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Effects of humic acid on copper adsorption onto few-layer reduced graphene oxide and few-layer graphene oxide

Shuang Yang ^a, Lingyun Li ^b, Zhiguo Pei ^{a,*}, Chunmei Li ^a, Xiao-quan Shan ^a, Bei Wen ^a, Shuzhen Zhang ^a, Lirong Zheng ^c, Jing Zhang ^c, Yaning Xie ^c, Rixiang Huang ^d

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, Beijing 100085, China

^b Supervision and Testing Center for Vegetable Quality, Ministry of Agriculture, The Institute of Vegetables and Flowers, Chinese Academy of Agricultural Sciences, Beijing 100081, China

^c Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

^d Department of Geology, Baylor University, One Bear Place #97354, Waco, TX 76798, USA

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ABSTRACT

The effects of humic acid (HA) on copper (Cu(II)) adsorption onto few-layer reduced graphene oxide (FRGO) and few-layer graphene oxide (FGO) were investigated using a batch equilibration method, micro-Fourier transform infrared spectroscopy, and extended X-ray absorption fine structure spectroscopy (EXAFS). The results showed that HA was adsorbed on FRGO through π - π interaction. The adsorbed HA introduced O-containing functional groups and negative charges to FRGO surfaces, increasing Cu(II) adsorption through chemical complexation and electrostatic attraction. In contrast, HA was adsorbed onto FGO mainly through polar interactions, due to its rich O-containing functional groups. The adsorbed HA had little effect on Cu(II) adsorption onto FGO because the shielding effect of HA on Cu(II) adsorption was offset by newly introduced adsorption sites of HA on FGO. EXAFS results suggested that Cu(II) was adsorbed on FRGO and FGO mainly through the coordination with their O-containing functional groups. When HA was added at pH 4.0 and 6.0, more Cu(II) was adsorbed on HA-coated FRGO. At pH 8.0, a portion of Cu(II) in solution precipitated on FRGO surface, while the presence of HA led to the formation of FRGO-HA-Cu ternary surface complexes instead of Cu(II) precipitation.

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1. Introduction

Graphene-based nanomaterials (GBNs) are ideal two-dimensional materials with thickness of only one atomic layer, and have recently attracted considerable attention

due to their distinct and unique physicochemical properties [1]. GBNs are considered promising candidates in many areas of nanotechnological applications, including their use as sorbents for the removal of recalcitrant contaminants from water [2–8]. However, rapid increase in the production and

* Corresponding author. Fax: +86 10 62923563.

E-mail address: peizg@rcees.ac.cn (Z. Pei).

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application of GBNs has triggered serious concerns about their potential adverse effects on both the environment and human health due to their inevitable release into the environment [9].

Humic acid (HA) is ubiquitous in natural waters and has been found to interact with nanomaterials in the environment [10]. The interactions between HA and nanomaterials not only alter the surface properties and environmental behavior of these nanomaterials, but also affect the adsorption of coexisting contaminants [10,11]. Hyung et al. [12] revealed that dissolved organic matter (DOM) could bind with carbon nanotubes in aquatic systems through π - π interaction, and the steric and electrostatic stabilization offered by DOM greatly enhanced their stability and transport in water [13]. Shi et al. [14] reported that the presence of HA helped inhibit the formation of fullerene aggregates and increased its dispersion in solution, consequently atrazine adsorption on fullerenes was enhanced. Additionally, HA could also coat on the surface of titanium dioxide and ferromagnetic oxide nanoparticles, making removal of heavy metals from water more effective [15,16]. As for GBNs, little information is available regarding the interactions between GBNs and HA, and their subsequent effects on the adsorption of coexisting contaminants. Previous studies usually examined the adsorption of contaminants by GBNs in single solute system [17–22]. Results showed that graphene oxide was an effective adsorbent for the removal of heavy metal from water due to the coordination between metal ion and O-containing functional groups of graphene oxide [17–19]. In addition, the adsorption of lead on graphene was attributed to the occurrence of electrostatic and Lewis acid–base interactions [23].

Though knowledge regarding HA interactions with carbon nanotubes is noteworthy and can help interpret the interactions between HA and GBNs, differences between carbon nanotubes and GBNs need to be considered. Compared to carbon nanotubes, GBNs are open layered structure and contain carbons of different saturation degrees and oxidation states. As a result, the differences in properties among GBNs are pronounced. Therefore, it is necessary to study the interactions between HA and GBNs with different structures and properties, and to examine their effects on the adsorption of coexisting contaminants.

