-existing ion species, temperature etc.) have been reported (Wittbrodt and Palmer, 1996) to have varying effects on the interaction of DOM and Cr(VI). For example, changes in ionic strength (representing background electrolyte concentration) of an

aqueous solution can cause some modifications of HA (Swift 1989, 1996) by making the phenolic and carboxylic functional groups either more or less accessible to Cr(VI), thereby altering the rate of reduction (Wittbrodt and Palmer, 1996). However, the effect on the adsorption process of the adsorption-reduction mechanism in the same reaction system is still unclear. That is, previous studies on the effect of aqueous factors on Cr(VI) removal by humic substances have mainly focused on Cr(VI) removal at the macro scale and not specifically on the processes of removal like adsorption and reduction respectively. Such a study will ensure the general applicability and stability of the Cr(VI) adsorbed on undissolved HA and the reduced Cr(III) under varying environments conditions.

In this study therefore, series of experiments were conducted to investigate Cr(VI) interaction with undissolved self-extracted peat soil HA from Northeast China (EHA) and from Sigma Aldrich (CHA). Specifically, the effects of physicochemical aqueous factors which included time, initial concentration, pH, ionic strength, co-existing ion species (both cations and anions) and temperature (thermodynamics) on adsorption and reduction processes respectively of Cr(VI) removal in the same reaction system by the two HAs were studied.

## 2. Materials and methods

### 2.1. Source of HA samples and extraction

Typical agricultural peat soil from North-East China (South-West Daqiao of Dunhua, Jilin Province) was obtained and naturally air-dried, ground to ensure homogeneity and subsequently passed through a 100-mesh sieve. The organic matter content of the peat soil as determined from Walkley-Black method was 11.64% while the pH value of 4.6 was measured at soil to 1 M KCl solution ratio of 1:2.5 (w:v). Sample was stored appropriately in sealed brown glass bottles before treatment.

International Humic Substances Society (IHSS) recommended protocol (Swift, 1996) for isolation of HA was used to extract HA from the peat soil. 0.1 M NaOH under an atmosphere of N<sub>2</sub> was added to a neutralized soil residue with 1 M NaOH (pH 7) to give a final solution to soil ratio of 10:1 (v:v) after shaking the residue for 24 h. The alkaline suspension was then allowed to settle overnight and supernatant collected by means of decantation. The supernatant was acidified with 6 M HCl with constant stirring to pH 1 and then allowed to settle for 12 h. The precipitate (HA) was separated by centrifugation. HA was re-dissolved by adding a minimum volume of 0.1 M KOH under N<sub>2</sub>. Solid KCl was added to attain a concentration of 0.3 M [K<sup>+</sup>] and then centrifuged at high speed to remove the suspended solids. HA was re-precipitated by adding 6 M HCl with constant stirring to pH 1 and suspension again allowed to stand again for 12 h. Supernatant was discarded after centrifuging the suspension at 3000 rpm for 25 min. Subsequently, HA precipitate was suspended in 0.1 M HCl/0.3 M HF solution in a plastic container and shaken overnight at 25 °C. The HCl/HF treatment process was repeated until the ash content was approximately 1%. Extracted HA was washed three times with deionized water, freeze-dried and then stored in sealed brown glass bottles after grinding to pass through 100-mesh sieve before use. CHA (ref no. 53680-50G) from Sigma Adrich Co. Ltd. was homogenized after sieving to remove coarse particulates.

### 2.2. Elemental composition, ash content and acidic groups of HA

The C, H, N contents of both CHA and EHA were analyzed with high-temperature combustion method (PE 2400 SERIES II analyzer, Pekin-Elmer, Inc.), and O content was calculated by the mass difference. The muffle furnace was utilized to determine the ash

content of samples by heating at 750 °C for about 5 h. The content of acidic functional groups (total acidic groups, carboxyls and phenols) was determined by a titration procedure described in detail by Li et al. (2008).

### 2.3. Batch experiments

For effect of time on Cr(VI) adsorption and reduction, series of 20 mL of Cr(VI) solutions with initial concentration of 5 mM were added into 20 mL amber glass bottles containing  $100.0 \pm 0.5$  mg CHA in one set and EHA in another set. The reaction solution contained a background electrolyte of 0.01 M CaCl<sub>2</sub> with a final pH of 3 (Fig. S1 and S2). Each solution was shaken at 25 °C using a horizontal incubator shaker with 200 rpm intensity of agitation. To ensure data quality all experiments were performed in triplicates. At time defined intervals (0.125, 0.25, 0.5, 1, 2, 4, 8, 16, 32 and 64 d), samples were taken and centrifuged at 3000 rpm for 5 min. Aliquots (10 mL) of the solution were analyzed immediately after being filtered through a 0.45 μm filter membrane. Vacuum filtration was then used to separate all undissolved HA from the reaction solutions. One HA sample each of the triplicates was freeze-dried for X-ray photoelectron spectroscopy (XPS). Desorption tests were performed on the other two HA samples with 20 mL 0.1 M NaOH for 1 d in order to dissolve HA completely so that the adsorbed Cr(VI) on HA could be determined. Cr(VI) concentration 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-OES SPECTROBLUE (SPECTRO Analytical Instruments GmbH, Germany) at 283.56 nm. As quality control measure hexavalent chromium standard solution was purchased from the National Centre of Analysis and Testing for Nonferrous Metals and Electronic Materials (NCATN) of China. This standard solution was used to calibrate the UV/vis spectrophotometer (SHIMADZU UV-1800) and the ICP-OES and established reliable working curves ( $R^2 > 0.999$ ). The relative standard deviations for the determination of low concentrations of total Cr (<5 limit of detection) and higher concentrations (>5 limit of detection) did not exceed 0.2 and 0.1 respectively. The Cr(III) concentration in the filtrate was then determined from the difference between total chromium and Cr(VI) concentrations.

