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Role of water chemistry on stability, aggregation, and dissolution of uncoated and carbon-coated copper nanoparticles



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ABSTRACT

Intentional or accidental release of copper nanoparticles (Cu-NPs) from consumer products during manufacturing, use, and end-of-life management could pose health and ecological risks. This paper presents a detailed study on the role of water chemistry on the fate of uncoated and carbon-coated Cu-NPs dispersed in aqueous cetyltrimethylammonium bromide (CTAB) surfactant in the presence and absence of humic acids (HAs). A range of water chemistry and HAs had minimum impact on hydrodynamic diameter and zeta-potential values of uncoated and carbon-coated Cu-NPs. The water pH significantly (p < 0.001) affected the aggregation of uncoated Cu-NPs uncoated Cu-NPs, however, the presence of HAs increased the stability of uncoated Cu-NPs. Although CTAB is considered as an efficient dispersant to stabilize Cu-NPs, the effect descended with time for uncoated Cu-NPs. The dissolution of Cu over time decreased with increasing pH for both uncoated (0.5–50% weight) and carbon-coated (0.5–40% weight) Cu-NPs. However, carbon-coated Cu-NPs exhibited significant dissolution (p < 0.001) at neutral pH than uncoated Cu-NPs may be due to the additional carbon it acquired during coating. Increasing HAs concentration from 0 to 15 mg L⁻¹ at pH 5.5 inhibited aggregations but enhanced dissolution of the uncoated and carbon-coated Cu-NPs. These findings inform risk analysis of Cu-NPs including how Cu-NPs fate, mobility and bioavailability are modulated by particles coating and dispersant, HAs presence, water chemistry and exposure time in dispersion media.

Credit author contribution statement

Ayenachew Tegenaw: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review, and Visualization, George A. Sorial: Conceptualization, Methodology, Validation, editing, and Supervision. Endalkachew Sahle-Demessie: Validation, Conceptualization, Supervision, Methodology and editing. Changseok Han: Methodology, Formal Analysis, and Data curation.

1. Introduction

Copper nanoparticles (Cu-NPs) have attracted a growing interest for catalysis, optical, electronic, conductive coatings/inks/pastes/slurry, nanofluids, and antimicrobial applications (Ingle et al., 2014; Jang et al., 2010; Umer et al., 2012). Nearly 200,000 kg of Cu and Cu_xO NPs were produced in 2010, and about 75%, 18%, 5.5%, and 1.5% of this

account were ended up in landfill, soil, water, and air, respectively (Keller et al., 2013). The release of Cu-NPs into the ecosystems during manufacturing, use, and end-of-life management via different exposure pathways is an emerging ecological concern (Taylor and Walker, 2016). Cu is required by all organisms to carry out fundamental biological functions for normal growth and development (Yruela, 2009). However, excessive Cu oxidizes important biomolecules such as lipids, proteins, deoxy (ribonucleic) acids, and modifies molecular oxygen to produce reactive oxygen radicals that damage cells, enzymes, and protein structures (Chen et al., 2000; Sarkar et al., 2011).

Past research has found that excess Cu can have detrimental environmental effects. Studies have shown that exposure to Cu-NPs could cause health effects including hepatotoxicity, nephrotoxicity, cytotoxicity, phytotoxicity, and genotoxicity (Hejazy et al., 2018; Ingle et al., 2014; Lei et al., 2008; Mosa et al., 2018; Prasad et al., 2016). Cu-NPs have been reported to impact the performance of key wastewater treatment processes such as nitrification, denitrification, anaerobic

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digestion and enhanced biological phosphorus removal (Mu et al., 2014; Yang et al., 2013). Cu-NPs could also inhibit the microbial degradation of several pesticides (Gaw et al., 2006; Gunasekara et al., 2005; Jindal et al., 2000; Kim et al., 2011; Liu et al., 2007). The U.S. Environmental Protection Agency (U.S. EPA) listed Cu and its compounds as toxic and priority pollutants under the Clean Water Act (CWA) and Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) at the Code of Federal Regulations (CFR) 40 CFR 401.15 and 40 CFR 302, respectively.

Although detailed review of Cu-NPs toxicity exist (Hejazy et al., 2018; Ingle et al., 2014); however, in the complex and dynamic environmental matrices the toxicity depends on the stability of the NPs in the encountered media and their transformations (Conway et al., 2015; Keller et al., 2017; Song et al., 2014). The stability of Cu-NPs is subject to pH, ionic strength, and electrolyte valence of the environmental media and the presence of natural organic matter (NOM) (Aiken et al., 2011; Arenas-Lago et al., 2019; Cornelis et al., 2014). Solution pH could impact the aggregation, dissolution, bioavailability, and toxicity of Cu-NPs by affecting the surface potential of the NPs (Adeleye et al., 2014; Peng et al., 2017; Xiao et al., 2018b). Dissolved organic matter (DOM) adsorbed to Cu-NPs surfaces could alter NPs surfaces physicochemical properties and enhance/suppress NPs aggregation/dissolution via electrostatic repulsion and/or steric interactions (Kloster et al., 2013; Wang et al., 2015; Xiao et al., 2018b). However, the complexation of polyvalent cations with the carboxylic groups of DOM could form intermolecular bridging effect that compresses the electrical double layer (EDL) of the NPs (Kloster et al., 2013; Zhang et al., 2009). The EDL compression caused by the intermolecular bridging effect could diminish ζ-potential values of NPs which in turn lead to NPs aggregation (Chen and Elimelech, 2007; Kloster et al., 2013; Zhang et al., 2009). The origin, composition, and properties of DOM also influence the fate and mobility of the NPs (Baken et al., 2011; Li et al., 2017).