In this work, we chose few-layer reduced graphene oxide (FRGO) and few-layer graphene oxide (FGO) with different π -electron density and O-containing functional groups as adsorbents to examine the interactions of HA with FRGO and FGO and their effects on Cu(II) adsorption. Cu(II) is an essential element for life at low concentration, but is toxic at high concentrations. It can be detected in most natural settings and accumulate in soils to a high level through the land application of fertilizers, sewage sludge, or wastewater irrigation [18]. The objectives of this study were (i) to examine the adsorption of HA on FRGO and FGO, (ii) to investigate the adsorption of Cu(II) on FRGO and FGO in the absence and presence of HA, and (iii) to provide an insight into the mechanisms of Cu(II) adsorption on FRGO and FGO using extended X-ray absorption fine structure spectroscopy (EXAFS).

2. Experimental

2.1. Materials

FGO was prepared by a modified Hummers method [24], and FRGO was obtained by thermal exfoliation/reduction using graphite oxide as a precursor [25]. Detailed process has been provided in the “Supplementary data”. Cu(NO₃)₂, NaNO₃, NaOH and HNO₃ are of analytical grade and were used as received. HA was isolated from a commercial peat (Klasmann–Deilmann GmbH, Germany) according to the procedure of the International Humic Substances Society [26]. The obtained HA was dried, pulverized gently in a mortar to pass through a 0.25-mm sieve, and stored in a glass vial at room temperature before use. The elemental compositions of HA are shown in Table S1. Solid-state ¹³C nuclear magnetic resonance (NMR) spectrum was acquired using cross-polarization and magic angle spinning on a 300-MHz NMR spectrometer (Varian, San Francisco). Spectra were acquired at a frequency of 75 MHz for ¹³C magic angle spinning rate of 13 kHz, contact time of 2 ms, 4 s recycle delay. The number of scans was from 5000 to 10,000 per sample. The results showed that percentages of aliphatic and aromatic carbon are 50.2% and 36.6%, respectively (Fig. S1 and Table S2).

2.2. Characterization of FRGO and FGO

The surface functional groups of FRGO and FGO were determined by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer PHI 550 ESCA/SAM, U.S.) and Boehm titration [27,28]. Scanning electron microscope (SEM) images were obtained on a field emission scanning electron microscope (SU-8020). Transmission electron microscope (TEM) images were collected with a H-7500 (Hitachi, Japan). The size and thickness of FRGO and FGO were measured by means of atomic force microscopy (AFM) (Veeco Instrument Inc., Plainview, N.Y.). Nitrogen specific surface areas of FRGO and FGO were estimated using an accelerated surface area system and Brunauer–Emmett–Teller (BET) equation to adsorption of N₂ at 77 K.

2.3. Adsorption of HA on FRGO and FGO

HA solution (60.0 mg L^{−1}) was prepared in 0.01 M NaNO₃ solution, to which 0.1 g L^{−1} NaN₃ was added to suppress the potential growth of bacteria. The obtained HA solutions were filtered through 0.22 μ m membrane filter before use. Adsorption of HA on FRGO and FGO as a function of solution pH were performed by mixing a certain amount of FRGO or FGO with 20.0 mL 0.01 M NaNO₃ solution containing 30.0 mg L^{−1} HA in 50.0 mL polyethylene centrifuge tubes. The pH was adjusted from 4.0 to 10.0 by the addition of 0.1 M HNO₃ or NaOH. The suspension was rotated continuously for 24 h at 23.0 $\pm$ 1 °C (apparent equilibrium was reached before this time, Fig. S2a). After centrifugation at 10,000 rpm for 20 min and filtration with a 0.22 μ m membrane filter, HA concentrations in the filtrate were determined by an ultraviolet and visible spectrophotometer (U-

3010, Hitachi, Japan) at 256 nm and calibrated with a total organic carbon analyzer (Shimadzu, Japan). Preliminary results showed no significant loss of HA after centrifugation and filtration.