The effects of pH, ionic strength, initial Cr(VI) concentration, temperature and co-existing cations or anions on Cr(VI) adsorption and reduction by HA were investigated. For pH dependence, the final pH of the reaction samples was varied from 2 to 6. With the exception of pH dependence experiment, all the other experiments were performed with a final pH of 3. Ionic strength was tested in the presence of 0.001, 0.01, and 0.1 M CaCl<sub>2</sub> background electrolyte. Sorption as a function of initial Cr(VI) concentration was studied by modifying the concentration from 0.625 to 10 mM. The effect of temperature on was conducted at three temperatures of 15, 25, and 35 °C. The background electrolyte was varied using 0.01 M each of cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) and anions (SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>) to test the effect of co-existing ion species on the adsorption and reduction rate.

### 2.4. XPS characterization and analysis

In this study, XPS characterization using Thermo escalab 250XI was employed to distinguish and verify the oxidation state of the chromium sorbed on HA. The X-ray excitation was provided by monochromatic AlK $\alpha$  with an excitation of energy of 1486.6 eV. The hydrocarbon component of adventitious carbon was used to correct the binding energies spectra at 284.8 eV. The fitting of XPS data was performed using XPSPEAK 41 software.

### 2.5. Data analysis

The fitting of kinetic experimental data was conducted in piecewise (rapid and slow phases) using pseudo-first and second order kinetics equations (S1) and (S2) respectively as shown in supplementary material. Both the Freundlich and Langmuir isothermal models were used to fit equilibrium experimental results. The Freundlich model and Langmuir can be expressed in equations (S4) and (S5) respectively. The thermodynamics parameters, Gibbs free energy change ( $\Delta G^0$ ) was calculated using equations (S6) and (S7). The standard enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ), of sorption were estimated from the van't Hoff equation which is expressed in equation (S8)

## 3. Results and discussion

### 3.1. Characterization of HA samples

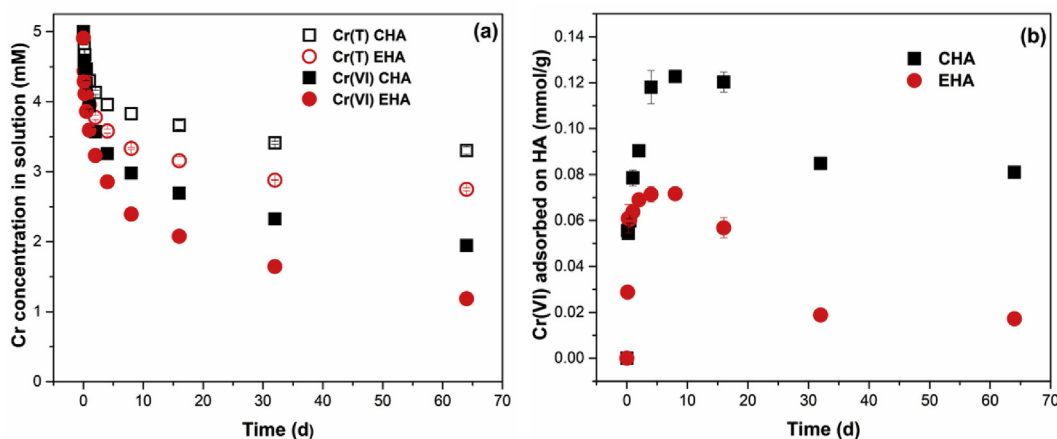
The detailed elemental compositions, atomic ratio, ash content and acidic functional groups are shown in Table S1. The bulk elemental composition analysis and elemental ratios of EHA and CHA showed that their (N + O)/C and H/C values were comparable (0.44 and 0.83, 0.43 and 0.80 respectively) which suggested that they had nearly the same content of polar C and degree of aromatic character. The total acidic groups, carboxyls, and phenols were 6.60, 3.45 and 3.15 mmol/g for EHA, and 4.76, 2.87 and 1.89 mmol/g for CHA respectively. That is both carboxyls and phenols of the total acidic functional group was higher for EHA than CHA. Considering that the O/C values for EHA and CHA are comparable (0.38 and 0.37 respectively), it also meant that CHA contained more low polar oxygen-containing functional groups like ether, ester and carbonyl than in EHA.

### 3.2. Effect of time on Cr(VI) adsorption and reduction

To determine the influence of time on Cr(VI) adsorption and reduction, the variations of Cr(VI) concentration in solution and on HA with time were investigated over 64 d. The entire process can be divided into fast and slow removal phases which are 0–8 d and 8–64 d for both HAs (Fig. 1a and b). The interaction of Cr(VI) and undissolved HA is established to follow an adsorption-reduction mechanism from our previous work (Zhang et al. 2018b, 2018c). Based on this assumption, it can be explained that, at the first phase (up to 8 d) of the removal process, Cr(VI) concentration in aqueous phase is very high as against available sorption sites and acidic functional groups (carboxyl and phenol groups) on undissolved HA. For this reason, the rate of Cr(VI) adsorption (molecular diffusion based PZC values) on the available sites on HA and subsequent complexation with the carboxyl content are very high (high activity) (Fig. 1b). Although, the electron donation rate for Cr(VI) reduction by the reductive functional group was also very high at this stage which is confirmed by the high initial Cr(III) production rate, the Cr(VI) removal process in the first 8 days was adsorption dominated. It is worth mentioning that the decrease in the initial Cr(T) from 4.94 to 2.75 mM and 4.94 to 3.28 mM for EHA and CHA respectively suggested that Cr was indeed adsorbed from the aqueous phase onto the undissolved HA.

At the second phase (after 8 d) when adsorption had reached equilibrium, available complexation sites and reductive functional groups of HA get exhausted (low activity) with time. The Cr(VI) removal rate at this stage was reduction dominated and the amount of Cr(VI) removed by CHA and EHA slows down.