Information on the role of water chemistry on Cu-NP is far less available than Ag, TiO₂, and ZnO NPs (Adeleye et al., 2014; Arenas-Lago et al., 2019; Conway et al., 2015; Jones and Su, 2012; Keller et al., 2017; Xiao et al., 2018a, 2018b). Moreover, there is a need of information regarding the role of water chemistry on Cu-NPs stability in consideration of capping (dispersants and coatings) agents (Li et al., 2007; Saterlie et al., 2012). Capping agents such as polymers and surfactants (cationic, anionic, and non-ionic) prevent NPs aggregation via electrostatic, steric or electro steric stabilization mechanisms (El Badawy et al., 2010). Capping agents change the surface properties of NPs and could exhibit surface charge-dependent toxicity of NPs (El Badawy et al., 2011; Saterlie et al., 2012). Cu-NPs were also coated with carbon at laboratory and mass production scales to enhance oxidation stability (Athanassiou et al., 2006; Eiroma et al., 2012; Li and Liu, 2009; Li et al., 2010). However, no research work has been done on uncoated verses carbon-coated Cu-NPs colloidal stability at a range of water chemistry in the presence and absence of DOM. Therefore, the goal of the current research was to investigate how water chemistry of the exposure media modulates the stability (aggregation and dissolution) of uncoated and carbon-coated Cu-NPs in view of potential ecological implications.

2. Material and methods

2.1. Cu-NPs

Two types of Cu-NPs (uncoated and carbon-coated Cu-NPs) were selected for this study. The uncoated and carbon-coated Cu-NPs in powder forms were obtained from US Research Nanomaterials, Inc. (Houston, Texas). As per the manufacturer, the uncoated and carbon-coated Cu-NPs were made by laser synthesis method and have the following common properties: 25 nm average particle size, 99.8% purity, $30-50 \text{ m}^2 \text{ g}^{-1}$ specific surface area, $0.15-0.35 \text{ g cm}^{-3}$ bulk density, 8.94 g cm⁻³ true density, and spherical shape. The uncoated

Cu-NP has a dark-brown color, whereas the carbon-coated Cu-NP is black.

2.2. The crystalline phases of Cu-NPs

The crystalline phases of uncoated and carbon-coated Cu-NPs were analyzed using X-ray diffractometer (XRD: PANalytical Xpert Pro 2 θ) with Cu-K α radiation source ($\lambda = 1.5415$ Å) operating at 40 kV and 40 mA. Phase identification and peak analysis were carried out by means of X'Pert accompanying software program PANalytical High Score Plus in conjunction with the Joint Committee on Powder Diffraction Standards (JCPDS) Database (Kobayashi et al., 2012; Yu et al., 2010). The elemental spectra of the uncoated and carbon-coated Cu-NPs were also analyzed using energy dispersive X-ray analysis (EDXA) installed in a scanning electron microscope (SEM: JSM-6490LV, JEOL) to verify the uncoated and carbon-coated Cu-NPs as Cu-NPs and imply the occurrence of oxidation due to oxygen presence.

2.3. Cu-NPs hydrodynamic diameter (D_h), zeta potential (ζ – potential), and morphology

A 100 mg of each Cu-NPs was dispersed separately in 1 L of 0.09 mM aqueous cetyl trimethylammonium bromide (CTAB) cationic surfactant solution using probe sonicator at 30 W for 10 min. Milli-Q water (deionized ultra-pure water, Millipore Corporation, "Type 1", as defined by ISO 3696 with resistivity (> 18 M Ω -cm) and conductivity $(< 0.056 \ \mu\text{S cm}^{-1})$ at 25 °C) was used in the preparation of 0.09 mM (i.e., the critical micelle concentration (CMC) value) CTAB solution. The uncoated and carbon-coated Cu-NPs were also prepared in the presence of 5 and 15 mg L^{-1} of HAs from Suwannee River (SRHA) and Sigma Aldrich (SAHA) to make a total of ten dispersions samples (five for uncoated Cu-NPs (HA-0, SRHA-5, SRHA-15, SAHA-5, and SAHA-15) and five for carbon-coated Cu-NPs (HA-0, SRHA-5, SRHA-15, SAHA-5, and SAHA-15). Particle sizer and ζ-potential analyzer (NanoBrook Omni, Brookhaven Instruments Corporation) was used to measure Dh and ζ-potential values of triplicate samples of all dispersions using dynamic light scattering (DLS) and phase analysis light scattering (PALS) techniques, respectively. Dispersions of the uncoated and carbon-coated Cu-NPs in polyvinylpyrrolidone (PVP) polymeric dispersant were also prepared and analyzed for Dh and ζ-potential measurements to see the effect of a different dispersing agent. PVP was selected for this study since it is an effective reducing agent, surface stabilizer and dispersant that modifies NPs surfaces (Koczkur et al., 2015). PVP is also a common and widely used dispersant for Cu-NPs (Umer et al., 2012).

The thermal stability and chemical analysis (functional groups) of SRHA and SAHA were analyzed using a thermogravimetric analyzer (TGA: Q500, TA Instruments) and a Fourier-transform infrared spectroscopy (FTIR: PerkinElmer 200), respectively. The FTIR spectra of uncoated Cu-NPs (alone and with SRHA/SAHA) and carbon-coated Cu-NPs (alone and with SRHA/SAHA) were also analyzed to see a change in the FTIR spectrum peak. The results and discussions of the TGA and FTIR analyses are presented in the Supplementary Data (S) in Figs. S3 and S4 and Section S1, S2.