2.4. Adsorption of Cu(II) on FRGO and FGO as affected by HA

All adsorption experiments were conducted in triplicate using a batch equilibration method at $23.0 \pm 1^\circ\text{C}$. Prior to the initiation of Cu(II) adsorption, a certain amount of FRGO or FGO was transferred to 50.0 mL polyethylene centrifuge tubes, mixed with 10.0 mL different concentrations of HA solution, and rotated continuously for 24 h. Afterwards, different volumes of Cu(II) stock solution were added to the tubes. The final volume of the equilibrium solution was adjusted to 20.0 mL with 0.01 M NaNO_3 solution. The initial concentrations of Cu(II) were 0.1–2.5 mM, and the initial concentrations of HA were 0, 15.0 and 30.0 mg L^{-1} . The suspension pH was adjusted to 5.0 ± 0.1 by addition of 0.1 M HNO_3 or 0.1 M NaOH . The suspension was rotated continuously for 24 h to ensure complete adsorption (apparent equilibrium was reached before this time, Fig. S2b). After centrifugation and filtration, the concentrations of Cu(II) in the filtrate were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (IRIS Advantage, Thermo Elemental). The adsorbed Cu(II) was calculated from the differences between the initial and final equilibrium concentrations. Mass balance calculations were conducted by determining Cu(II) left in the equilibrium solution after Cu(II) adsorption onto FRGO or FGO, and the adsorbed Cu(II) on FRGO or FGO, which was extracted with 5.0% HNO_3 solution (30 mL) for three times. The total recovery was calculated from the sum of Cu(II) in the solution phase and the adsorbed Cu(II) on FRGO or FGO divided by the initial amount of Cu(II) added. The average recoveries of Cu(II) were $\geq 97.0\%$ for both FRGO and FGO, indicating that the loss of Cu(II) in the adsorption process was negligible.

The pH effect on Cu(II) adsorption on FRGO or FGO in the absence and presence (15.0 and 30.0 mg L^{-1}) of HA was conducted using a batch adsorption approach as mentioned above. The initial concentration of Cu(II) was 0.2 mM. After equilibrium was reached, suspension was centrifuged and filtered, and Cu(II) concentrations in the filtrate were determined by ICP-AES.

2.5. Electrophoretic mobilities (EPMs) measurement

The suspension for EPMs measurement was prepared by mixing a certain amount of FRGO or FGO with 20.0 mL 0.01 M NaNO_3 solution including different concentrations of HA (0, 15.0 and 30.0 mg L^{-1}). The solution pH was adjusted using 0.1 M HNO_3 or NaOH . The suspension was rotated continuously for 24 h at room temperature ($23.0 \pm 1^\circ\text{C}$). The EPMs were determined on a ZetaSizer Nano ZS (Malvern Instruments, Worcestershire, U.K.). Five independent EPMs measurements were collected for each sample to ensure accurate and reproducible data.

2.6. Micro-Fourier transform infrared (μ -FTIR) spectroscopy

μ -FTIR spectra were recorded on NICOLET in 10 MX (Thermo Scientific). Samples for μ -FTIR analysis were prepared by mixing a certain amount of FRGO or FGO with 20.0 mL HA solution in polyethylene centrifuge tubes. After equilibrium, the suspensions were centrifuged, and the supernatant was discarded. HA-adsorbed FRGO or FGO were washed with 0.01 M NaNO_3 solution, and then freeze-dried overnight. Microsamples were pressed on a diamond bracket and μ -FTIR spectra were measured. The resolution for μ -FTIR spectra was 4 cm^{-1} , and a total of 100 scans were collected for each spectrum. Difference spectra of HA-adsorbed samples were obtained by subtracting the spectrum of sole FRGO or FGO from the corresponding spectrum of HA-adsorbed FRGO or FGO.

2.7. X-ray absorption spectroscopy

The adsorbed samples were prepared according to above adsorption procedures, where the initial concentrations of Cu(II) and HA were 0.2 mM and 30.0 mg L^{-1} , respectively. Three pH values (4.0, 6.0 and 8.0) were selected in the experiments. After centrifugation, the supernatant was discarded. Cu K-edge (8979 eV) X-ray absorption spectra of these wet pastes were collected at 1W1B beamline of the Beijing Synchrotron Radiation Facility using a Si (111) double-crystal monochromator. Data for all adsorption samples were collected in fluorescence mode under ambient conditions. An average of three scans was performed to achieve an adequate signal to noise ratio. The data were Fourier transformed over k -region of $3.3\text{--}12.0 \text{ \AA}^{-1}$. Fitting was performed in k -space yielding optimal values for coordination numbers (N) and atomic distances (R), energy offset (E_0), and Debye–Waller factors (σ^2). Phase shifts and backscattering amplitudes were obtained from theoretical calculations using FEFF 8.0 [29]. Data analysis was performed using program WinXAS 3.1.