For purposes of determining the reduction rates, both the first and second order kinetic models were utilized. The piecewise (0–8 d and 8–64 d) fitting technique was used to fit the



**Fig. 1.** (a) Removal of Cr(VI) by CHA and EHA over 64 d (b) Content of Cr(VI) adsorbed on HA over 64 d. Final pH = 3 and T = 25 °C. [Cr(VI)]<sub>0</sub> = 5 mM, [HA] = 100 mg, I = 0.01 M CaCl<sub>2</sub>. Error bars represent SEM (n = 3).

experimental data (Fig. S4). Details of the piecewise fitting parameters are also shown in Table S2. The second order kinetic model fitted better than the first order. The second order kinetic is developed based on the assumption that the reaction rate is related to both the concentration of Cr(VI) and the content of reductive functional groups. That is, the rate of Cr(VI) reduction is a function of initial Cr(VI) concentration and the reductive functional groups content of HA. The values of the rate constant during the rapid removal phase ( $k_{rap}$ ) varied in the order: 0.05089 d<sup>-1</sup> (EHA) > 0.03665 d<sup>-1</sup> (CHA). That of the slow removal phase was in the order: 0.00794 d<sup>-1</sup> (EHA) > 0.00334 d<sup>-1</sup> (CHA). By the end of day 8, 40% and 52% of the initial Cr(VI) concentration had been removed by CHA and EHA respectively. This dropped to 35% and 50% respectively after day 8–64. By the end of the entire interaction process of 64 d, 0.77 (±0.01) and 0.61 (±0.02) mmol/g of Cr(VI) were removed by EHA and CHA respectively. Of the removed Cr(VI) concentration, 98% and 54% were reduced to Cr(III) by EHA and CHA respectively.

As established in this study, the increase in Cr(III) concentration in solution with time at the expense of Cr(VI) suggests that Cr(VI) was indeed reduced by HA. As this is the case in the liquid phase, it is equally important to establish the variations of the valence state of chromium sorbed on HA in order to verify the extent of Cr(VI) reduction in the solid phase. To this end, XPS Cr2p was utilized to distinguish between different chromium species. The oxidation state variation of chromium on both HA samples with time (4, 8, 16, and 64 d) are shown in Fig. S5. It can be deduced that with time the intensity of XPS Cr2p in absolute terms increased. This confirms earlier observation that Cr(VI) indeed moved from aqueous phase onto the solid phase with time. For both HA samples, the intensity of Cr(III) kept increasing from 4 d up to 64 d as Cr(VI) reduced. This observation is consistent with the results from the chemical experiment conducted which indicated the increase in Cr(III) concentration with time. Moreover, the percentage of Cr(III) distribution on CHA as shown in Table S3 increased from 66.33% at 4 d to 75.99% at 64 d. Similarly for EHA, Cr(III) distribution increased from 69.55% at 4 d to 78.79% at 64 d. All these results clarify the fact that Cr(VI) was reduced to Cr(III) by both CHA and EHA on their surfaces.

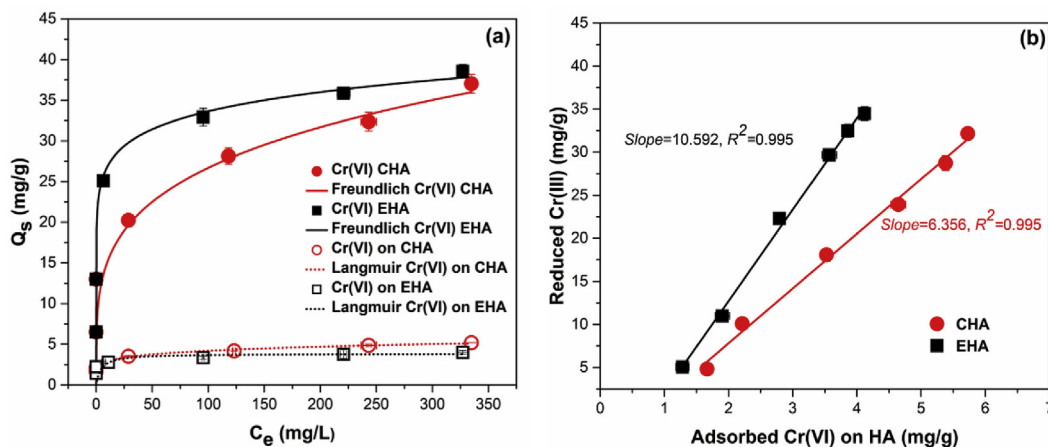
According to our previous studies, phenols compared to carboxyls act as main the electron donors (Zhang et al. 2017, 2018b). That is, the higher the phenol content, the higher the reduction capacity of HA. Carboxyls on the other hand are considered more likely to act as ligand for Cr complexation instead of being oxidized.

Based on this assertion it was expected that EHA with phenol content of 3.15 mmol/g compared to CHA with 1.89 mmol/g to have higher reduction capacity under the same experimental conditions.

### 3.3. Effect of initial Cr(VI) concentration

The effect of initial concentration of Cr(VI) on adsorption and reduction by HA was investigated using initial Cr(VI) concentrations of 32.5–520 mg/l. The Freundlich and Langmuir equilibrium models were used to fit total Cr(VI) removed amount and Cr(VI) adsorbed on HA data respectively as shown in Fig. 2a. According to Yuwei and Jianlong (2011), the Freundlich model assumes that the adsorbent surface is energetically heterogeneous, where the adsorbed molecules are interactive and the sorption quantity rises infinitely with the increasing concentration of adsorbate in the liquid phase. The Langmuir model on other hand assumes the adsorbent surface is structurally homogeneous and the binding sites have the same affinity for the adsorbate, where only monolayer adsorption occurs without interactions among adsorbed molecules (Ren et al., 2013). The Freundlich model fitted better with the total removed Cr(VI) data by both CHA and EHA compared with Langmuir model resulting from higher correlation coefficient of 0.787 and 0.850 respectively (Table S4). This implied that both CHA and EHA have energetically heterogeneous surfaces which are known characteristic of HA. The Langmuir model was however used for adsorbed Cr(VI) content on HA data in order to determine the maximum amount of sorption (Table S5).