The morphology of the uncoated and carbon-coated Cu-NPs was determined using transmission electron microscope (TEM: JEM-2100, JEOL) operating at 200 kV after the dispersions in CTAB solution were placed and dried separately on 200 mesh TEM Au grids (Ted Pella, Inc.).

2.4. Role of water chemistry on Cu-NPs D_h and ζ -potential

We investigated the role of water chemistry on the stability of Cu-NPs after sonication in triplicates for a total of ten dispersions (Section 2.4). The dispersions were adjusted to three ionic strengths (1, 10, and 20 mM) of Na⁺ (using NaCl) and Ca²⁺ (using CaCl₂), respectively. All samples were prepared in three pH values (5.5, 7.0, and 8.5) using 0.1 M HCl/NaOH solution and stirred for 15 min. The selection of HAs (5 and 15 mg L^{-1}), ionic strengths of both Na⁺ and Ca²⁺ (1, 10, and 20 mM), and pH (5.5, 7.0, and 8.5) values was based on environmental considerations of most agricultural soils and aquatic (surface and ground waters) ecosystems, and water/wastewater treatment processes in which Cu-NPs may be released and/or transported (Fondriest Environmental Inc, 2013; French et al., 2009; Gao et al., 2017; Kobayashi et al., 2012; McCauley et al., 2009; Rodrigues et al., 2009; Sobek et al., 2007; Yu et al., 2010; Zazouli et al., 2007). A total of 540 subsamples (37.5 mL each in a 50 mL tube) were analyzed for D_b and ζpotential measurements using DLS and PALS techniques, respectively. The account of the 540 subsamples was as follows: two Cu-NPs (uncoated and carbon-coated), five dispersions for each Cu-NPs (HA-0, SRHA-5, SRHA-15, SAHA-5, and SAHA-15), six ionic strengths (1, 10, 20 mM Na⁺ and 1, 10, 20 mM Ca²⁺), three pH (5.5, 7.0, and 8.5), and three replicates, i.e., 2*5*6*3*3 = 540 subsamples.

Statistically significant differences between D_h and ζ -potential values were evaluated by *t*-tests using Microsoft Excel 2016 software. The specific analysis of the applied *t*-test was "*t*-test: two-sample assuming unequal variances" with a more stringent alpha value of 0.001 (Johnson, 2013). The statistically significant differences were determined based on the obtained probability value (p-value) of one-tailed distribution *t*-test.

2.5. Role of water chemistry on Cu-NPs aggregation and dissolution

The role of water chemistry on aggregation and dissolution of Cu-NPs in HA-0, SAHA-5, and SAHA-15 solutions after sonication (Section 2.4) was investigated for a total of six dispersions (three for uncoated Cu-NPs and three for carbon-coated Cu-NPs) as a function of time (0.01, 0.5, 1, 2, 3, 6, 9, 12, 15, 30, and 60 d). The criteria of choosing SAHA over that of SRHA for this experiment was due to insignificant differences in D_b and ζ-potential values between SRHA and SAHA solutions in both uncoated and carbon-coated Cu-NPs (see Section 3.2) and SRHA is (acted as) a standard or reference HA. The six dispersions in triplicate were adjusted to the ionic strength of 10 mM Ca²⁺. The Ca²⁺ was selected due to the influence of polyvalent cations to undergo complexation with HAs to produce intermolecular bridging effect that cause reduction of surface ζ-potential and aggregation of the NPs and 10 mM was chosen in consideration of most likely environmental compartments in which the NPs may undergo (Kloster et al., 2013; Wang et al., 2015; Xiao et al., 2018b). The pH was also adjusted to 5.5, 7.0, and 8.5 using 0.1 M HCl/NaOH solution. A total of 594 sealed vials (50 mL) with 37.5 mL solution were then placed in a mechanical tumbler at 12 ± 1 revolution per min (rpm). Three sealed vials were used at each pH level to measure D_h and dissolved Cu for dispersions matrix. The pH of each sample was also measured during the course of the experiment to observe pH variation.

The dissolved Cu ion concentration of each sample was then analyzed using atomic absorption spectroscopy (AAS: PerkinElmer AAnalyst 300) following centrifugal ultrafiltration process (10 kDa pore size Amicon centrifugal ultrafiltration tubes at 6000 rpm for 30 min at 20 °C) and acidification of 5 mL of the sample with 5 mL of concentrated HCl solution (Zhang et al., 2011). The 10 kDa pore size Amicon centrifugal ultrafiltration tubes have two compartments (the upper and the lower). The lower compartment is for the collection of dissolved ionic Cu after passing through the 10 kDa ultrafiltration membrane, whereas the undissolved NPs remain in the upper compartment. The dissolved Cu ions cannot pass through the 10 kDa ultrafiltration membrane without the use of centrifuge. The maximum pore size of the 10 kDa ultrafiltration membrane is ~3 nm (Conway et al., 2015; Erickson, 2009; Sweeney et al., 2006). A mass balance of uncoated and carbon-coated Cu-NPs was also conducted at all pH and HA values using 15 min samples to evaluate the lost Cu during processing.

