Tannic acid promotes ion release of copper oxide nanoparticles: Impacts from solution pH change and complexation reactions

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A B S T R A C T

The increasing number of applications in which copper oxide nanoparticles (CuO NPs) are used, may lead to potential release of CuO NPs into the environment. However, the impact of natural organic matters on the behavior and fate of CuO NPs in aquatic media is still largely unknown. In this study, the dissolution and aggregation of CuO NPs under the exposure of tannic acid (TA) were monitored over a period of 72 h, with a focus on assessing the contributions of solution pH changes and complexation reactions. Results showed that the total amount of Cu^{2+} released from CuO NPs increased in the presence of TA especially at the highest TA concentration of 73.5 μmol/L. Although TA was observed to wrap around the CuO NPs, the aggregation of CuO NPs was not strongly influenced by TA and by the solution pH as investigated in this study. The kinetics of Cu^{2+} release were fitted using the modified pseudo second-order model and the rate of dissolution was assessed to be highest at TA = 14.7 μmol/L. At pH = 4, the increased H^+ concentration was responsible for increased Cu^{2+} release, whereas the complexation reaction between Cu^{2+} and TA dominated at pH = 7. These findings suggested that the effects of TA on the dissolution of CuO NPs were a combination of solution pH change and complexation reaction, the relative fractions of which also depended on the solution pH. Additionally, the percentage of Cu^{2+} released from the CuO NPs was found to increase upon decreasing concentrations of CuO NPs. Our work helps to further understand how and to which extent natural organic matters affect the behavior and fate of CuO NPs.

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1. Introduction

Due to the excellent physiochemical properties, engineered metal-based nanoparticles (NPs) have been increasingly used for consumer products, and thus may be inevitably discharged into the environment in the course of storage, transportation, application, or through the incorrect waste disposal. Copper oxide NPs are one of the five most commonly used NPs (Leitch et al., 2012), including use in products like catalysts, gas sensors, heat transfer fluids, semiconductors, photovoltaic cells (Wang et al., 2016a), and recently pesticides (Le Van et al., 2016). Previous studies have reported unintentional effects of CuO NPs on both aquatic (Gunawan et al., 2011; Kahru and Dubourguier, 2010; Li et al., 2012; Zhao et al., 2013) and terrestrial organisms (Pradhan et al., 2016). To identify

and understand their risks to ecosystems and human health, it is essential to further explore the fate and behavior of CuO NPs in the environment.

Soluble metal-based NPs, such as CuO NPs may transform or redistribute in suspension through dissolution, aggregation or even agglomeration as soon as they are released into the environment (Quik et al., 2014). This may lead to alteration of their fate and behavior, and consequently of their effects on ecosystems (Liu et al., 2016). It is commonly assumed that metal ions produced from the dissolution of metal-based NPs are responsible for their toxicity because the toxic metal ions, as opposed to their particulate counterparts, can be directly taken up by organisms (Lexmond and Van Der Vorm, 1982; Xia et al., 2011) and then can exert adverse effects. This increases the mobility of CuO NPs and their hazardous dimension. However, more and more evidence is becoming available in supporting the option that the particulate forms of metal-based NPs can also enter the organisms by endocytosis (Le Van et al., 2016), and then exert toxic effects (Lee et al., 2008; Yang

et al., 2017). Particles that have settled or are adsorbed to sediments or soils may also produce toxicity to the surrounding organisms, such as fungi and bacteria (Pradhan et al., 2016). Besides, aggregation can modify the overall diffusion-layer thickness of NPs, and thus affect the dissolution of NPs (Liu et al., 2016). Thereupon the risk assessment of CuO NPs can be assessed accurately only if their dissolution and aggregation processes are fully understood.

Under environmentally realistic conditions, the fate of metal-based NPs has been determined to be highly dependent on environmental factors such as pH (Miao et al., 2015; Midander et al., 2009) and natural organic matter (NOM) (Omar et al., 2014; Son et al., 2015). Nevertheless, it is still unclear how NOM interacts with soluble metal-based NPs, which resulted in inconsistent findings. Fulvic acid was found to suppress the dissolution of Ag NPs (Gunsolus et al., 2015), while NOM including humic acid, fulvic acid, bovine serum albumin, and sodium alginate, in all cases increased the release of Cu^{2+} from Cu NPs (Wang et al., 2015). Gunsolus et al. (2015) explained that this can be attributed to amongst all 1. The diversity and variability in chemical composition of NOM especially for HA-like structures with large molecular weight; 2. Different mass ratios of NPs to NOM; 3. Different analytical methods; 4. Lack of discrimination between free metal ions and ion-NOM complexes. Theoretically, the introduction of more H^+ can promote the dissolution of soluble metal-based NPs by influencing the following reaction (Bian et al., 2011).

$$M_aO_b + H^+ \leftrightarrow M^{(2b/a)+} + H_2O \qquad (1)$$

M_aO_b: metal oxide NPs; $M^{(2b/a)+}$: metal ions released from NPs.