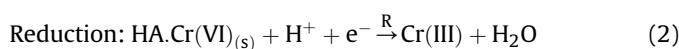
The results of isothermal adsorption by CHA and EHA are shown in Fig. 2a. It can be observed from adsorption isotherms by EHA and CHA that, at an adsorption quantity of 23 mg/g and 13 mg/g respectively, the equilibrium concentration  $C_e$  was almost zero. This confirms that the Cr(VI) adsorption process could not only involve partitioning. Adsorption of heavy metals like Cd(II), Pb(II) and Ni(II) on SOM generally involves partitioning (Febrianto et al., 2009; Bradl, 2004) where the concentrations in the solid phase and the aqueous phase can be in equilibrium. However, Cr(VI) adsorption on SOM does not only involves partitioning but also reduction to Cr(III), which makes it difficult in real terms to establish an equilibrium point. It was therefore expected that unlike other heavy metals, Cr(VI) adsorption isotherms will be quite different. At low (32.5–130 mg/L) initial Cr(VI) concentrations, adsorption and reduction by HA increased sharply with increase initial concentration. Beyond 130 mg/L, the rate of increase of both



**Fig. 2.** (a) Adsorption equilibrium of Cr(VI) at various initial concentrations ranging from 0.625 to 10 mM by HA (b) Correlation between reduced Cr(III) and adsorbed Cr(VI) remaining on HA, [HA] = 100 mg, I = 0.01 M CaCl<sub>2</sub> at final pH 3 and 25 °C over 20 d.

adsorption and reduction decreases. This is due to the fact that the content of high reductive functional groups is limited as established in our previous study. Therefore any further Cr(VI) addition in the aqueous phase beyond the maximum level fails to be reduced. The Cr(VI) removal at this stage was virtually determined by the reduction process. For adsorption, the increase in initial Cr(VI) concentration did not have corresponding increases in the amount of Cr(VI) sorbed. This is because the amount of Cr(VI) sorbed was limited by the adsorption capacity of HA. Therefore when the maximum capacity is reached, the amount of Cr(VI) reduced by content of reductive functional groups determines the extra amount of Cr(VI) that can sorbed on HA by creating more available sorption sites on the surface.

In theory the adsorption-reduction mechanism of Cr(VI) removal by undissolved HA can be described by;



We therefore suspected a relationship between the reduced Cr(III) amount and the sorbed Cr(VI) content on HA. To verify the kind of relationship, the reduced Cr(III) amount which was determined after subtracting the sorbed Cr(VI) content on HA from the total amount of Cr(VI) removed as shown in Fig. 2a was plotted against the sorbed Cr(VI) content on HA as shown in Fig. 2b. It was observed that there was a linear relationship between them, and the slope of EHA was higher (10.592) than that of CHA (6.356). It was again observed that the ratio of the slopes of EHA and CHA (1.67) were related to their phenolic content (reductive functional group) ratio (1.66) as established in our previous study. Adsorption of Cr(VI) on HA under the conditions of this study was complexation and the higher content of reductive functional group for EHA than CHA meant that after desorption, more Cr(VI) remained on CHA than EHA. This is because more Cr(VI) might have been reduced to Cr(III). This could explain the difference in the Cr(VI) content sorbed on EHA and CHA after desorption test and hence the shift to the right of the linear relationship between reduced Cr(III) and the adsorbed Cr(VI) content on HA. The difference in the slopes on the other hand also meant that at any given amount of sorbed Cr(VI) on HA, EHA had higher reduction rate constant  $k$ , than CHA corroborating earlier observations.

### 3.4. Effect of pH on Cr(VI) adsorption and reduction

Presumably, one of the key steps that underpins Cr(VI) retention by undissolved HA especially under strongly acidic conditions has been established to be electrostatic adsorption to HA surface (Zhang et al., 2017). Electrostatic adsorption is triggered by electrostatic force, but in the pH condition of 3, HA will be negatively charged (PZC 1.06 and 1.12) for CHA and EHA respectively. Therefore, the molecular diffusion would have been the main driving force. As adsorption of Cr(VI) onto HA is the balance result of electrostatic repulsion and molecular diffusion, with decreasing pH the electrostatic repulsion decreases, and the molecular diffusion dominate. On the other, as pH increases, electrostatic repulsion increases.

The effects of final pH (2.27–5.85) on the adsorption and reduction of Cr(VI) by undissolved HAs were investigated as shown in Fig. 3a and b. This pH range was chosen to ensure that HA remained in the undissolved form (average mass of HA in liquid phase 3.214 and 3.932 mg for CHA and EHA respectively), which is also typical of contaminated sites associated with electroplating and leather tanning industries (Liu et al., 2011; Dermentzis et al., 2011). The retention of Cr(VI) by undissolved HA under the conditions of this study was highly pH-dependent. Both EHA and CHA removed maximum quantities of Cr(VI) (98.98 and 90.20% respectively) in strongly acidic (pH 2.3) media. It however decreased to 30.66% and 27.04% respectively at slightly acidic pH of 5.86. At pH of 3,  $\text{HCrO}_4^-$  is usually the predominant Cr(VI) ion species. Cr(VI) adsorption at this condition implies that  $\text{HCrO}_4^-$  weakly binds through complexation to negatively charged HA functional groups (which are exposed under such conditions) on the surface. Additionally, as pH increases, the electrostatic repulsion increases with lower molecular diffusion which also reduced the amount of Cr(VI) removed.

It can be deduced from Fig. 3a and b that, although higher amount of Cr(VI) adsorbed onto CHA (0.34–0.11 mmol/g) compared to EHA (0.08–0.02 mmol/g), the overall reduced Cr(III) by EHA was higher (0.95–0.29 mmol/g) than CHA (0.53–0.16 mmol/g). This implies that in a typical adsorption-reduction process of the retention of Cr(VI) by undissolved HA, Cr(VI) reduction to Cr(III) by reductive functional groups may be the key limiting factor. That is, the amount of Cr(VI) removed by undissolved HA is principally determined by the reduction capacity of the HA (phenol and hydroxyl content). Similar observation has been in our previous study (Zhang et al., 2017).