3. Results and discussion

3.1. The crystalline phases and morphology of Cu-NPs

The XRD spectra of the uncoated and carbon-coated Cu-NPs recorded in the 20 range of 20°-80° are shown in Fig. 1a-b. The diffraction peaks observed in the uncoated and carbon-coated Cu-NPs at 43.3°, 50.4°, and 74.2° correspond to (111), (200), and (220) planes of Cu crystal, respectively (Fig. 1a-b; Table S1). The diffraction peaks observed in the uncoated and carbon-coated Cu-NPs at 29.5°, 36.4°, 42.3°, and 61.4° correspond to (110), (111), (200), and (220) planes of Cu₂O crystals, respectively (Fig. 1a-b; Table S1). The diffraction peaks observed in uncoated Cu-NPs at 35.4° and 38.6° correspond to (111) and (111) planes of CuO crystal, respectively (Fig. 1a; Table S1). The results are in good agreement with the reported values of JCPDS no. 04-0836 for Cu crystals (Kobayashi et al., 2012; Yu et al., 2010), JCPDS no. 05-0667 for Cu₂O crystals (Giannousi et al., 2014; Khan et al., 2016), and JCPDS no. 80-1268 for CuO crystals (Lanje et al., 2010; Zhu et al., 2004). The presence of Cu₂O and CuO could be due to oxidation of Cu at ambient atmosphere (Bojko et al., 2000; Iijima et al., 2006; Platzman et al., 2008; Suzuki et al., 1997). The oxidation of uncoated Cu-NPs produced both Cu₂O and CuO, whereas the oxidation of carboncoated Cu-NPs yielded only Cu₂O. The result furnishes the information that although the coating of Cu-NPs with carbon slows oxidation compared to uncoated one; however, Cu-NPs are prone to oxidation. The average crystalline sizes of the uncoated and carbon-coated Cu-NPs based on Scherrer's formula, were estimated to be about 20 nm (Purushothaman and Muralidharan, 2009).

The elemental spectra conducted on the uncoated and carboncoated Cu-NPs using EDXA in conjunction with SEM verified the NPs as Cu by showing strong peaks of Cu at 1, 8, and 9 kev (Fig. 1c-d, f-g). The presence of elemental oxygen on the EDXA spectra in the uncoated and carbon-coated Cu-NPs (Fig. 1d, g) also reinforced the oxidation of the uncoated and carbon-coated Cu-NPs by XRD analysis (Fig. 1a–b). The morphology of the uncoated and carbon-coated Cu-NPs in CTAB dispersant after TEM analysis is shown in Fig. 1e, h. The TEM images showed polydisperse spherical NPs in the size range of 5–50 nm with mean value of 25 nm for the uncoated and carbon-coated Cu-NPs (Fig. 1e, h). Up to 100 nm or higher clusters of Cu-NPs were also observed in the additional TEM images provided in Fig. S1.

3.2. Cu-NPs D_h and ζ – potential

The D_h and ζ -potential values of uncoated Cu-NPs in all dispersions (HA-0, SRHA-5, SRHA-15, SAHA-5, and SAHA-15) after DLS and PALS measurements analyses were in the range of 245-315 nm and +41-(+49) mV, respectively (Fig. 1i–j). Correspondingly, the D_h and ζ -potential values of carbon-coated Cu-NPs in all dispersions were in the range of 120–140 nm and +35-(+47) mV, respectively (Fig. 1i–j). The D_h value of NPs is the combined diameter of the particle and the surrounding fluid layer/media adsorbed on the NPs surfaces (Bhattacharjee, 2016). From the point of coating carbon-coated Cu-NPs could have larger D_h value than the uncoated Cu-NPs. However, the carbon-coated Cu-NPs were coated with carbon during synthesis that may control their sizes. In addition, the thickness of the fluid layer adsorbed on uncoated and carbon-coated Cu-NPs may vary and significantly affects the D_h value. Thus, microscopic images are needed to verify the actual size of the NPs. The analysis of the results showed that there were significant D_h differences (p = 0.001) and insignificant ζ potential difference (p = 0.122) between uncoated and the corresponding carbon-coated Cu-NPs of each tested dispersion. Moreover, there were insignificant differences in D_h values (p = 0.172) and ζ potential values (p = 0.280) among all tested dispersions of uncoated and carbon-coated Cu-NPs. On the other hand, uncoated Cu-NPs were stable in PVP dispersant having average D_h of 290 $~\pm~$ 10 nm and $\zeta\text{-}$ potential of +9 ± 2 mV (Fig. S2a); however, carbon-coated Cu-NPs



Fig. 1. XRD spectra of: (a) uncoated Cu-NPs and (b) carbon-coated Cu-NPs; uncoated Cu-NPs: (c) SEM image, (d) EDXA spectra, and (e) TEM image; carbon-coated Cu-NPs: (f) SEM image, (g) EDXA spectra, and (h) TEM image; uncoated and carbon-coated Cu-NPs: (i) D_h and (j) ζ-potential.

were aggregated in PVP dispersant having average Dh of 2200 \pm 200 nm and ζ -potential of -7 ± 3 mV (Fig. S2b). The stability of Cu-NPs by CTAB cationic surfactant is through electrostatic stabilization mechanism, whereas in the case of PVP polymer the stability is through steric stabilization due to the adsorption of PVP on Cu-NPs surfaces. However, adsorption of PVP polymer on the surfaces of the carbon-coated Cu-NPs (already coated with carbon) resulted in larger $D_{\rm b}$ value (the $D_{\rm b}$ value of NPs is the combined diameter of the particle and the surrounding fluid layer adsorbed on the NPs surfaces). The PVP is an uncharged polymer that does not protonate/deprotonate; thus it has lower ζ -potential value and its stabilization effect is through steric repulsion (Csempesz and Csáki, 2000; El Badawy et al., 2010). The lower limit of 30 mV ζ-potential absolute value is a general term and may not apply to sterically stabilized NPs with PVP or other uncharged polymers (Csempesz and Csáki, 2000; El Badawy et al., 2010). The result showed that CTAB is a good dispersant for uncoated and carboncoated Cu-NPs than PVP. This scenario implies that the type of dispersant plays a key role in the stability of NPs during synthesis and nanopowder dispersion and in aqueous ecosystems in which such NPs could be released (Bakshi, 2009; Chen et al., 2003; Mulvaney, 1996).

