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# Influence of water chemistry on colloid-size Cu-based pesticides particles: A case of Cu(OH)<sub>2</sub> commercial fungicide/bactericide

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#### HIGHLIGHTS

• Cu-based pesticides contain smaller fractions of other trace and heavy metals.

• Colloid-size Cu-based pesticides comprise a fraction of nanoscale particles.

• The presence of Ca<sup>2+</sup> promotes colloidal instability and immobility.

• Solution pH < 7 modulates the dissolution and bioavailability of Cu.

• Humic acids presence ultimately reduces dissolution of Cu at pH < 7.

#### A R T I C L E I N F O

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#### ABSTRACT

The intensive, widespread, and ever-increasing applications of Cu-based pesticides in agriculture could potentially increase environmental exposures via different routes. Unlike ionic/bulk forms, the fate, transport, and toxicity of colloid-size Cu-based pesticides are not well studied. This paper provides evaluation outcomes of granule and dispersion characterizations, stability, and dissolution of colloid-size particles of Cu(OH)<sub>2</sub> commercial pesticide product at a range of water chemistry. The evaluated product contained about 35% weight of metallic Cu equivalent and Cu(OH)<sub>2</sub> particles with sizes < 1  $\mu$ m of which a fraction of nanoscale particles exist. The presence of Ca<sup>2+</sup> at ionic strengths of >0.01 M and 0.001–0.2 M significantly influenced (p < 0.001) particle size (PS) and  $\zeta$ -potential values, respectively at all investigated pH values. Cu dissolution at pH 5.5 was significant (p < 0.001) and exceeded Cu dissolutions at pH 7.0 by 87–90% and at pH 8.5 by 87–95% in all dispersions. The order of Cu dissolution was PH 5.5 > pH 7.0 > pH 8.5 in all dispersions. Cu dissolution was relatively reduced by 53% by increasing HA from 0 to 15 mg L<sup>-1</sup>, however, the overall Cu dissolution of Cu at pH < 7. The findings provide an insight into how water chemistry influences the fate and transport of colloid-size cu-based pesticides particles.

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#### 1. Introduction

Copper-based commercial pesticides play crucial roles in intensive agriculture to enhance food production and security for the ever-growing world population by controlling pests, pathogens,

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https://doi.org/10.1016/j.chemosphere.2019.124699 0045-6535/© 2019 Elsevier Ltd. All rights reserved. and diseases (Kanhed et al., 2014; Schneider et al., 2011). However, annually applied pesticides amount not reaching the target organisms exceeds 99% (Bolognesi, 2003; Carriger et al., 2006; Gavrilescu, 2005; Pimentel, 1995). This gigantic portion persists in agricultural soils via off-target deposition and foliage wash-off and enters other ecosystems mostly as runoff to adversely impact the biotic and abiotic components (De Oliveira-Filho et al., 2004; Komárek et al., 2010; Larsbo et al., 2016; Wang et al., 2009). Cu is







required by all organisms to carry out fundamental biological functions for healthy growth and development (Tapiero et al., 2003). However, excessive Cu oxidizes important biomolecules (lipids, proteins, and deoxyribonucleic acid/DNA) and modifies molecular oxygen to produce reactive oxygen species (ROS) mainly through the Haber-Weiss and Fenton reactions (Festa and Thiele, 2011; Pham et al., 2013). Moreover, Cu-based pesticides are among the most toxic pesticides to soil microorganisms and aquatic species (Bünemann et al., 2006). Thus, elevated Cu amount in agricultural soils is becoming a worldwide concern (Dewey et al., 2012; El Hadri et al., 2012).

The unique physicochemical and biological properties and novel applications of nanomaterials (NMs) have paved the way to extend the use of bulk/ionic forms of Cu-based pesticides in agricultural and non-agricultural sectors into colloid-size (1-1000 nm) Cubased pesticides (Ho et al., 2018; Matsunaga et al., 2009). Although nano-pesticides and nano-fertilizers have yielded 20-30% overall improved efficiency than their conventional counterparts, researchers have suggested large-scale critical evaluation of nano-agrochemicals and their conventional agrochemicals in realistic agricultural conditions to avoid unjustified expectations or associated fears/uncertainties (Kah, 2015; Kah et al., 2018). Due to their small sizes and high surface-to-volume ratios, NMs are potentially more reactive, bioaccumulative and toxic than their larger counterparts (Heinlaan et al., 2008). Currently, there is no evidence that NMs will lead to other toxicological endpoints than those recognized for ionic/bulk forms (Donaldson and Poland, 2013). However, small size, high surface area, guantum effect, and unique properties of nanoparticles (NPs) may lead to intricate or newfangled biological effects that are not yet fully realized (Wang et al., 2016).

Whenever colloid-size Cu-based pesticides are released to the environment, the particles may encounter various environmental media and undergo transformations (Conway et al., 2015; Lowry et al., 2012; Mudunkotuwa et al., 2012). According to DLVO (Derjaguin-Landau-Verwey-Overbeek) theory, the colloidal stability of particles is affected by the water chemistry of the exposure media (Hotze et al., 2010; Wang et al., 2011). Various studies have shown the impacts of pH, ionic strength, and electrolyte type/valence of the solution on the stability and dissolution of Cu-based NPs (Adeleye et al., 2014; Arenas-Lago et al., 2019; Peng et al., 2017; Xiao et al., 2018). HA, a primary constituent of dissolved organic matter (DOM), also plays a crucial role in the fate, transport, and toxicity of Cu-based colloids by acting as a ligand that interacts with the particles to enhance/suppress the stability and dissolution of the particles via electrostatic and steric stabilization (Aiken et al., 2011; Jones and Su, 2012; Wang et al., 2015; Xiao et al., 2018). However, the presence and extent of HAs with polyvalent cations promote colloidal aggregation through bridging effect caused by electrical double layer (EDL) compression (Liu et al., 2013; Xiao et al., 2018). The origin, compositions, and properties of HAs also influence the particles-HA or metal-HA interactions (Shen et al., 2015; Wang et al., 2015).