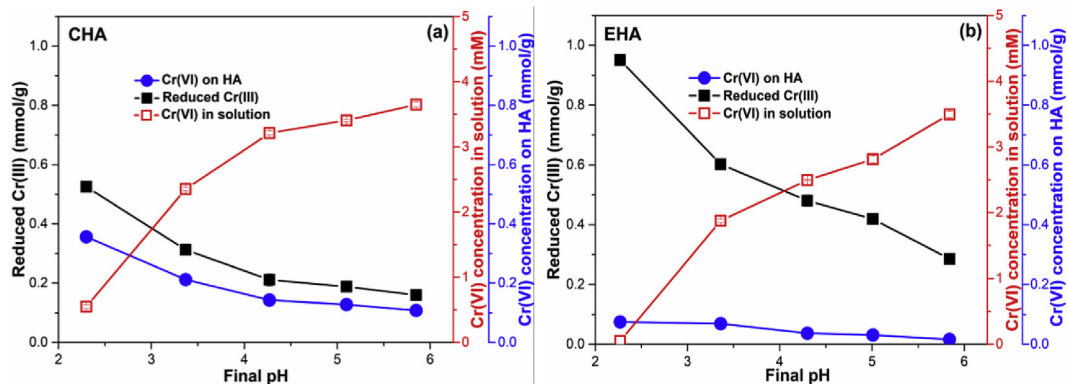


Fig. 3. pH dependencies for the adsorption and reduction of Cr(VI) from solution with (a) CHA and (b) EHA.  $[Cr(VI)]_0 = 5$  mM,  $[HA] = 100$  mg,  $I = 0.01$  M  $CaCl_2$  at  $25^\circ C$  over 20 d. Error bars represent SEM ( $n = 3$ ).

### 3.5. Effect of co-existing ion species

In a typical soil environment, HA may co-exist with varying background electrolytes bind to it. The dependence of adsorption and reduction on the co-existing ion species was investigated using

four cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) and four anions ( $SO_4^{2-}$ ,  $HCO_3^-$ ,  $NO_3^-$ ,  $Cl^-$ ).

Plots of total Cr(VI) retention quantity ( $Q_s$ ) versus equilibrium concentration of Cr(VI) in solution ( $C_e$ ) fitted with the Freundlich and Langmuir isotherm models were used to assess the effects of

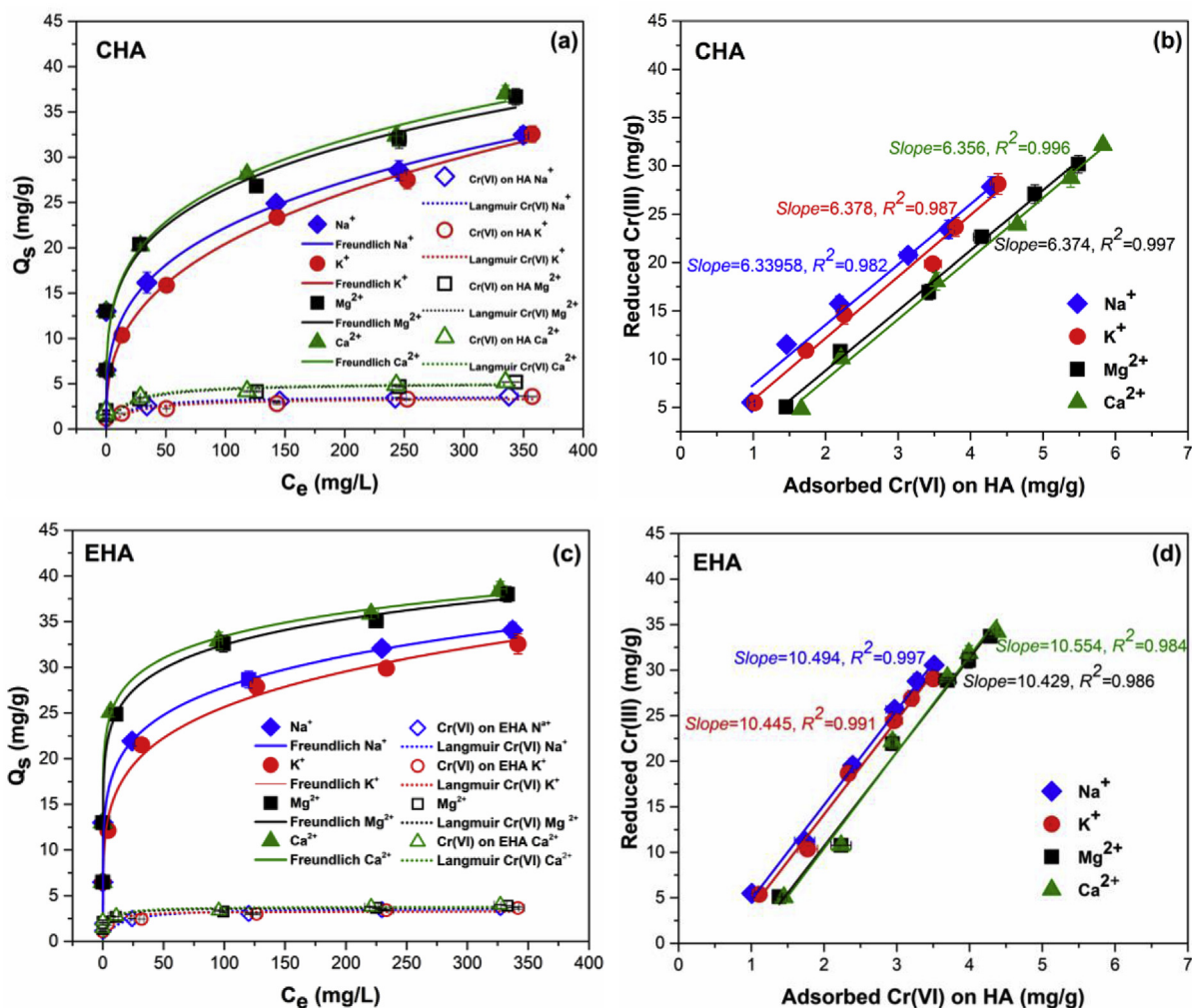


Fig. 4. Effect of various co-existing cation species on adsorption and reduction of Cr(VI) by CHA (a) and EHA (c); Correlation between reduced Cr(III) and adsorbed Cr(VI) remaining on CHA (b) and EHA (d). Final pH 3 and  $25^\circ C$  over 20 d. Initial Cr(VI) concentration in the range of 0.625–10 mM with 100 mg HA. Error bars represent SEM ( $n = 3$ ).