3.3. Role of water chemistry on D_h and ζ – potential values of Cu-NPs

The role of solution pH, ionic strength, electrolytes valence, and SRHA/SAHA on D_h and ζ -potential values of uncoated and carboncoated Cu-NPs dispersed in aqueous CTAB solution after DLS and PALS measurements are shown in Fig. 2 and Fig. 3 and Tables S2–S5, respectively. The D_h and ζ -potential values of uncoated Cu-NPs in all tested dispersions across all ionic strength of Na⁺ (1–20 mM) at pH 5.5, 7.0, and 8.5 were in the range of 255–365 nm and +43-(+53) mV, 248–345 nm and +39-(+54) mV, and 250–335 nm and +40-(+51) mV, respectively (Fig. 2a–c; Fig. 3a–c; Tables S2 and S4). The D_h and ζ -potential values of uncoated Cu-NPs in all tested dispersions for ionic strength of Ca²⁺ (1–20 mM) at pH 5.5, 7.0, and 8.5 were also in the range of 280–375 nm and +38-(+52) mV, 285–360 nm and +33-(+54) mV, and 280–365 nm and +32-(+53) mV, respectively (Fig. 2d–f; Fig. 3d–f; Tables S2 and S4). Correspondingly, the D_h and ζ -potential values of carbon-coated Cu-NPs in all tested dispersions across all ionic strength of Na⁺ at pH 5.5, 7.0, and 8.5 were in the range of 117–133 nm and +34-(+46) mV, 119–138 nm and +34-(+45) mV, and 120–143 nm and +32-(+43) mV, respectively (Fig. 2g–i; Fig. 3g–I; Tables S3 and S5). The D_h and ζ -potential values of carbon-coated Cu-NPs in all tested dispersions across all ionic strength of Na⁺ at pH 5.5, 7.0, and 8.5 were in the range of 117–138 nm and +34-(+46) mV, and 120–143 nm and +32-(+43) mV, respectively (Fig. 2g–i; Fig. 3g–I; Tables S3 and S5). The D_h and ζ -potential values of carbon-coated Cu-NPs in all tested dispersions across all ionic strength of Ca²⁺ at pH 5.5, 7.0, and 8.5 were also in the range of 123–135 nm and +34-(+45) mV, 123–139 nm and +32-(+46) mV, and 124–141 nm and +32-(+43) mV, respectively (Fig. 2j-I; Fig. 3j-I; Tables S3 and S5).

The results showed significant differences in D_h values (p = 0.0004) between uncoated and the corresponding carbon-coated Cu-NPs at a range of water chemistry while the effects on ζ-potential values differences were less significant (p = 0.091). The effect of the other factors including ionic strengths of Na⁺ and Ca²⁺ (1–20 mM), pH values (5.5–8.5) and presence of SRHA/SAHA solutions (0–15 mg L^{-1}) was not significant on the D_h (p = 0.070 for uncoated and p = 0.196 for carbon-coated) and ζ -potential (p = 0.247 for uncoated and p = 0.228 for carbon-coated) values among the uncoated and carbon-coated Cu-NPs. The differences in the thermal degradation steps and the main functional groups present in the analyzed SRHA/SAHA samples accounts for the variations in the D_h and ζ -potential values (Figs. S3 and S4; Section S1, S2). Although the ζ-potential values of carbon-coated Cu-NPs decreased by < 20% compared to uncoated Cu-NPs; however, the ζ-potential values of uncoated and carbon-coated Cu-NPs in any dispersion was above +30 mV. This shows that the uncoated and



Fig. 2. Hydrodynamic diameter of: uncoated Cu-NPs in aqueous solutions of Na⁺ (a, b, c) and Ca²⁺ (d, e, f); carbon-coated Cu-NPs in Na⁺ (g, h, i) and Ca²⁺ (j, k, l) at selected pH in the absence and presence of SRHA and SAHA. * Triplicate measurements with triplicate run (30 s per run) were taken and obtained after ~15 min of ionic strength and pH adjustments.



Fig. 3. ζ -Potential of: uncoated Cu-NPs in aqueous solutions of Na⁺ (a, b, c) and Ca²⁺ (d, e, f); carbon-coated Cu-NPs in Na⁺ (g, h, i) and Ca²⁺ (j, k, l) at selected pH in the absence and presence of SRHA and SAHA. * Triplicate measurements with triplicate run (30 s per run) were taken and obtained after ~15 min of ionic strength and pH adjustments.



Fig. 4. Hydrodynamic diameter of uncoated Cu-NPs (a, b, c) and carbon-coated Cu-NPs (d, e, f) at selected pH as a function of time in the absence and presence of SAHA.

carbon-coated Cu-NPs may be stable at a range of water chemistry. The stability of uncoated and carbon-coated Cu-NPs in aqueous CTAB surfactant was due to electrostatic stabilization by CTAB (El Badawy et al., 2012; Li et al., 2007; Mandel et al., 2011). Thus, uncoated and carbon-coated Cu-NPs dispersed in CTAB or related surfactants may be stable in aqueous ecosystems of similar media characteristics as the tested water chemistry parameters. This in turn may favor the mobility of these NPs in aqueous ecosystems. However, long-term stability could not be achieved as in the case of uncoated Cu-NPs and may be for carbon-coated Cu-NPs as well (Fig. 4; Tables S6 and S7).