Unlike ionic/bulk forms, the fate, transport, and toxicity of colloid-size Cu-based pesticides are not well studied. There is also a need of information regarding PS, chemical speciation, surface chemistry, and impact of water chemistry on stability of colloid-size Cu-based commercial pesticides and miscellaneous products which are not provided by manufacturers. In this context, the current research presents a detailed evaluation of a colloid-size Cu-based commercial pesticide product at a range of water chemistry of the exposure media or solution. The primary objective of this study was to analyze the granular and dispersion characterizations, colloidal stability, and dissolution of colloid-size Cu-based pesticide particles.

#### 2. Material and methods

#### 2.1. Pesticide (fungicide/bactericide)

CuPRO® 2005 T/N/O, dry flowable, pesticide product was selected for this study. As per the manufacturer (SePRO Corporation), the pesticide consists of 538 g (53.8%) of Cu(OH)<sub>2</sub> (metallic Cu equivalent of 350 g (35%)) as an active ingredient and 462 g (46.2%)of inert ingredients per kg of product, respectively. The inert ingredients include wetting, antifoam, dispersing, disintegrating, binding, and acid-base neutralizing agents and water-soluble carrier for good dispersity, high retention, better efficacy, and improved shelf life of the active ingredient (Chen and Lin, 2005; Lefiles et al., 1995). The application rate of this pesticide is  $0.84-11.21 \text{ kg ha}^{-1}$  (typically  $0.84-4.20 \text{ kg ha}^{-1}$ ) depending on type/size/stage of crops/trees. The pesticide is used against fungal and bacterial diseases on a wide range of crops using ground and areal applications at a concentration of about 2200–30,000 mg L<sup>-1</sup> (typically 2200–11,100 mg  $L^{-1}$ ) in water dispersion. The manufacturer also recommends higher spray rates for short time intervals during periods of frequent rains and persistent severe disease conditions.

#### 2.2. Experimental measurements

Samples of CuPRO® 2005 T/N/O were analyzed for elemental and mineral compositions and colloidal dispersion characterization using different spectroscopy and microscopy techniques. The stability, aggregation, and dissolution of the colloidal dispersions were also assessed at a range of water chemistry (pH, ionic strength, electrolyte type/valence, and HAs). To ensure better quality results and reproducible data of dynamic light scattering (DLS) and phase analysis light scattering (PALS) techniques, the concentration of this pesticide was set at  $100 \text{ mg L}^{-1}$  as  $Cu(OH)_2$  in all experiments conducted (Sousa and Teixeira, 2013). The manufacturer recommended 2200–30,000 mg  $L^{-1}$  of this pesticide for agricultural applications (Section 2.1). This value is about 1200–16,000% higher than the value selected for this study. Thus, the  $100 \text{ mg L}^{-1}$  as Cu(OH)<sub>2</sub> is high compared to environment levels; however, it is too low as compared to the manufacturer's recommended value. A dissolution study was conducted with 750 mg  $L^{-1}$  CuO-NPs (Misra et al., 2011). Recent phytotoxicity studies were conducted with 25–2100 mg L<sup>-1</sup> Cu-based nano/micro/bulk/ionic pesticides on a wide range of crops (Adhikari et al., 2012; Cota-Ruiz et al., 2018; Hong et al., 2016; Lee et al., 2008; Strayer-Scherer et al., 2018; Zhao et al., 2016). Some acute aquatic toxicity studies were also conducted with 0.30–217 mg L<sup>-1</sup> of CuO-NPs across several organisms (Blinova et al., 2010; Jo et al., 2012; Manusadžianas et al., 2012; Mortimer et al., 2011).

#### 2.3. Elemental and mineral compositions

Elemental compositions were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES: Thermo Scientific iCAP 6000 Series) after triplicate samples were digested following United States Environmental Protection Agency (US EPA) method 3051 (Agazzi and Pirola, 2000). Energy dispersive X-ray analysis (EDXA) installed in a scanning electron microscope (SEM: JSM-6490LV, JEOL) was also used for elemental compositions determination. X-ray diffraction (XRD: PANalytical X'Pert Pro) with Cu-K $\alpha$  radiation source ( $\lambda = 1.5415$  Å) operating at 40 kV and 40 mA was used to determine the mineral compositions. Peak analysis and phase identification were carried out using Joint Committee on Powder Diffraction Standards (JCPDS) database (Devamani and Alagar, 2013; Singh et al., 2009).

#### 2.4. Agglomerate size of particles

Many colloidal granules tend to agglomerate after production due to their high surface area-to-volume ratios (Ju-Nam and Lead, 2008). Thus, agglomerate size of particles was determined using SEM at different magnifications.