2.8. Isotherm models

Adsorption data were fitted to Freundlich and Langmuir equations using software Origin 7.5. Freundlich and Langmuir equations can be expressed as $Q = K_f C^n$ and $Q = K_L Q_{\text{max}} C / (1 + K_L C)$, respectively, where Q (mg g^{-1}) is the amount of adsorbed Cu(II) by FRGO and FGO, C (mg L^{-1}) is the equilibrium concentration in solution, K_f is an empirical constant related to adsorption capacity ($\text{mg}^{(1-n)} \text{ g}^{-1} \text{ L}^n$), n is Freundlich exponent, Q_{max} is maximum adsorption capacity (mg g^{-1}), and K_L is adsorption equilibrium constant.

3. Results and discussion

3.1. Characterization of FRGO and FGO

The surface morphology of FRGO and FGO was characterized by SEM and TEM. It is found that both FRGO and FGO are closely agglomerated together as thin and randomly aggregated nanosheets (Fig. S3), and have typically wrinkled, sheet-like

structures (Fig. S4). BET analysis shows that the specific surface areas (A_{BET}) of FRGO and FGO are 589.5 and 75.3 $\text{m}^2 \text{g}^{-1}$, respectively. The thickness and size of FRGO and FGO were measured by AFM (Fig. S5). The results show that the thickness of FRGO is 1.872 nm, corresponding to about 5 layers of graphene, which is close to the calculated result (about 4.4 layers of graphene) using the scaling law: layer number = $2600/A_{\text{BET}}$ [30]. The lateral length of FRGO is in the range of 0.3–1.2 μm . For FGO, its thickness is 1.158 nm (about 3 layers of graphene), and the lateral length is 0.7–2.0 μm .

XPS provides useful information about surface functional groups of FRGO and FGO. In Fig. 1a, the spectrum of FRGO shows a dominant peak of $\text{sp}^2 \text{C}=\text{C}$ at 284.6 eV, which was attributed to the graphitic structure. Several small peaks of C–O at 285.9 eV, C=O at 287.3 eV, and O–C=O at 288.9 eV were assigned to carbon atoms attached to different oxygen-containing moieties. The spectrum of FGO shows three types of carbon bonds: the carbon $\text{sp}^2 \text{C}=\text{C}$ at 284.8 eV in the basal plane of FGO, the carbon in C–O at 286.8 eV and the carbonyl carbon in C=O at 288.5 eV (Fig. 1b). These results indicated that the surface of FGO had large numbers of functional groups.

3.2. Adsorption of HA on FRGO and FGO

The adsorption of HA on FRGO and FGO as a function of pH is shown in Fig. 2. The results show that the adsorption of HA on both FRGO and FGO are pH-dependent, where their adsorption capacities decrease as pH increases. Compared to FRGO, the pH-dependency of HA adsorption on FGO is more pronounced. This suggests the primary contribution of polar interactions to the adsorption of HA, as FGO has higher density of polar groups (Fig. 1). With increasing solution pH, the functional groups on both FGO/FRGO and HA become more deprotonated (Fig. S6), the electrostatic repulsion between them inhibits the adsorption of HA on FRGO and FGO, consistent with previous observations about HA adsorption on other adsorbents [13,31].

In the examined pH range, it is found that FRGO showed much larger adsorption capacity compared to that of FGO. This is possibly because the relatively lower surface area of FGO does not provide sufficient adsorption sites for HA. Interestingly, in terms of surface area normalized adsorption capacity, the adsorption of HA on FGO was higher than that on FRGO at pH < 6.5 (Fig. S7), which was opposite to the trend

Fig. 2 – Adsorption of HA on FRGO and FGO as a function of solution pH. Initial concentration of HA was 30.0 mg L^{-1} in 0.01 M NaNO_3 solution. Data are means of three separate experiments. Error bars represent standard deviation.

shown in Fig. 2. Considering the different surface properties of FRGO and FGO, it is significant that HA was adsorbed on FRGO and FGO with different adsorption mechanisms. FRGO has rich π electrons and hydrophobic surface. It is speculated that π – π interaction and/or hydrophobic interaction are the main driving force [12]. Compared to FRGO, FGO contains fewer π -electrons, but more O-containing groups on its surfaces. It is possible that HA is adsorbed on FGO through polar interactions with these functional groups of FGO.