3.4. Role of water chemistry on aggregation of Cu-NPs

The impact of pH and SAHA on aggregation of uncoated and carboncoated Cu-NPs in aqueous CTAB solution at 10 mM Ca²⁺ as a function of time (15 min–60 d) after D_h measurement using DLS technique is shown in Fig. 4 and Tables S6 and S7. The D_h values of uncoated Cu-NPs in SAHA-0, SAHA-5, and SAHA-15 solutions at pH 5.5 for the entire time interval were in the range of 170–2480 nm, 150–2080 nm, and 160–1230 nm, respectively (Fig. 4a–c; Table S6). The D_h values of uncoated Cu-NPs in SAHA-0, SAHA-5, and SAHA-15 solutions at pH 7.0 were in the range of 300–2060 nm, 300–1120 nm, and 300–1160 nm, respectively (Fig. 4a-c; Table S6). The D_h values of uncoated Cu-NPs in SAHA-0, SAHA-5, and SAHA-15 solutions at pH 8.5 were also in the range of 300-3780 nm, 320-1170 nm, and 300-1210 nm, respectively (Fig. 4a-c; Table S6). The D_h of uncoated Cu-NPs in the absence of SAHA was significantly impacted by solution pH (p = 0.007 for pH 5.5 verses pH 7.0; p = 0.0002 for pH 5.5 verses pH 8.5, and p = 0.012 for pH 7.0 verses pH 8.5) (Fig. 4a; Table S6). This may be due to the replacement of Br⁻ by OH⁻ that transform CTAB to cetyltrimethylammonium hydroxide (CTAOH) at basic pH values (Balakrishnan et al., 2004). This implies that the NPs may lose the support of the electrostatic stabilization of CTAB that could lead to aggregation and precipitation of the uncoated Cu-NPs as time increased (Al-thabaiti et al., 2015). However, this significant effect of pH on the D_b of uncoated Cu-NPs in the absence of SAHA was significantly attenuated by the presence of SAHA-5 (p = 0.324) and SAHA-15 (p = 0.164) solutions (Fig. 4b-c; Table S6). This could be due to the steric and/or electrosteric stabilization of uncoated Cu-NPs by HAs (Adeleye and Keller, 2014; Yang et al., 2009). Furthermore, time had a significant impact (p = 0.0001) on the D_h of uncoated Cu-NPs at day 60 (compared to D_h at 15 min) at all tested pH values and SAHA concentrations. This may be attributed to the inadequacy of CTAB to keep the NPs stability in a longer period of time (Sui et al., 2006). Time also

significantly impacted the D_h of uncoated Cu-NPs in the absence of SAHA at pH 7.0 on day 3 (130% increase) and at pH 8.5 on day 0.5 (1000% increase) (Table S6). The percent change (increase/decrease) in the D_h values at each time interval for all tested samples in all pH values is also shown in Table S6. Thus, uncoated Cu-NPs dispersed in CTAB surfactant are prone to aggregation at solution pH \geq 7.0 in the absence of SAHA and in a longer time at all tested pH values in the presence and absence of SAHA solution.

On the other hand, the D_h values of carbon-coated Cu-NPs in SAHA-0. SAHA-5, and SAHA-15 solutions for the entire time interval were in the range of (130-165, 120-195, and 125-165 nm) at pH 5.5, (130-250, 120-180, and 130-180 nm) at pH 7.0, and (130-260, 125–215, and 125–160 nm) at pH 8.5, respectively (Fig. 4d-f; Table S7). Generally, the D_h of carbon-coated Cu-NPs at any tested pH, SAHA, and time values was in the range of 120-260 nm. Thus, solution pH, SAHA concentration, and exposure time had minimum impact (p > 0.001) on aggregation of carbon-coated Cu-NPs compared to uncoated Cu-NPs (Fig. 4d-f; Table S7). This may be due to the steric repulsion effect of carbon on carbon-coated Cu-NPs which prevents the particles from aggregation, whereas uncoated Cu-NPs lacks the steric repulsion effect due to the absence of carbon-coating (Kloster et al., 2013; Wang et al., 2015; Xiao et al., 2018b). Table S7 shows the details of percent change in the D_h values of carbon-coated Cu-NPs at any given time at a range of water chemistry in the presence and absence of HAs. This implies that carbon-coated Cu-NPs may stay stable in aqueous ecosystems under similar water chemistry ranges as the tested values. Thus, water chemistry and time had minimum impact on aggregation of carbon-coated Cu-NPs, whereas they had significant impact (p < 0.001) on aggregation of uncoated Cu-NPs.

The morphology of the uncoated and carbon-coated Cu-NPs in SAHA-0 solutions after 15 min and 3 d are shown in Fig. 5a–d. The uncoated Cu-NPs showed aggregation after 3 d by forming clusters of particles (Fig. 5b). However, the carbon-coated Cu-NPs did not form clusters after 3 d (Fig. 5d). The results of the SEM microscopic images clearly support the results and discussions of section 3.4.