### 2.5. Particle size, $\zeta$ -potential, and dissolved Cu of colloidal dispersions

A 100 mg as Cu(OH)<sub>2</sub> of the pesticide was added in 1 L of Milli-Q water (deionized ultra-pure water, Millipore Corporation, "Type 1", as defined by ISO 3696), Suwannee River HA (SRHA: 5 and 15 mg  $L^{-1}$ ), and Sigma Aldrich HA (SAHA: 5 and 15 mg  $L^{-1}$ ) solutions, respectively, and stirred for 15 min without sonication. The five colloidal dispersions in triplicate were then analyzed for PS and ζ-potential measurements using DLS and PALS techniques (Nano-Brook Omni, Brookhaven Instruments), respectively. The PS and ζpotential values of SRHA and SAHA samples (100 mg  $L^{-1}$ ) were also measured after the HAs suspensions were filtered through 0.45 µm filter unit which yielded the dissolved HA portion. The standard operating procedures (SOP) of DLS and PALS methods are shown in the Supplementary Information (S) document (Section S1, S2; Figs. S1 and S2). The dissolved Cu of each colloidal dispersion sample was analyzed using atomic absorption spectrophotometer (AAS: PerkinElmer AAnalyst 300) after centrifugal ultrafiltration process (10 kDa Amicon ultra-15 centrifugal filter unit at 5000×g for 30 min at 20 °C) and acidification (5 mL of each ultra-filtered sample with 5 mL concentrated HCl) (Zhang et al., 2011). The maximum pore size of the 10 kDa ultrafiltration membrane is ~3 nm (Conway et al., 2015; Erickson, 2009; Sweeney et al., 2006).

#### 2.6. Characterization of SRHA and SAHA samples

SRHA and SAHA samples were characterized for thermal gravimetric analysis (TGA) and the corresponding derivative thermal analysis (DTA) to determine their thermal stability. TGA and DTA were conducted using thermogravimetric analyzer (TGA Q500, TA Instruments) by measuring the weight and rate of weight change of the HAs samples (~5 mg) in the range of 30-600 °C temperature at a scan rate of 10°C min<sup>-1</sup> under helium gas  $(20 \text{ mLmin}^{-1})$ . Such a high temperature is for the complete thermal decomposition/degradation of HAs. Generally, the temperature is in the range of 20–1000 °C depending on type/source/composition of HAs; however, TGA curves are flat after 600 °C in most cases without impurities like clay (De Souza and Bragança, 2018; Elsheikh et al., 2017; Huculak-Maczka et al., 2018; Oliveira et al., 2009; Santos et al., 2007). FTIR analysis was also conducted using FTIR spectrometer (Cary 600 Series, Agilent Technologies) to determine main functional groups of SRHA and SAHA samples.

#### 2.7. Colloidal particles morphology

Samples of colloidal dispersions in Milli-Q and SRHA (5 and 15 mg  $L^{-1}$ ) solutions (Section 2.5) were placed and dried on separate transmission electron microscope (TEM) grids (Au, 200 meshes, Ted Pella, Inc.). The as-prepared TEM grids were then analyzed for particles imaging/morphology using TEM (JEM-2100, JEOL) operating at 200 kV.

#### 2.8. Influence of water chemistry on PS and $\zeta$ -potential values

Triplicate samples of the five colloidal dispersions in Section 2.5 were adjusted to three ionic strengths (0.001, 0.01, and 0.02 M) of  $Na^+$  and  $Ca^{2+}$ , respectively. The samples were then adjusted to

three pH values (5.5, 7.0, and 8.5) using 0.1 M HCl/NaOH solution and stirred for 15 min. A total of 270 subsamples were analyzed for PS and  $\zeta$ -potential measurements using DLS and PALS techniques, respectively to assess the effect of water chemistry on colloidal stability. The selection of HAs (5 and 15 mg L<sup>-1</sup>), ionic strengths of both Na<sup>+</sup> and Ca<sup>2+</sup> (0.001, 0.010, and 0.020 M), and pH (5.5, 7.0, and 8.5) values was based on environmental considerations of most agricultural soils ecosystem in which the pesticide product is directly applied and aquatic ecosystems in which the colloids and/ or ions may be transported (Fondriest Environmental Inc, 2013; French et al., 2009; Gao et al., 2017; McCauley et al., 2009; Rodrigues et al., 2009; Sobek et al., 2007; Zazouli et al., 2007). Milli-Q water solution was used as a baseline. Statistically significant differences among PS and  $\zeta$ -potential values, respectively were evaluated using *t*-tests (p = 0.001) using Excel 2016.

### 2.9. Influence of water chemistry on particles aggregation and dissolution

Colloidal dispersions in Mill-Q and SAHA (5 and 15 mg  $L^{-1}$ ) were selected from Section 2.5 to investigate the influence of water chemistry on aggregation and dissolution of particles. Samples of the three colloidal dispersions in triplicates were adjusted to 0.01 M  $Ca^{2+}$  and three pH values (Section 2.8). A total of 297 sealed vials (50 mL) with 37.5 mL solution were then placed in a mechanical tumbler at  $12 \pm 1$  revolution per minute (rpm). Three sealed vials were sacrificed at each pH level and each matrix. Samples were then taken at the end of 0.01, 0.5, 1, 2, 3, 6, 9, 12, 15, 30, and 60 d for PS and dissolved Cu measurements using DLS and AAS techniques. respectively. The dissolved Cu of each sample was analyzed after centrifugal ultrafiltration and acidification processes (Section 2.5). Statistically significant differences among PS and dissolved Cu values were evaluated using t-tests (Section 2.8). The experimental dissolved Cu at the first dissolution time (0.01 d or 15 min) was also compared with the expected theoretical dissolved Cu based on solubility product of Cu(OH)<sub>2</sub> and MINEQL+5 chemical equilibrium modeling system software. The solubility product constant  $(K_{sp} = [Cu^{2+}] [OH^{-}]^{2})$  of Cu(OH)<sub>2</sub> at equilibrium is  $2.20 \times 10^{-20}$ . The effect of water chemistry on the dissolution study as a result of saturation was also dealt by contrasting K<sub>sp</sub> with solubility product quotient  $(Q_{sp} = [Cu^{2+}] [OH^{-}]^2)$  at the three pH values. The values of  $[OH^{-}]$  at pH 5.5, 7.0, and 8.5 are  $3.1623 \times 10^{-9}$ ,  $1 \times 10^{-7}$ , and  $3.1623 \times 10^{-6}$  M, respectively. MINEQL+5 was performed by selecting chemical components (H<sub>2</sub>O, H<sup>+</sup>, Ca<sup>2+</sup>, and Cu<sup>2+</sup>), scanning thermodynamic data, reviewing the same input data as the experimental value (setting total concentrations and calculation parameters), running the calculation, and extracting output data (Rachou and Sauvé, 2008; Xie et al., 2016).