To reveal the adsorption mechanisms of HA on FRGO and FGO, a μ -FTIR study was performed (Fig. 3). For FRGO, peak at 1581 cm^{-1} was assigned to benzene ring C=C stretching vibration (Fig. 3a). Peaks that appeared at 1734 and 1245 cm^{-1} were the results of carboxyl C=O and epoxy C–O stretching vibrations, respectively. For HA, peak at 3367 cm^{-1} was assigned to the –OH stretching vibration. The shoulder peak at 1713 cm^{-1} was assigned to the C=O stretch of –COOH group, and the peak at 1632 cm^{-1} corresponded to the aromatic C=C stretching vibration and the ketone C=O stretching vibration of HA [32,33]. When HA was adsorbed on FRGO (Fig. 3d), it was found that the peaks of HA attributable to hydroxyl group (3367 cm^{-1}) and to carboxyl group (1713 cm^{-1}) exhibited no significant shift, suggesting that these polar groups were not involved in adsorption. As a result, the shift of peak at 1632 to 1596 cm^{-1} can be attributed to the occurrence of π – π interaction between aromatic moiety of HA and FRGO surface. It is noticeable that π – π interaction weakens the double band character of aromatic rings of HA and causes a

Fig. 1 – C1s XPS spectra of FRGO (a) and FGO (b).

Fig. 3 – μ -FTIR spectra of FRGO (a), HA (b), HA-adsorbed FRGO (c), difference spectrum of HA adsorbed on FRGO (d), FGO (e), HA-adsorbed FGO (f), and difference spectrum of HA adsorbed on FGO (g).

red-shift of C=C stretching vibration bands (Fig. 3d). This finding is supported by Hyung and Kim [12], who indicated that π - π interaction was the main driving force for the adsorption of natural organic matter on multi-walled carbon nanotubes. Furthermore, when HA is adsorbed on FRGO through π - π interaction, the hydrophobic surface of FRGO will be shielded by the aromatic moiety of HA, leaving the polar moiety of HA (carboxyl and phenolic groups, etc.) free in the opposite direction. The EMPs results revealed that ionization of these adsorbed HA further increased the surface negatively charged density of FRGO (Fig. S6a). As a result, the adsorbed HA enhanced the steric and electrostatic stabilization of FRGO and facilitated the dispersion of FRGO in aqueous solution. As shown in Fig. S8, suspension of FRGO alone became transparent quickly after settling. When HA and FRGO were mixed together, it is found the aqueous solution appeared dark and turbid even after settling for 4 days, suggesting FRGO remained suspending in solution in the presence of HA.

Compared to FRGO, μ -FTIR results reveal that HA has different adsorption mechanism on FGO due to its less π electron density and rich O-containing functional groups. For FGO, the broad peak at 3380 cm^{-1} corresponded to -OH stretching vibration (Fig. 3e). In low wavenumbers range, FTIR spectra of FGO showed carboxyl C=O (1725 cm^{-1}), aromatic C=C (1622 cm^{-1}), and carboxyl O=C-O (1383 cm^{-1}) stretching vibrations. When HA was adsorbed on FGO (Fig. 3f), the bands of FGO at 3380 and 1725 cm^{-1} were shifted to 3389 and 1721 cm^{-1} , suggesting the interaction between HA and FGO. The difference spectrum of HA adsorbed on FGO was shown in Fig. 3g, where the -OH stretching vibration, carboxyl C=O and ketone C=O stretching vibration of HA shifted significantly from 3367 , 1713 and 1632 to 3410 , 1729 and 1645 cm^{-1} , respectively, indicating that these polar functional groups were involved in the adsorption of HA on FGO [34,35].

The effect of HA on the electrokinetic properties of FGO is reported in Fig. S6. It is shown that the increase of HA concentrations had a negligible effect on the EMPs of FGO, consistent with the result of Chowdhury et al. [36]. Addition of HA,

however, enhanced the stabilization of FGO in water (Fig. S8). Because HA did not affect the EMPs of FGO, steric repulsion imparted by the adsorbed HA macromolecules may be the dominant mechanism in FGO stabilization [36,37].