For NOM, the deprotonation of surface carboxyl and phenolic hydroxyl moieties may raise the H^+ concentration in solution (Philippe and Schaumann, 2014), thus affecting the surface charge and dissolution of metal-based NPs (Hypothesis 1). In addition to increasing the H^+ concentration, NOM may complex with Cu^{2+} because of intra- and inter-molecular chelation with functional groups in NOM (Kim et al., 1999; Wang et al., 2015). This may lower the free metal ion concentration on the right-hand side of equation (1) and cause the reaction to proceed to the right (Hypothesis 2). Due to electrostatic repulsion and steric hindrance (Wang et al., 2016b), the adsorbed NOM may prevent aggregation and enhance dissolution of metal-based NPs (Hypothesis 3). Moreover, Wang et al. (2016b) reported that the NOM-mediated dissolution and aggregation of soluble metal-based NPs were pH-dependent. It was thus assumed in this study that the added NOM may enhance the dissolution of CuO NPs and its impact would be the combined effect of H^+ and of complexation reactions between Cu^{2+} and NOM (general hypothesis). To our knowledge, it remains unknown how and to which extent changes of pH and complexation reactions contribute to the effects of NOM on environmental processes of metal-based NPs.

To cope with the issues indicated above and to test our hypothesis shown above, our study aims at systematically investigating the dissolution and aggregation processes of CuO NPs in the presence of tannic acid (TA, $pK_{a1} = 4.9 \pm 0.5$, $pK_{a2} = 7.4 \pm 0.6$) (Lin et al., 2009; Liu et al., 2012), with a focus on the contributions of varying solution pH and complexation reaction between Cu^{2+} and TA. TA was chosen as it has been ideally characterized in terms of composition and properties (Liu et al., 2012). It is well known that phenolic hydroxyl groups in TA (Fig. S1) are commonly present in NOM (Chang and Juang, 2004) and can strongly complex with Cu^{2+} (Hernandez et al., 2006). TA is thus a well suited NOM type for qualitative and quantitative analysis and to gain mechanistic understanding of the impact of NOM on the dissolution of CuO NPs. Experiments were performed according to a full-factorial design to prevent the influence of fixed mass ratios of TA and CuO NPs.

Relatively simple and well-controlled testing methods, i.e. the ion selective electrode and the complex titration method were used for the quantification of free Cu^{2+}, and Cu^{2+} and TA complexes respectively.

2. Materials and methods

2.1. Test compounds

Uncoated copper oxide nanoparticles (CuO NPs, nano-spheres, nominal particle size 40 nm as provided by the supplier, purity 99.5%) were purchased from the Aladdin Reagent Company (Shanghai, China). Tannic acid (TA, purity $\geq$ 99.8%) was purchased from the Jicang Company (Tianjin, China). $Cu(NO_3)_2 \cdot 2.5H_2O$ (purity $\geq$ 98.0%) for generating the complexation titration curves and $NaNO_3$ (purity $\geq$ 99.0%) for preparing the background solution were all purchased from the Alfa Aesar Company (Tianjin, China). The background solution was composed of $NaNO_3$ (0.02 mol/L) dissolved in ultrapure water (pH 6.68) and was applied for preparing the suspensions of NPs.

2.2. Experimental design

To study the influence of TA on the fate and behavior of CuO NPs, and to quantify the contributions of solution pH change and complexation reactions between TA and released Cu^{2+} to the effects of TA on the dissolution and aggregation of CuO NPs, three experiments were set up as follows:

(1) Assessment of the effects of TA on the dissolution and aggregation processes of CuO NPs (TA-CuO NPs). TA was first dissolved in the background solution and diluted to concentrations of 0, 5.9, 14.7, and 73.5 μmol/L. Different amounts of CuO NPs were weighed and then added in the spiked TA solutions to reach the nominal concentrations of 0, 50, 125, and 250 mg/L.

(2) Assessment of the effects of pH on the dissolution and aggregation processes of CuO NPs (pH-CuO NPs). As shown in Fig. 1, the solution pH values were significantly decreased with the increasing concentrations of TA. Thereupon, to identify the influence of the pH change on dissolution and aggregation of CuO NPs, the pH values of CuO NPs suspension were fixed at 4 ± 0.2, 5 ± 0.2, 6 ± 0.2, 7 ± 0.2 respectively using either NaOH or HNO_3. A pH buffer was not used in this
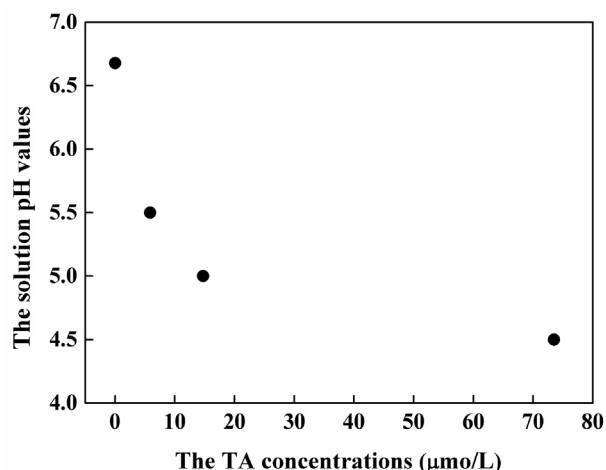

Fig. 1. Relationship between the TA concentrations and the solution pH.