#### 3. Results and discussion

#### 3.1. Elemental and mineral compositions

Elemental compositions of this pesticide after ICP-AES analysis are shown in Fig. 1a and b. The product contained  $360 \pm 4$  g  $(36 \pm 0.4\%)$  of Cu per kg of product, and trace amounts of Al, Ca, Fe, K, Na, Mg, P, Pb, S, Si, Ti, and Zn (Fig. 1a and b). The analysis was also conducted for other elements but their concentrations were below the method detection limit (MDL) (Fig. 1a and b). Similarly, EDXA results showed about 36.3% weight of product as Cu and smaller amounts of Al, Ca, Fe, Na, P, and Si (Fig. 1c and d). The detection of trace amount of Au may be due to contamination of SEM sample holder. The ICP-AES ( $36 \pm 0.4\%$ ) and EDXA (36.3%) results of Cu are consistent with the manufacturer's reported value of 35% (Section 2.1) with 0.6-1.4% error. The intensive, widespread, and ever-



**Fig. 1.** Cu-based particles: elemental concentrations using ICP-AES in (a) g kg<sup>-1</sup> of product and (b) % weight of product, (c) SEM images of agglomerated particles, (d) elemental spectra using EDXA, and (e) X-ray diffraction spectra using XRD.

increasing use of this and other inorganic commercial pesticides, fertilizers, wood preservatives, antifouling agents, and miscellaneous products could also increase the amount of Cu and other heavy metals in the environment (Dewey et al., 2012; El Hadri et al., 2012). Excessive presence of Cu and other heavy metals due to such applications may cause adverse effects to soil microorganisms (Wyszkowska et al., 2013), aquatic species (Niyogi et al., 2008), human health (Mahmood and Malik, 2014), and water/wastewater treatment processes (Sanches et al., 2010; Yang et al., 2013).

The XRD spectra of the product recorded in the range of  $20^{\circ}-80^{\circ}$  at  $2\theta$  scan are shown in Fig. 1e. The observed diffraction peaks at  $23.8^{\circ}$ ,  $33.9^{\circ}$ ,  $35.9^{\circ}$ ,  $37.9^{\circ}$ ,  $39.8^{\circ}$ ,  $51.8^{\circ}$ ,  $53.3^{\circ}$ ,  $54.9^{\circ}$ ,  $62.9^{\circ}$ ,  $64.7^{\circ}$ ,  $68.4^{\circ}$ ,  $73.4^{\circ}$ , and  $76.1^{\circ}$  correspond to (021), (002), (111), (022), (130), (006), (150), (061), (200), (152), (221), (202), and (222) planes of Cu(OH)<sub>2</sub>, respectively (Fig. 1e). The diffraction lines are consistent with the reported standard values of JCPDS No. 13-0420,

35-0505, and 80-0656 (Devamani and Alagar, 2013; Singh et al., 2009). However, the detection of quartz showed the presence of impurities and that of malachite ( $Cu_2CO_3(OH)_2$ ), cornetite ( $Cu_3CO_4(OH)_3$ ), and tenorite (CuO) indicated transformations (Fig. 1e). The average crystalline size of the particles was estimated to be about 90 nm using Scherrer formula (Khan et al., 2016).

#### 3.2. Agglomerate size of dry flowables

The morphology of dry flowables analyzed using SEM at different magnifications are shown in Fig. 2a–c. The particles were observed as spherical agglomerates having an agglomerate size of  $5-250 \,\mu\text{m}$  at X50 magnification (Fig. 2a). However, SEM image taken at a higher magnification of  $\times 2,500$  uncovered the presence of polydisperse particles of irregular shape with sizes <1  $\mu$ m (Fig. 2c). The result showed that the particles are agglomerated



**Fig. 2.** Cu-based particles: SEM images of dry flowable agglomerates at magnifications of (a)  $\times$  50, (b) X500, (c) X2,500; TEM images of colloidal dispersions in (d) Milli-Q water, (e) 5 mg L<sup>-1</sup> SRHA, and (f) 15 mg L<sup>-1</sup> SRHA dispersions.

unintentionally after synthesis/production may be due to their small sizes. However, the agglomerated particles need to be dispersed in a solution to get the primary granule size. Agglomerates are reversible clusters whereas aggregates are irreversible clusters (Sokolov et al., 2015).

## 3.3. Particle size, $\zeta$ -potential, and dissolved Cu of colloidal dispersions

The PS,  $\zeta$ -potential, and dissolved Cu values of colloidal dispersions in Milli-Q, SRHA (5 and 15 mg L<sup>-1</sup>), and SAHA (5 and 15 mg L<sup>-1</sup>) solutions measured using DLS, PALS, and AAS techniques, respectively are shown in Fig. S3a-c. The PS and  $\zeta$ -potential values were about 766 ± 21 nm and  $-38 \pm 2$  mV in Milli-Q, 773 ± 46 nm and  $-40 \pm 2$  in 5 mg L<sup>-1</sup> SRHA, 782 ± 52 nm and  $-42 \pm 2$  in 15 mg L<sup>-1</sup> SRHA, 787 ± 61 nm and  $-48 \pm 4$  in 5 mg L<sup>-1</sup> SAHA, and 778 ± 40 nm and  $-55 \pm 2$  in 15 mg L<sup>-1</sup> SAHA solutions (Fig. S3a, b). The result showed that there were nonsignificant (p > 0.001) PS and  $\zeta$ -potential differences between 0, 5, and 15 mg L<sup>-1</sup> HA solutions of the five colloidal dispersions (Fig. S3a, b). However, there was a non-significant relative increase in  $\zeta$ -potential values in the order of Milli-Q < SRHA (5 and