3.3. Effects of HA on Cu(II) adsorption

Adsorption isotherms of Cu(II) on FRGO and FGO in the absence and presence of HA are shown in Fig. 4. Freundlich and Langmuir models were applied to fit the adsorption data. At the 95% confidence interval, it was found that the R^2 values of the Langmuir model were higher than those of the Freundlich model, indicating that the Langmuir model fitted the adsorption data better than the Freundlich model (Table 1). The Q_{max} values of Cu(II) adsorption on FRGO and FGO in the absence of HA were 11.40 and 73.36 mg g^{-1} (Table 1), respectively, suggesting that FGO was a more effective adsorbent for Cu(II) due to its numerous O-containing functional groups [17,19]. Table S3 shows the amount of different O-containing functional groups (such as carboxyl, lactone, and hydroxyl groups) on FGO. It was found that the content of carboxyl groups was higher than the sum of lactone and hydroxyl groups. Considering the strong complexation capability of carboxyl groups, it was possible that carboxyl groups played a more important role in Cu(II) adsorption than other O-containing functional groups.

When HA was added, it was found that the adsorption of Cu(II) on FRGO increased with increasing initial HA concentrations from 0 to 30.0 mg L^{-1} , suggesting that HA facilitated the adsorption of Cu(II) on FRGO (Fig. 4a). Q_{max} was used to compare the adsorption of Cu(II) (Table 1). Obviously, Q_{max} values increased from 11.40 to 18.60 mg g^{-1} when HA concentrations increased from 0 to 30.0 mg L^{-1} . As mentioned above, HA was adsorbed on FRGO mainly through π - π interaction between the aromatic fractions of HA and the aromatic surfaces of FRGO, leaving O-containing functional groups (carboxyl and phenolic groups, etc.) of HA available. Undoubtedly, the adsorbed HA introduced more O-containing functional groups and negative charges to FRGO surface, increasing the adsorption of Cu(II) through chemical complexation and electrostatic attraction. In addition, the adsorbed HA increased FRGO dispersion in solution and made more adsorption sites on FRGO available (Fig. S8), which also facilitated the adsorption of Cu(II) on FRGO to some extent.

Compared to FRGO, the presence of HA had little effects on the adsorption of Cu(II) on FGO (Fig. 4b), despite much HA had been adsorbed on FGO at pH 5.0 (Fig. 2). To date, very limited studies were available regarding the effects of HA on metal adsorption on FGO [17,38]. As mentioned above, HA was adsorbed on FGO through polar interactions. Obviously, these adsorbed HA shielded the surface of FGO and occupied parts of surface sites on FGO, which would decrease the adsorption of Cu(II). Meanwhile, the adsorption of HA also introduced new adsorption sites for metal adsorption because HA had various functional groups that can bind Cu(II) [39]. Depending on the properties of used HAs, HAs could impart different effects on metal adsorption on FGO [17,38]. For example, Zhao et al. [17] suggested that HA with high aromatic content (57.0%) effectively shielded the FGO surface with its aromatic moiety, and decreased the adsorption of cadmium and cobalt

Fig. 4 – Adsorption isotherms of Cu(II) on FRGO (a) and FGO (b) in the absence and presence of different concentrations of HA in 0.01 M NaNO₃ background electrolyte at pH 5.0 ± 0.1. Data are means of three separate experiments. Error bars represent standard deviation. The solid lines are Langmuir model simulation, and the dashed lines are Freundlich model simulation.

Table 1 – Parameters for Langmuir and Freundlich models of Cu(II) adsorption on FRGO and FGO in the absence and presence of HA.

HA concentrations (mg L ⁻¹)	Langmuir			Freundlich		
	Q _{max}	K _L	R ²	K _f	n	R ²
FRGO						
0	11.40	0.49	0.99	4.23	0.30	0.93
15.0	13.40	0.65	0.99	5.40	0.29	0.95
30.0	18.60	0.46	0.97	6.40	0.34	0.98
FGO						
0	73.36	0.11	0.97	16.58	0.33	0.95
15.0	79.64	0.09	0.98	14.43	0.37	0.98
30.0	82.91	0.09	0.99	15.84	0.37	0.97

Statistical confidence interval was set at the 95% level.

on FGO. In our case, the aromatic and carboxylic contents of the HA are 36.6% and 13.1%, respectively. No striking changes in Cu(II) adsorption on FGO by HA coating indicated that the shielding effect of HA on Cu(II) adsorption was offset by the newly introduced adsorption sites of HA on FGO (Fig. 4). To further verify this conclusion, we chose fulvic acid (FA) to study the effect of FA on Cu(II) adsorption on FGO. Compared to HA, FA has higher polarity, lower aromaticity and is more hydrophilic (Table S1) [38]. As shown in Fig. S9, the presence of FA increased the adsorption of Cu(II) on FGO, suggesting

that FA increased the adsorption sites on FGO surface and facilitated the adsorption of Cu(II).