3.5. Role of water chemistry on dissolution of Cu-NPs

The impact of pH and SAHA on dissolution of uncoated and carboncoated Cu-NPs in aqueous CTAB solution at 10 mM Ca²⁺ as a function of time (15 min-60 d) after AAS analysis is shown in Fig. 6 and Tables S8 and S9. The result showed that the dissolution of Cu at a range of water chemistry and time was from 5 to 500 g kg^{-1} (0.5–50% weight) for uncoated Cu-NPs and from 5 to 400 g kg⁻¹ (0.5–40% weight) for carbon-coated Cu-NPs (Fig. 6a-f; Tables S8 and S9). The highest Cu dissolution was at pH 5.5 and the lowest at pH 8.5 for all scenarios (Fig. 6a-f; Tables S8 and S9). The dissolved Cu in SAHA-0, SAHA-5, and SAHA-15 solutions as a function of time at pH 5.5 was in the range of 290–500 g kg $^{-1}$, 155–400 g kg $^{-1}$, and 370–480 g kg $^{-1}$ for uncoated and in the range of 170-400 g kg^{-1} , 150-330 g kg^{-1} , and 300–385 g kg⁻¹ for carbon-coated Cu-NPs, respectively (Fig. 6a–f; Tables S8 and S9). The dissolved Cu in SAHA-0, SAHA-5, and SAHA-15 solutions as a function of time at pH 7.0 was in the range of 13-85 g kg⁻¹, 16-110 g kg⁻¹, and 16-170 g kg⁻¹ for uncoated and 75-160 g kg⁻¹, 160-230 g kg⁻¹, and 185-250 g kg⁻¹ for carboncoated Cu-NPs, respectively (Fig. 6a-f; Tables S8 and S9). The dissolved Cu in SAHA-0, SAHA-5, and SAHA-15 solutions as a function of time at pH 8.5 was in the range of 5–25 g kg $^{-1}$, 5–30 g kg $^{-1}$, and 8–30 g kg $^{-1}$ for uncoated and 5–27 g kg⁻¹, 5–30 g kg⁻¹, and 7–40 g kg⁻¹ for carbon-coated Cu-NPs, respectively (Fig. 6a-f; Tables S8 and S9). Generally, the dissolution of Cu in SAHA-0, SAHA-5, and SAHA-15 solutions of uncoated and carbon-coated Cu-NPs increased with decreasing pH.

The dissolution of Cu in SAHA-0, SAHA-5, and SAHA-15 solutions as a function of time from 15 min to 60 d decreased at pH 5.5 and 7.0 but increased at pH 8.5 (Fig. 6a–f; Tables S8 and S9). The overall decrease of Cu dissolution in SAHA-0, SAHA-5, and SAHA-15 solutions as a function of time at pH 5.5 from 15 min to 60 d time interval was 35%, 53%, and 15% weight for uncoated Cu-NPs and 48%, 44%, and 11% weight for carbon-coated Cu-NP, respectively (Fig. 6a–f; Tables S8 and S9). The overall decrease of Cu dissolution in SAHA-0, SAHA-5, and



Fig. 5. SEM images of uncoated Cu-NPs (a, b) and carbon-coated Cu-NPs (c, d) in SAHA-0 solution at pH 7 after 15 min and 3 d.



Fig. 6. Dissolved Cu ions of uncoated Cu-NPs (a, b, c) and carbon-coated Cu-NPs (d, e, f) at selected pH as a function of time in the absence and presence of SAHA.

SAHA-15 solutions as a function of time at pH 7.0 was also 80%, 82%, and 88% weight for uncoated Cu-NPs and 45%, 21%, and 14% weight for carbon-coated Cu-NP, respectively (Fig. 6a–f; Tables S8 and S9). However, the overall increase of Cu dissolution in SAHA-0, SAHA-5, and SAHA-15 solutions as a function of time from 15 min to 60 d at pH 8.5 was 270%, 323%, and 182% for uncoated Cu-NPs and 342%, 373%, and 295% for carbon-coated Cu-NPs, respectively (Fig. 6a–f; Tables S8 and S9). The decreased Cu dissolution at pH 5.5 and 7.0 as a function of time may be due to the formation of insoluble complexes of Cu (Conway et al., 2015), whereas the increased Cu dissolution at pH 8.5 as a function of time was attributed to the formation of soluble complexes of Cu at alkaline pH (Doelsch et al., 2010; Temminghoff et al., 1997).

The dissolved Cu in all solutions as a function of time at pH 7.0 and 8.5 was lower than the dissolved Cu at pH 5.5 by 65–95% and 85–99% for uncoated Cu-NPs and by 4-65% and 84-99% for carbon-coated Cu-NPs, respectively (Fig. 6a-f; Tables S8 and S9). Furthermore, the dissolved Cu at pH 8.5 was lower than the dissolved Cu at pH 7.0 by 2--94% and 70–97% for uncoated and carbon-coated Cu-NPs, respectively (Fig. 6a-f; Tables S8 and S9). However, the dissolved Cu at pH 8.5 was slightly greater than the dissolved Cu at pH 7.0 for uncoated Cu-NPs after day 15 (Tables S8 and S9). Thus, the dissolved Cu at pH 5.5 was significant (p = 0.0003) for uncoated and carbon-coated Cu-NPs. However, carbon-coated Cu-NPs exhibited significant dissolution (p = 0.0001) of Cu at pH 7.0 compared to uncoated Cu-NPs in all dispersions (Fig. 6a-f; Tables S8 and S9). This may be due to the interaction of the additional carbon (the carbon-coated Cu-NPs acquired during coating) at pH 7.0 with the Cu-NPs to produce more Cu⁺² ions in the presence of aqueous CTAB solution assisted by pH drop (-0.35),