15 mg L<sup>-1</sup>) < SAHA (5 and 15 mg L<sup>-1</sup>) solutions (Fig. S3a, b). This may be due to the origin, composition, and property of HAs that can influence the binding potential and surface properties of colloidal particles (Hyung et al., 2007; Shen et al., 2015). The differences in the thermal degradation steps and the main functional groups present in the analyzed HAs samples also reinforce the slight variations in ζ-potential values (Figs. S4 and S5; Section S3). The average PS values of SAHA and SRHA samples were about 290 ± 22 nm and 275 ± 15 nm, respectively (Fig. S3d) after 0.45 µm filtration, whereas the corresponding average ζ-potential values of SAHA and SRHA samples were about  $-52 \pm 3$  mV and  $-49 \pm 4$  mV, respectively (Fig. S3e).

The initial quantity of Cu added to all dispersions was 538 g per kg of product as  $Cu(OH)_2$  or 350 g per kg of product as Cu (Section 2.2). The concentration of dissolved Cu in the colloidal dispersions after AAS analysis (Section 2.5) was in the range of 2-3 g (0.2–0.3%) per kg of product, i.e., equivalent to 0.37–0.56% weight of Cu(OH)<sub>2</sub> or 0.57–0.86% weight of total Cu (Fig. S3c). The result showed that Cu(OH)<sub>2</sub> is slightly soluble in water under normal conditions. It has been observed that the concentration of dissolved Cu decreased non-significantly in the presence of HA (Fig. S3c). This may be due to the effect of HAs to reduce dissolution (Conway et al., 2015; Liu

and Hurt, 2010). There was also a relatively very low dissolved Cu variation between colloidal particles in SRHA and SAHA dispersions (Fig. S3c). This may be due to the fact that the origin, composition, and properties of HAs can influence the free Cu<sup>2+</sup>–HA binding potential (Shen et al., 2015). The differences in the thermal degradation steps and the main functional groups present in the analyzed HAs samples also reinforce the variations in the dissolved Cu ion concentrations (Figs. S4 and S5; Section S3).

#### 3.4. Particles morphology in colloidal dispersions

The particles morphology in Milli-Q and SRHA (5 and 15 mg L<sup>-1</sup>) colloidal dispersions analyzed using TEM technique is shown in Fig. 2d–f. The TEM imaging analysis uncovered the presence of spherical particles with sizes <20 nm (Fig. 2d–f). The result showed that a fraction of colloidal particles of this pesticide is within the nanoscale range (1–100 nm). The observation of nanoscale particles in this pesticide product is important and merits for further investigation of the fate, transport, and toxicity of particles of this pesticide.

#### 3.5. Influence of water chemistry on PS and $\zeta$ -potential values

The influence of water chemistry on PS of colloids dispersed in Milli-Q, SRHA (5 and 15 mg  $L^{-1}$ ), and SAHA (5 and 15 mg  $L^{-1}$ ) solutions after DLS measurement is shown in Fig. 3. Solution pH had non-significant influence (p > 0.001) on PS of all dispersions across all ionic strengths of Na<sup>+</sup> (Fig. 3a–d). However, solution pH had significant influence (p < 0.001) on PS of all dispersions with 0.02 M  $Ca^{2+}$  solution at all tested pH values and with 0.01 M  $Ca^{2+}$  solution at pH 5.5 solutions, respectively (Fig. 3e and f). The PS increase when the pH decreased (Fig. 3a-f) may be attributed to particles aggregation caused by the reduction of the protective effect of  $Cu^{2+}$ -HA binding due to increasing competition of H<sup>+</sup> ions on active HA binding sites (Celi et al., 2001; Meador, 1991). The significant influence (p < 0.001) on PS of 0.01 M  $Ca^{2+}$  solution at pH 5.5 and 0.02 M  $Ca^{2+}$  solution at all tested pH values may be due to particles aggregation resulted from the intermolecular bridging effect caused by the complexation of  $Ca^{2+}$  and HAs (Liu et al., 2013; Xiao et al., 2018).

Increasing the ionic strengths of Na<sup>+</sup> (0.001–0.02 M) did not influence the PS of all dispersions across all pH values (Fig. 3a-c). However, increasing the ionic strengths of  $Ca^{2+}$  from 0.001 to 0.01 M at pH 5.5 and from 0.01 to 0.02 M at all pH had significantly influenced (p < 0.001) the PS of all dispersions (Fig. 3d-f). This may be due to the intermolecular bridging effect caused by the complexation of Ca<sup>2+</sup> that leads to EDL compression, aggregation and PS increase (Liu et al., 2013; Xiao et al., 2018). The increase in HAs (SRHA and SAHA) content from 0 to 15 mg L<sup>-1</sup> resulted in nonsignificant (p > 0.001) PS difference for all ionic strengths of Na<sup>+</sup> and  $Ca^{2+}$  across all pH values, respectively (Fig. 3a–f). However, the significant influence (p < 0.001) on PS for 0.01 M Ca<sup>2+</sup> at pH 5.5 and  $0.02 \text{ Ca}^{2+}$  across all pH values, respectively (Fig. 3e and f) ascertains the intermolecular bridging effect caused by the complexation of Ca<sup>2+</sup> with HAs (Liu et al., 2013; Xiao et al., 2018). Thus, the presence of Ca<sup>2+</sup> (>0.01 M) at all investigated pH values modulates the colloidal stability, fate, and transport of such particles in agricultural soil and other ecosystems.