It is possible that solution pH may affect the surface charge of adsorbents and the ionic species of metals. Therefore, the adsorption of Cu(II) on FRGO and FGO with or without HA at different equilibrium solution pH were also studied (Fig. 5). In the single solute system, it is observed that adsorption of Cu(II) increased at pH 4.0–7.5, and then maintained high loading level at pH > 7.5 (Fig. 5). The pH dependence of adsorption reactions of Cu(II) was due, in part, to the

Fig. 5 – Effect of pH on Cu(II) adsorption on FRGO (a) and FGO (b) in the absence and presence of different concentrations of HA. Initial concentrations of Cu(II) was 0.2 mM in 0.01 M NaNO₃ background electrolyte. Data are means of three separate experiments. Error bars represent standard deviation.

preferential adsorption of hydrolyzed Cu(II) species in comparison to free Cu ion [40]. Another reason was that an increase of solution pH increased the number of negatively charged sites on FRGO and FGO, which further promoted the adsorption of cationic Cu(II) (Fig. S6). When HA was added, it was found that HA increased the adsorption of Cu(II) significantly at pH < 8.0 on FRGO. At pH above 8.0, HA had little effect on the adsorbed amount of Cu(II) on FRGO (Fig. 5a). In comparison, the presence of HA had negligible effects on the adsorption of Cu(II) on FGO over the entire pH range (Fig. 5b).

3.4. EXAFS analysis

EXAFS was used to identify the surface complexation and the coordination environment of adsorbed Cu(II) on FRGO and FGO. Identification of such complex formation provides an insight into the adsorption mechanisms and species of Cu(II). The k^3 -weighted EXAFS spectra for the adsorbed Cu(II) on FRGO and FGO at pH 4.0, 6.0 and 8.0, and reference sample of aqueous Cu(II) ions are presented in Fig. 6a. Except sample FRGO at pH 8.0, it was found that spectra of all samples were dominated by a single sinusoidal wave mainly from the backscattering off of O atoms in the first atomic shell.

The corresponding radial structure functions (RSFs) are shown in Fig. 6b. For all adsorbed samples, two peaks were observed in the RSF spectra at ~ 1.5 and ~ 2.5 Å. The first peak in the RSF spectra occurring at ~ 1.5 Å corresponds to the backscattering oxygen atoms of the first shell. When Cu(II) was adsorbed on FRGO without HA at pH 4.0 and 6.0, the EXAFS fitting reveals that the Cu–O shell consists of 3.90 and 4.01 O atoms at an effective Cu–O distance of 1.94 Å

(Table 2). The second peak at ~ 2.5 Å is evidenced from Cu–C backscatter. The best fit of the second shell leads to 2.32 and 3.0 C atoms at a bond distance of 2.92 and 2.91 Å, respectively, suggesting that Cu(II) was adsorbed on FRGO surfaces mainly through the coordination with O-containing functional groups of FRGO rather than Lewis acid–base interaction [23]. When solution pH was increased to 8.0 (Fig. 6b), the magnitude of the second peak (at ~ 2.5 Å) increased. Compared to that at pH 4.0 and 6.0, it is found that this peak is a combination of Cu–C and Cu–Cu backscatter, including 7.0 C atoms at a bond distance of 2.90 Å, and 3.60 Cu(II) atoms at a bond distance of 2.92 Å (Table 2). The Cu–Cu bond distance is very close to that in Cu(OH)₂ [41]. Therefore, it is speculated that a portion of Cu may precipitate from aqueous solution onto FRGO surface at high pH range.

When Cu(II) was adsorbed on FRGO in the presence of HA at pH 4.0 and 6.0, the fitting results showed that the coordinated C atom numbers of the second peak increased from 2.32 and 3.0 to 3.31 and 3.80, suggesting that more Cu(II) was adsorbed on the coated HA (Table 2). When solution pH was increased to 8.0, interestingly, it was found that the intensity of the second peak at 2.5 Å decreased compared to that in the absence of HA (Fig. 6). The second shell was best fitted with 3.60 C atoms at an average distance of 2.94 Å (Table 2). This result indicated that the adsorbed HA increased the amount of adsorption sites on FRGO and caused most of Cu(II) to be adsorbed as FRGO–HA–Cu ternary surface complexes rather than precipitation.