the co-existing ion species on reduction and adsorption respectively as shown in Fig. 4a,c. For cations, results from the plots showed that monovalent ( $K^+$  and  $Na^+$ ) and divalent ( $Ca^{2+}$  and  $Mg^{2+}$ ) cations have varying effect on the sorption capacity and intensity of both CHA and EHA samples. Divalent cations for both samples showed higher adsorption capacity and intensity compared to monovalent cations as shown in Table S6. This observation suggested a possible cation bridging of divalent cations between Cr(VI) and HA which ultimately enhances the adsorption capacity of HA. All the cations had almost the same slopes of reduction implying similar reduction rate constants. However, divalent cations had higher overall removed Cr(VI) than monovalent cations (Fig. 4b, d). The gaps in the lines of best fit suggested different Cr(VI) adsorption amounts with different cations with the higher for divalent cations.

It was suspected that co-existing anions will compete with  $HCrO_4^-$  ions for active binding sites of HA leading to an inhibitive effect. The adsorption equilibrium results showed inhibition to Cr(VI) adsorption and hence reduction in the order of  $NO_3^- < Cl^- < HCO_3^- < SO_4^{2-}$  for both CHA and EHA as shown in Fig. S6a,c. Fitting parameters of co-existing anions are shown in Table S7. This suggests that under the conditions of this experiment, co-existing anions did not have very serious adverse or inhibitory effect on adsorption and reduction as shown in Fig. S6b,d. It is

possible that the concentration of anions tested in these experiments were low to have any adverse effect on adsorption. For reduction, the anions had comparable slopes and hence did not affect Cr(VI) reduction.

### 3.6. Effect of ionic strength

Changes in ionic strength have also been reported to possibly cause some structural changes in humic substances (Swift, 1989) which makes reactive functional groups either more or less accessible to Cr(VI). Such a condition can affect Cr(VI) adsorption and reduction quantities. For this study, the effects of three different initial concentrations (0.001, 0.01 and 0.1 M) of background electrolyte ( $CaCl_2$ ) on Cr(VI) adsorption and reduction were investigated for both CHA and EHA (Fig. 5). Again, the Freundlich isotherm model was used to fit ionic strength equilibrium data for Cr(VI) removal, while the Langmuir model was used for adsorption equilibrium data. The fitting results of the ionic strength data are shown in Table S8.

Unlike Cr(VI) sorption to FA and dissolved HA (Wittbrodt and Palmer, 1996), ionic strength showed positive effect on Cr(VI) adsorption to undissolved CHA and EHA especially at higher Cr(VI) concentrations. Adsorption of Cr(VI) on both undissolved HA samples through complexation increased with increasing ionic