Correspondingly, the impact of water chemistry on  $\zeta$ -potential values of colloidal particles dispersed in Milli-Q, SRHA, and SAHA solutions after PALS measurement is shown in Fig. S6. The pH of the solutions had non-significant influence (p > 0.001) on  $\zeta$ -potential values of all dispersions across all ionic strength of Na<sup>+</sup> and Ca<sup>2+</sup>, respectively (Fig. S6a-f). The increase in ionic strengths of Na<sup>+</sup> (0.001–0.02 M) had non-significant influence (p > 0.001) on  $\zeta$ -

potential values of all dispersions at all tested pH values (Fig. S6a-c). However, the increase in ionic strengths of  $Ca^{2+}$  (0.001–0.02 M) had a significant influence (p < 0.001) on  $\zeta$ -potential values of all dispersions at all pH values (Fig. S6d-f). That means there were significant reductions (p < 0.001) in  $\zeta$ -potential values of all dispersions in Ca<sup>2+</sup> solution across all pH values. This may be attributed to the intermolecular bridging effect caused by the complexation of  $Ca^{2+}$  leading to particles aggregation (Liu et al., 2013; Xiao et al., 2018). Colloidal dispersion with a ζ-potential value between -20 and + 20 mV is considered as unstable and results in particles aggregation and settling (Crosgrove, 2005). Generally, the  $\zeta$ -potential values in Ca<sup>2+</sup> solution are insufficient to maintain colloidal stability (Crosgrove, 2005). Thus, the presence of  $Ca^{2+}$  (0.001–0.2 M) at all investigated pH values modulates the  $\zeta$ potential values and the subsequent colloidal stability and mobility of the particles in agricultural soils and other ecosystems.

### 3.6. Influence of water chemistry on particles aggregation and dissolution

Influence of pH and SAHA content on particles aggregation in 0.01 M Ca<sup>2+</sup> solution as a function of time after PS measurement using DLS technique is shown in Fig. 4a-c. The influence of time on PS of Milli-Q and SAHA (5, and 15 mg L<sup>-1</sup>) SAHA dispersions at pH 7.0 and pH 8.5 was negligible in all dispersions, respectively (Fig. 5a-c); however, it had a minimal impact (p > 0.001) at pH 5.5 (Fig. 4a–c). There were significant PS differences (p < 0.001) at pH 5.5 in Milli-Q and  $5 \text{ mg L}^{-1}$  SAHA solutions for the entire time, whereas up to day 1 in 15 mg  $L^{-1}$  (Fig. 4a–c). This may be due to the reduction of the protective effect of Cu<sup>2+</sup>-HA binding due to increasing competition of H<sup>+</sup> ions on active HA binding sites as the pH decreases leading to aggregation and PS increase (Celi et al., 2001; Meador, 1991). However, there was a non-significant PS difference (p > 0.001) between pH 7.0 and pH 8.5 in all dispersions (Fig. 4a–c). The increased content of SAHA  $(0-15 \text{ mg L}^{-1})$  had also a non-significant influence (p > 0.001) on PS at all pH values as a function of time (Fig. 4a–c). Thus, solution pH below 7 and HAs content modulate the colloidal stability and transport of particles in agricultural soils and other ecosystems.

Correspondingly, the influence of pH and SAHA content on particles dissolution in 0.01 M Ca<sup>2+</sup> as a function of time after AAS analysis is shown in Fig. 4d-f. Based on the result, time had a nonsignificant influence (p > 0.001, by < 4.5%) on the dissolution of Cu at pH 5.5 in all colloidal dispersions (Fig. 4d-f). However, time had a significant influence (p < 0.001) on the dissolution of Cu in all dispersions at pH 7.0 and 8.5, respectively (Fig. 4d-f). The overall increase of Cu dissolution as time increased from 15 min to 60 d in Milli-Q, 5 mg L<sup>-1</sup> SAHA, and 15 mg L<sup>-1</sup> SAHA dispersions was about 65%, 80%, and 30%, respectively at pH 7.0 and 194%, 360%, and 280%, respectively at pH 8.5 (Fig. 4d-f). Thus, the overall increase of Cu dissolution as a function of overall time increase was in the order of pH 5.5 < pH 7.0 < pH 8.5 in all dispersions. The reason for such dissolution increase with increased time at pH 8.5 was that HA may form soluble complexes with Cu especially at alkaline pH (Doelsch et al., 2010; Temminghoff et al., 1997). The change of pH during the extended period of the experiment was up to +0.6 at pH 5.5, -0.4 at pH 7.0, and -0.8 at pH 8.5 in all solutions. The fluctuations of pH values may be due to the effects of the inert ingredients present in the pesticide product and the inability of 0.01 M HCl or NaOH solution to maintain pH stability over time.