When Cu(II) was adsorbed on FGO without HA, it is found that an increase of solution pH had little effect on these RSF spectra (Fig. 6). Fitting results show that ~ 3.7 O atoms at a bond distance of ~ 1.94 Å occur in the first shell peak and

Fig. 6 – Raw (solid) and fitted (dashed) EXAFS spectra (χ -function) (a) and Fourier transformation of EXAFS spectra (b) for the adsorbed Cu(II) on FRGO and FGO at pH 4.0, 6.0 and 8.0, and Cu(II) reference compound of aqueous Cu(NO₃)₂.

Table 2 – EXAFS fitting results for adsorbed Cu on FRGO and FGO in the absence and presence of HA.

Samples	Cu–O shell			Cu–C shell			Cu–Cu shell		
	R (Å) ^a (±0.02)	N ^b (±20%)	σ^2 (Å ²) ^c (±0.0005)	R (Å) ^a (±0.02)	N ^b (±20%)	σ^2 (Å ²) ^c (±0.0005)	R (Å) ^a (±0.02)	N ^b (±20%)	σ^2 (Å ²) ^c (±0.0005)
FRGO									
pH 4.0	1.94	3.90	0.003	2.92	2.32	0.006			
pH 6.0	1.94	4.01	0.005	2.91	3.00	0.007			
pH 8.0	1.95	4.20	0.004	2.90	7.00	0.008	2.92	3.60	0.01
FRGO-HA									
pH 4.0	1.94	3.80	0.004	2.91	3.31	0.01			
pH 6.0	1.94	3.88	0.005	2.90	3.80	0.01			
pH 8.0	1.95	3.90	0.004	2.94	3.60	0.009			
FGO									
pH 4.0	1.95	3.58	0.003	2.90	2.52	0.006			
pH 6.0	1.94	3.76	0.005	2.92	3.43	0.010			
pH 8.0	1.94	3.82	0.005	2.91	2.92	0.011			
FGO-HA									
pH 4.0	1.95	3.57	0.003	2.90	2.69	0.009			
pH 6.0	1.94	3.78	0.004	2.90	3.45	0.011			
pH 8.0	1.94	3.84	0.004	2.92	3.17	0.009			

Blank cells: no data. Estimated standard deviations of the least square fitting routine are given in parentheses.

^a Bond distances.

^b Coordination number.

^c Debye Waller factor.

~3.0 C atoms at a bond distance of 2.91 Å occur in the second shell peak (Table 2). Compared to FRGO, the RSF spectra of adsorbed Cu(II) on FGO at pH 8.0 was significantly different, where the second peak mainly arose from Cu–C backscatter. The results suggest that most of Cu(II) in solution was adsorbed on FGO surfaces instead of precipitation because more adsorption sites were available on GO surfaces. The complexation information of Cu(II) on FGO in the presence of HA was also examined (Table 2). It is found that the fitting data are similar to that without HA, suggesting that Cu(II) was adsorbed through the coordination with O-containing functional groups. However, it was difficult to distinguish these functional groups from FGO or from the coated HA by EXAFS alone.

4. Conclusions

The present study showed HA was adsorbed on both FRGO and FGO through different mechanisms, and consequently exerted different effects on the adsorption of Cu(II) on FRGO and FGO. The results suggested that HA was adsorbed on FRGO mainly through π – π interaction. The adsorbed HA introduced O-containing functional groups and negative charges to FRGO surface, increasing the adsorption of Cu(II) through complexation and electrostatic attraction. While HA was adsorbed on FGO through polar interactions. On the one hand, these adsorbed HA shielded the surface of FGO and occupied parts of surface sites on FGO, which would decrease the adsorption of Cu(II). On the other hand, the adsorbed HA can introduce new adsorption sites for Cu(II) adsorption onto the FGO surface. Depending on the properties of HA, HA could impart different effects on Cu(II) adsorption on FGO. In this study, the results suggest that HA had little effect on Cu(II) adsorption onto FGO. EXAFS results suggest that O-containing

functional groups of FRGO and FGO were the main adsorption sites for Cu(II). Compared to FGO, FRGO had fewer O-containing functional groups on its surfaces, which led to a portion of Cu(II) precipitate on FRGO surfaces at pH 8.0. The addition of HA increased the amount of adsorption sites on FRGO, causing most of Cu(II) to be adsorbed on FRGO surfaces as FRGO-HA-Cu ternary surface complexes at the examined pH range.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2014.03.057>.

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