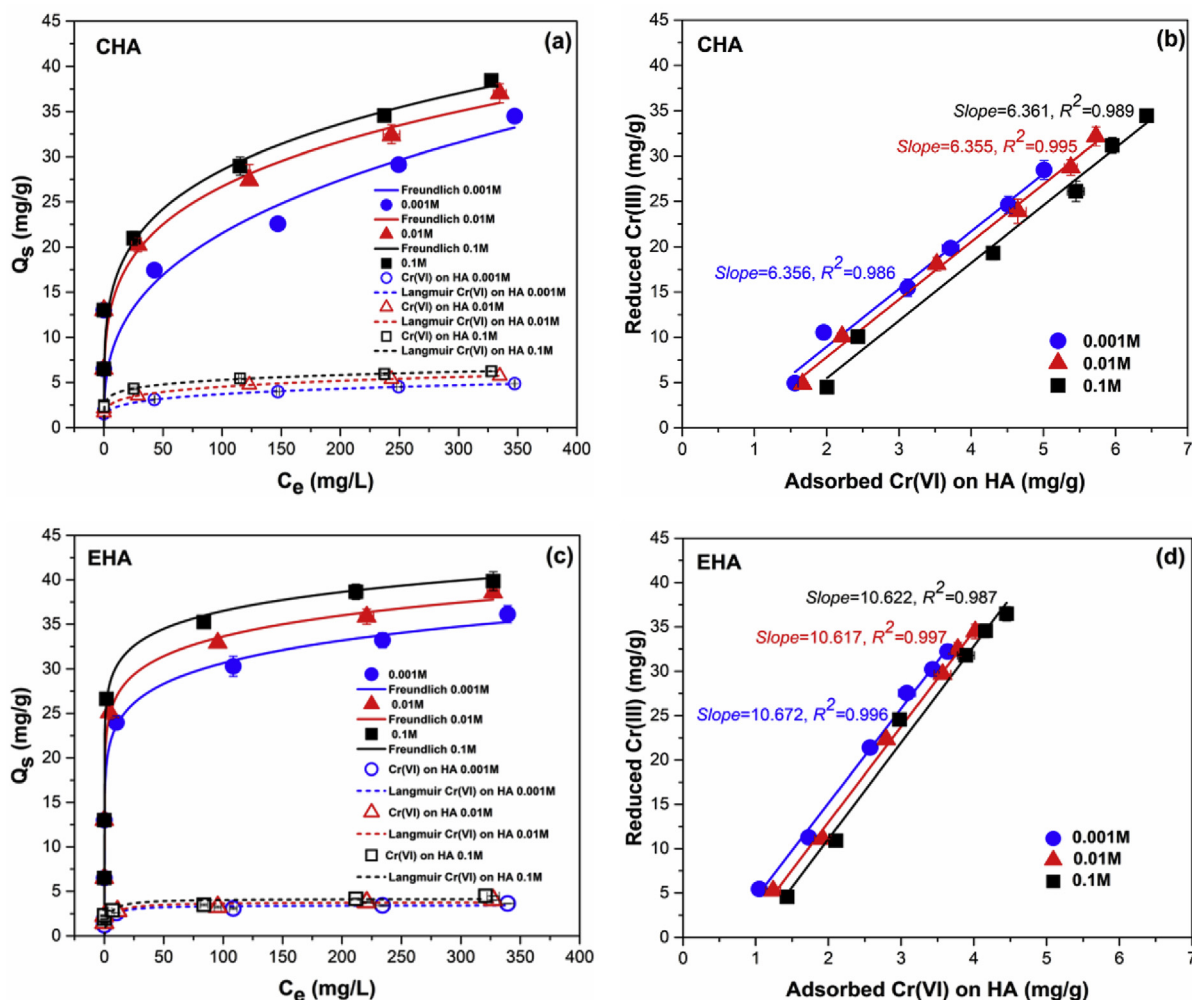


Fig. 5. Effect of various ionic strength of Cr(VI) adsorption and reduction by CHA (a) and EHA (c); Correlation between reduced Cr(III) and adsorbed Cr(VI) remaining on CHA (b) and EHA (d). Final pH 3 and 25 °C over 20 d. Initial Cr(VI) concentration in the range of 0.625–10 mM with 100 mg HA. Error bars represent SEM ( $n = 3$ ).

strength of the background electrolyte. This was because as the concentration of  $\text{CaCl}_2$  increases, more  $\text{Ca}^{2+}$  (divalent cation) ions are introduced and available for a possible cation bridging between  $\text{HCrO}_4^-$  of Cr(VI) and negatively-charged functional groups (ionized carboxyl groups) of HA confirming results from the ions species experiment.  $\text{Ca}^{2+}$  is known to be a flocculating agent of natural systems because of its ability to form efficient outer sphere bridge units with SOM (Rowley et al., 2018).

Again, exchangeable bridges attributed to  $\text{Ca}^{2+}$  are reported to usually have a larger residence time than those of monovalent cations, due to the charge-to-hydration radius ratio which prevents monovalent cations from efficiently countering electrostatic repulsion that exists between negatively-charged surfaces (Iskrenova-Tchoukova et al., 2010; Sutton et al., 2005). Elsewhere, Kalinichev and Kirkpatrick (2007) modeled the interaction between SOM and  $\text{Ca}^{2+}$  and established that  $\text{Ca}^{2+}$  could form direct cation bridges with carboxylate and to a lesser extent, phenolic and other  $-\text{OH}$  functional groups. This is consistent with the assertion by Bonn and Fish (1993) that significant humate structural modifications can occur when divalent cation concentrations are greater than 2 mM. Although  $\text{Ca}^{2+}$  could precipitate with chromate, we assumed the conditions of this experiment would not facilitate such a reaction and hence was neglected.

To find out whether increase in ionic strength ( $\text{Ca}^{2+}$ ) affected Cr(VI) reduction rates, correlations between reduced (III) amount

and Cr(VI) adsorbed on HA were utilized. Again the shifts to the right of the linear correlations meant an increase in Cr(VI) sorption on HA through complexation (Fig. 5b,d). It can be observed that the increase in ionic strength did not change the reduction rate constant, it however had positive effect on the overall amount of Cr(VI) removed. Comparing the difference in the isotherms of the Cr(VI) removed at various ionic strengths to that of the sorbed Cr(V) content on HA, it can be observed that increases in ionic strength slightly increased the reduced Cr(III) amount. This may be attributed to the fact that the cation bridging effect of  $\text{Ca}^{2+}$  through complexation made the reductive functional groups of HA more accessible to Cr(VI). This is because from reaction equation (2) Cr(VI) reduction is a function of adsorption, reductive functional groups content and protons. So at a constant protons and reductive functional groups content, an increase in adsorption will slightly increase the reduced Cr(III) amount.

### 3.7. Effect of temperature and thermodynamics

The effect of temperature on the sorption amount of Cr(VI) by HA was investigated at different temperatures of 15 °C to 35 °C (288–308 K). Based on the adsorption-reduction interaction mechanism between Cr(VI) and HA and under the conditions of this experiment (pH 3), the movement of Cr(VI) from aqueous phase onto HA solid phase was dominated by molecular complexation.