The average dissolved Cu amounts in Milli-Q, 5 SAHA, and  $15 \text{ mg L}^{-1}$  SAHA dispersions as a function of time were about  $41.5 \pm 0.8$ ,  $19.5 \pm 0.8$ , and  $30.5 \pm 0.6$  g, respectively at pH 5.5, about  $3.9 \pm 0.7$ ,  $3.9 \pm 0.9$ , and  $3.9 \pm 0.5$  g, respectively at pH 7.0, and about  $2.4 \pm 0.8$ ,  $2.5 \pm 0.9$ , and  $2.4 \pm 0.9$  g, respectively at pH 8.5 per kg of



Fig. 3. Cu-based particles average size in aqueous solutions (0.001, 0.01, and 0.02 M) of Na<sup>+</sup> (a, b, c) and Ca<sup>2+</sup> (d, e, f) at selected pH in Milli-Q. SRHA, and SAHA dispersions.

product (Fig. 4d-f). There were significant differences (p < 0.001) in dissolved Cu amounts between pH 5.5 and 7.0 and between pH 5.5 and 8.5 in all dispersions; however, there was non-significant difference (p > 0.001) in dissolved Cu amounts between pH 7.0 and pH 8.5 in all dispersions (Fig. 4d-f). The dissolution of Cu at pH 5.5 was significant (p < 0.001) and it was more than the dissolution of Cu at pH 7.0 by 87–90% and at pH 8.5 by 87–95% in all dispersions (Fig. 4d-f). However, the dissolution of Cu at pH 7.0 was about 35–39% more than the dissolution of Cu at pH 8.5 in all dispersions. Thus, the order of dissolution of Cu in Milli-Q, 5 and  $15 \text{ mg L}^{-1}$ SAHA dispersions was pH 5.5 > pH 7.0 > pH 8.5, respectively (Fig. 4d-f). The highest dissolution of Cu at pH 5.5 may be due to the growing competition of H<sup>+</sup> ions on active binding sites as the pH decreases (Celi et al., 2001; Meador, 1991). This highest level Cu dissolution at pH 5.5 may increase the bioavailability and mobility of Cu from agricultural soils of acidic pH to other biotic and abiotic ecosystems via foliage wash-off and run-off.

Increasing SAHA content from 0 to  $5 \text{ mg L}^{-1}$  reduced the dissolution of Cu from 41.5 to 19.5 g kg<sup>-1</sup> of product (by 53%) at pH 5.5 (Fig. 4d and e). This may be due to the strong affinity of SAHA for binding Cu<sup>2+</sup> leading to block the active sites that suppress the

dissolution of Cu ions (Erickson et al., 1996). Increasing SAHA content from 5 to  $15 \text{ mg L}^{-1}$  increased the dissolution of Cu from 19.5 to  $30.5 \text{ g kg}^{-1}$  of product (by 55%) at pH 5.5 compared to the dissolution at  $5 \text{ mg L}^{-1}$  (Fig. 4e and f). This may be due to the complexation of HA with  $Cu^{2+}$  to enhance dissolution of colloidal particles (Li et al., 2011; Miao et al., 2010; Mudunkotuwa et al., 2012). However, increasing SAHA content from 0 to  $15 \text{ mg L}^{-1}$ decreased the overall dissolution of Cu from 41.5 to  $30.5 \text{ g kg}^{-1}$  of product (by 26.5%). Thus, HAs interaction with  $Cu^{2+}$  relatively reduce or promote the dissolution or release of Cu ions depending on solution pH and HAs content (Bian et al., 2011; Miao et al., 2010), but ultimately HA reduced the overall dissolution of Cu at pH < 7. On the other hand, the increased content of SAHA from 0 to 15 mg L<sup>-1</sup>) did not influence the dissolution of Cu at pH 7.0 and pH 8.5 in all dispersions (Fig. 4d–f). Thus, solution pH < 7, increasing time at alkaline pH, and HAs content modulate the dissolution, bioavailability, and mobility of Cu in agricultural soils and other ecosystems.

The experimental dissolved Cu ion at the three pH values was also compared to the theoretical dissolved Cu ion obtained from solubility product and MINEQL +5 analyses. The experimental and



Fig. 4. Cu-based particles average size (a, b, c) and dissolved Cu (d, e, f) in aqueous solution (0.01 M Ca<sup>2+</sup>) at selected pH as a function of time in Milli-Q and SAHA.

theoretical results are shown in Fig. 5. The dissolved Cu ion in Milli-Q water dispersion at pH 5.5, 7.0, and 8.5 were  $1.23 \times 10^{-4}$ ,  $9.95 \times 10^{-6}$ , and  $3.93 \times 10^{-6}$  M, respectively (Fig. 5a). The dissolved Cu ion in 5 mg L<sup>-1</sup> SAHA dispersion at pH 5.5, 7.0, and 8.5 were  $5.71 \times 10^{-5}$ ,  $8.81 \times 10^{-6}$ , and  $2.22 \times 10^{-6}$  Å, respectively (Fig. 5a). The dissolved Cu ion in  $15 \text{ mg L}^{-1}$  SAHA dispersion at pH 5.5, 7.0, and 8.5 were  $9.29 \times 10^{-5}$ ,  $9.81 \times 10^{-6}$ , and  $2.79 \times 10^{-6}$  M, respectively (Fig. 5a). The dissolved Cu ion using solubility product equation at pH 5.5, 7.0, and 8.5 were  $2.20 \times 10^{-3}$ ,  $2.20 \times 10^{-6}$ , and  $2.20 \times 10^{-9}$  M, respectively (Fig. 5a). The dissolved Cu ion using MINEQL+5 at pH 5.5, 7.0, and 8.5 were 6.81  $\times$  10<sup>-4</sup>, 8.35  $\times$  10<sup>-7</sup>, and 8.45  $\times$  10<sup>-9</sup> M, respectively (Fig. 5a). The dissolution of Cu was in the order of: solubility product > MINEQLE+5 > Milli-Q > 15 mg  $L^{-1}$  SAHA >5 mg  $L^{-1}$  SAHA at pH 5.5; Milli-Q > 15 mg L<sup>-1</sup> SAHA >5 mg L<sup>-1</sup> SAHA > solubility product > MINEQLE+5 at pH 7.0; and Milli-Q > 15 mg  $L^{-1}$  SAHA  $>5 \text{ mg L}^{-1} \text{ SAHA} > \text{MINEQLE}+5 > \text{ solubility product at pH 8.5}$ (Fig. 5a). The theoretical Cu dissolution was higher than the experimental values at pH 5.5; however, the theoretical Cu dissolution was lower than the experimental values at  $pH \ge 7$  (Fig. 5a). Thus, pH < 7is the dominant factor to influence the theoretical and experimental Cu dissolution; however, the presence of HAs suppressed Cu dissolution.