whereas uncoated Cu-NPs lacks such interaction due to the absence of carbon. The pH drop may be due to the inadequacy of 0.01 M HCl/ NaOH solution to maintain pH stability over time. However, the complexation of both uncoated and carbon-coated Cu-NPs at pH 8.5 produce only very low magnitude (concentration) of soluble complexes of Cu such as $Cu_2(OH)_2^{+2}$, $Cu(OH)_3^{-}$, $Cu(OH)_4^{-2}$, $CuOH^+$, $Cu(OH)_2$ (aq), $CuCl_3^-$, $CuCl_2_{(aq)}$, $CuCl_4^{-2}$, and $CuCl^+$. Thus, there was insignificant dissolution differences between uncoated and carbon-coated Cu-NPs in all tested dispersions at pH 8.5 (Tables S8 and S9). The highest level of Cu dissolution at pH 5.5 for the uncoated and carbon-coated Cu-NPs and at pH 7.0 for carbon-coated Cu-NPs may increase the bioavailability and mobility of Cu in aqueous ecosystems. Thus, the application and release of Cu-NPs at $pH \le 7$ may increase the dissolution of Cu-NPs and the subsequent environmental bioavailability and mobility. The change of pH during the extended period of the experiment was up to +0.25, -0.35, and -0.70 at pH 5.5, 7.0, and 8.5, respectively. This pH variation may be due to the inadequacy of 0.01 M HCl/NaOH solution to maintain pH stability over time. The lost Cu due to processing was found to be $\leq 0.1\%$ weight of Cu-NPs used in each dispersions of uncoated and carbon-coated Cu-NPs at all pH and HA values (Fig. S5). This amount is considered negligible as compared to the dissolved Cu amounts presented in Fig. 6a-f; Tables S8 and S9. It is also observed that the concentration of ionic copper was decreasing as the pH increased, whereas the concentration of particulate Cu was increasing as the pH increased (Fig. S5).

The use of SAHA-5 at pH 5.5 reduced the dissolved Cu of uncoated and carbon-coated Cu-NPs of SAHA-0 by 20–50% and 3–20%, respectively as a function of time (Fig. 6a–b, d-e; Tables S10 and S11).

However, SAHA-15 at pH 5.5 enhanced the dissolution of uncoated and carbon-coated Cu-NPs of SAHA-0 by 10-40% and 10-70%, respectively as a function of time (Fig. 6b-c, e-f; Tables S10 and S11). This finding demonstrates the dual function of HAs (reduction and enhancement) towards NPs dissolution (Slowey, 2010; Waples et al., 2005). On the other hand, SAHA-5 and SAHA-15 at pH 7.0 increased the dissolved Cu of uncoated Cu-NPs of SAHA-0 by 10-275% and 10-250% and carboncoated Cu-NPs of SAHA-0 by 50-110% and 60-150%, respectively as a function of time (Fig. 6b-c, e-f; Tables S10 and S11). Furthermore, SAHA-5 and SAHA-15 at pH 8.5 increased the dissolved Cu of uncoated Cu-NPs of SAHA-0 by 0-15% and 0-75% and carbon-coated Cu-NPs of SAHA-0 by 0-40% and 0-75%, respectively as a function of time (Fig. 6b-c, e-f; Tables S10 and S11). The impact of increasing SAHA concentration on Cu dissolution may be due to the adsorption of more Cu by active binding sites of SAHA (Boudesocque et al., 2007). The analysis of this result implies that depending on its concentration HA can inhibit or enhance the dissolution of both uncoated and carboncoated Cu-NPs at pH < 7.0. Thus, the application and release of uncoated and carbon-coated Cu-NPs at pH \leq 7 in the presence of HAs may increase the dissolution of Cu-NPs and the subsequent environmental bioavailability and mobility.

4. Conclusion

The environmental stability of both uncoated and carbon-coated Cu-NPs is dependent on the type of dispersant, water chemistry, exposure time, and the presence of humic acids. Water chemistry and the presence of humic acids had minimum impact on hydrodynamic diameter and ζ -potential of both uncoated and carbon-coated Cu-NPs. Solution pH, humic acids, and time had minimum impact on aggregation of carbon-coated Cu-NPs; however, the significant effect of pH and time on aggregation of uncoated Cu-NPs was significantly attenuated by the presence of humic acids. Although cetyltrimethylammonium bromide (CTAB) is considered as an efficient dispersant to stabilize Cu-NPs, the effect descended with time for uncoated Cu-NPs. Carbon-coated Cu-NPs exhibited significant dissolution at pH 7.0 compared to uncoated Cu-NPs in all dispersions may be due to the additional carbon it acquired during coating. Humic acid concentration of 5 mg L^{-1} inhibited Cu dissolution while a humic acid concentration of 15 mg L^{-1} enhanced Cu dissolution at pH 5.5, respectively for the uncoated and carboncoated Cu-NPs. Thus, the application and release of uncoated and carbon-coated Cu-NPs at pH \leq 7 could increase the dissolved Cu amount and the subsequent environmental bioavailability and mobility to adversely affect the biotic and abiotic components of the ecosystems. The findings in this study provide information into the potential mobility and bioavailability of uncoated and carbon-coated Cu-NPs at a range of water chemistry.

Supplementary data

Detailed discussion of TGA analysis of SRHA/SAHA and FTIR analysis of SRHA/SAHA with and without uncoated and carbon-coated Cu-NPs is presented in Sections S1 and S2. Analytical tables of XRD, D_h , ζ -potential, aggregation, and dissolution data of uncoated and carbon-coated Cu-NPs are provided in the supplementary data (Tables S1–S11). Analytical figures of more TEM images (Fig. S1), D_h of uncoated and carbon-coated Cu-NPs in PVP dispersant (Fig. S2), thermogravimetric analysis of SRHA/SAHA samples (Fig. S3), FTIR spectroscopy analysis of SRHA/SAHA with and without uncoated and carbon-coated Cu-NPs samples (Fig. S4) and mass balance of dissolved Cu (Fig. S5) are also located in the supplementary data.

Disclaimer

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Appendix A. Supplementary data

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