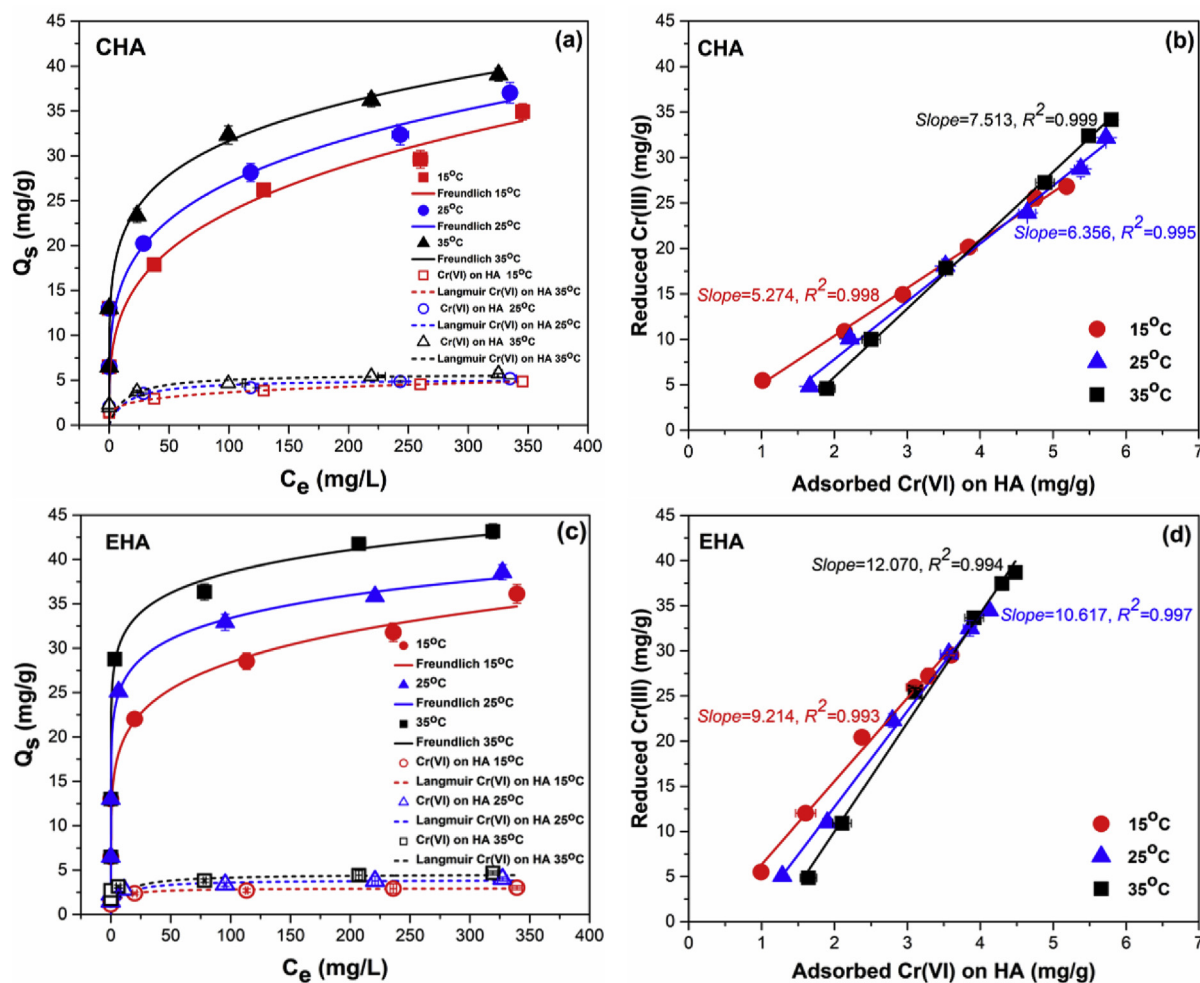


Fig. 6. Effect of temperature of Cr(VI) adsorption and reduction by CHA (a) and EHA (c); Correlation between reduced Cr(III) and adsorbed Cr(VI) remaining on CHA (b) and EHA (d). Final pH 3 over 20 d. Initial Cr(VI) concentration in the range of 0.625–10 mM with 100 mg HA.



Freundlich fitting parameters are shown in Table S9.

Molecular complexation is all about molecules moving from high concentration areas (Cr(VI) in aqueous phase) to low concentration areas (sorption sites on HA), or mixing together. Both scenarios are dependent upon the movement of the molecules, and are therefore susceptible to the effects of temperature. In a typical chemisorption process, as temperature is increased, the process of diffusion occurred more rapidly as a result of greater amount of energy in the molecules, and the faster molecules spread out onto HA solid phase more quickly. This ultimately increased both adsorption and reduction rate between Cr(VI) and the reactive functional groups of HA. The plot of Cr(VI) retention quantity as a function of temperature as shown in Fig. 6 revealed that increases in temperature increased both adsorption of Cr(VI) by both HA samples. The slopes of the correlations between reduced Cr(VI) and adsorbed Cr(VI) were quite different from each other. The slope increased with increase in temperature suggesting that the higher the temperature the higher the reduction rate constant,  $k$ . From equation (S8) van't Hoff plot of  $\ln K_c$  against  $1/T$  gives slope and intercept equal to  $-ΔH/R$  and  $ΔS^0/R$  respectively (Peng et al., 2012). The van't Hoff plots for the sorption of Cr(VI) on both CHA and EHA are shown in Fig. S6.

The observations as shown in Table S10 suggest an endothermic nature of the adsorption and reduction processes which was evident in the positive  $ΔH^0$  values. For adsorptions, 2.341 and 2.602  $\text{kJmol}^{-1}$  were recorded for both CHA and EHA respectively while reduction recorded 16.326 and 26.845 for CHA and EHA respectively. It also implied that there was an interaction between the adsorbent (HA) and adsorbate (Cr(VI)). The positive values of  $ΔS^0$  for adsorption and reduction processes were suggestive of some changes on the surface structure of the adsorbent and again indicates the trend of system to equilibrium (Li et al., 2008). The Gibbs standard free energy change ( $ΔG^0$ ) is used to determine the spontaneity of a reaction process where negative values indicate a spontaneous reaction mechanism. Adsorption values ranged from  $-0.006$  to  $-0.169$   $\text{kJmol}^{-1}$  and  $-0.039$  to  $-0.223$   $\text{kJmol}^{-1}$  for CHA and EHA respectively. It ranged from  $-0.038$  to  $-1.178$   $\text{kJmol}^{-1}$  and  $-0.324$  to  $-1.959$   $\text{kJmol}^{-1}$  for reduction CHA and EHA respectively, all indicating a spontaneous nature of the adsorption and reduction processes by undissolved HA. The decreasing degree of induction with increasing temperature proved the positive effect of higher temperature on Cr(VI) adsorption.

#### 4. Conclusions

This study investigated the retention of Cr(VI) on undissolved HA extracted from peat soil from Northeast China and commercial HA from sigma and the effect of traditional physicochemical aqueous factors. The adsorption-reduction mechanism of Cr(VI) removal by undissolved HA has been verified under varying conditions. The overall Cr(IV) amount removed by CHA and EHA were 0.61 and 0.77  $\text{mmol/g}$  respectively. Sorption isotherms suggested that both CHA and EHA have energetically heterogeneous surfaces. Like earlier reports of the interaction between Cr(VI) and DOM, adsorption and reduction of Cr(VI) on both undissolved HA samples were highly pH dependent with the processes decreasing with increase in pH. The positive effect of divalent cations ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) on adsorption and reduction was suggestive of cation bridging between Cr(VI) and HA functional groups. This was confirmed by the positive effect of the ionic strength ( $\text{Ca}^{2+}$ ) on the adsorption amount and reduction rate. Other co-existing ions ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$ ) however, had little effect on adsorption and reduction. Furthermore, the effect of temperature and thermodynamics revealed for both CHA and EHA that the adsorption and reduction processes was endothermic (positive

$ΔH^0$ ), irreversible (positive  $ΔS^0$ ) and spontaneous in nature according to  $ΔG^0$  values. In all, EHA proved to be more efficient for Cr(VI) removal than CHA.

#### Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (Grant 41672239) and China Geological Survey (1212011121173).

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.08.067>.

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