Similarly, the  $Q_{sp}$  value in Milli-Q water dispersion at pH 5.5, 7.0, and 8.5 were  $1.23\times10^{-21},~9.95\times10^{-20},$  and  $3.93\times10^{-17},~respec$ tively (Fig. 5b). The  $Q_{sp}$  value in 5 mg L<sup>-1</sup> SAHA dispersion at pH 5.5, 7.0, and 8.5 were  $5.71 \times 10^{-22}$ ,  $8.81 \times 10^{-20}$ , and  $2.22 \times 10^{-17}$ , respectively (Fig. 5b). The  $Q_{sp}$  value in 15 mg L<sup>-1</sup> SAHA dispersion at pH 5.5, 7.0, and 8.5 were  $9.29 \times 10^{-22}$ ,  $9.81 \times 10^{-20}$ , and  $2.79 \times 10^{-17}$ , respectively (Fig. 5b). The Q<sub>sp</sub> value from solubility product equation at pH 5.5, 7.0, and 8.5 were  $3.16 \times 10^{-21}$ ,  $1.00 \times 10^{-21}$ , and  $3.16 \times 10^{-17}$ , respectively (Fig. 5b). The Q<sub>sp</sub> value from MINEQL+5 at pH 5.5, 7.0, and 8.5 were 6.81  $\times$  10<sup>-21</sup>, 8.35  $\times$  10<sup>-21</sup>, and 8.45  $\times$  10<sup>-20</sup>, respectively (Fig. 5a). All theoretical and experimental values of Q<sub>sp</sub> were less than the K<sub>sp</sub> value at pH 5.5. That means the solution was unsaturated and ions concentration was less than equilibrium concentration; therefore, the reaction was proceeded forward to reach equilibrium concentration, and more solids would dissolve. On the contrary, all theoretical and experimental values of Q<sub>sp</sub> were greater than the K<sub>sp</sub> value at pH 8.5. This implied that the solution was supersaturated and ions concentration was greater than equilibrium concentration; therefore, the reaction proceeded in reverse to reach equilibrium concentration, and precipitation would occur. At solution pH 7.0, the experimental Q<sub>sp</sub> was greater than K<sub>sp</sub> which implies that the



Fig. 5. Cu-based particles theoretical (solubility product constant and MINEQL+5) and experimental: (a) dissolved Cu ion and (b) Q<sub>sp</sub> values.

solution was supersaturated and the reaction proceeded in reverse, precipitation would occur; however, the theoretical  $Q_{sp}$  was less than the  $K_{sp}$ , which means the solution was unsaturated, proceeded forward to reach equilibrium, and more solids will dissolve. Generally, the reaction was supersaturated ( $Q_{sp} > K_{sp}$ ) at pH < 7 and unsaturated ( $Q_{sp} < K_{sp}$ ) at pH > 7.0. The  $Q_{sp}$  value was in the order of Milli-Q > solubility product >15 mg L<sup>-1</sup> SAHA >5 mg L<sup>-1</sup> >MINEQL+5 at pH 5.5. However, at pH  $\ge$  7 the  $Q_{sp}$  values are very close to each other (Fig. 5b). The dissolution equilibrium was greatly impacted by solution pH, and the presence of HA had minimum impact on the dissolution equilibrium.

#### 4. Conclusion

The evaluated colloid-size Cu-based commercial pesticide product contained about 35% weight of metallic Cu equivalent and smaller amounts of other elements. The pesticide product also contained Cu(OH)<sub>2</sub> particles with sizes < 1 µm of which a fraction of nanoscale particles exist. The presence of Ca<sup>2+</sup> at ionic strengths of >0.01 M and 0.001–0.2 M significantly influences (p < 0.001) the PS and  $\zeta$ -potential values, respectively at all investigated pH values. This in turn modulates the colloidal stability, fate, and transport of such particles in agricultural soil and other ecosystems. Thus, divalent cations (>0.01 M) play a critical role in the aggregation of particles than monovalent cations at all investigated pH values. The dissolution of Cu at pH 5.5 was significant (p < 0.001) and it was more than the dissolution of Cu at pH 7.0 by 87–90% and at pH 8.5 by 87–95% in all dispersions. The order of dissolution of Cu in 0, 5, and 15 mg L<sup>-1</sup> SAHA dispersions was pH 5.5 > pH 7.0 > pH 8.5, respectively. However, the overall increase of Cu dissolution as a function of overall time increase (15 min-60 d) was in the order of pH 5.5 < pH 7.0 < pH 8.5 in all dispersions. HAs interaction with Cu<sup>2+</sup> relatively reduce or promote the dissolution or release of Cu ions depending on solution pH and HAs content, but ultimately HAs reduce the dissolution of Cu at pH < 7. Thus, solution pH < 7, increasing time at alkaline pH, and HAs content can modulate the dissolution, bioavailability, and mobility of Cu in agricultural soils and other ecosystems. The findings in this study provide an insight into the proper characterization and assessment of colloid-size inorganic commercial pesticides at a range of water chemistry. However, porous media transport and toxicity studies at laboratory and field levels need to be done to get comprehensive information on effects of pH, ionic strength and electrolyte type, and HAs on the fate, transport, and toxicity of colloidal particles of such product.

#### Disclaimer

The views expressed in this manuscript are those of the authors and do not necessarily represent the views or policies of the US EPA.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.124699.

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