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Citation

Xiao, Y. L., Tang, W., Peijnenburg, W. J. G. M., Zhang, X. H., Wu, J., Xu, M., ... Tu, L. H. (2022). Aggregation, solubility and cadmium-adsorption capacity of CuO nanoparticles in aquatic environments: effects of pH, natural organic matter and component addition sequence. *Journal Of Environmental Management*, 310.
doi:10.1016/j.jenvman.2022.114770

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Aggregation, solubility and cadmium-adsorption capacity of CuO nanoparticles in aquatic environments: Effects of pH, natural organic matter and component addition sequence

Yinlong Xiao^{a,*},¹, Wei Tang^{a,1}, Willie J.G.M. Peijnenburg^{b,c}, Xiaohong Zhang^a, Jun Wu^a, Min Xu^a, Hong Xiao^a, Yan He^a, Ling Luo^a, Gang Yang^{a,**}, Chao Chen^a, Lihua Tu^d

^a College of Environmental Sciences, Sichuan Agricultural University, Chengdu, 611130, PR China

^b National Institute of Public Health and the Environment, Center for the Safety of Substances and Products, P. O. Box 1, 3720, BA, Bilthoven, the Netherlands

^c Institute of Environmental Sciences (CML), Leiden University, P. O. Box 9518, 2300, RA, Leiden, the Netherlands

^d College of Forestry, Sichuan Agricultural University, Chengdu, 611130, PR China

ARTICLE INFO

Keywords:

Copper oxide nanoparticles
Natural organic matter
Cadmium adsorption
Aggregation
Solubility
Addition sequence

ABSTRACT

Nanoparticles (NPs), heavy metals and natural organic matter may co-exist in the water bodies. Currently, knowledge on their interaction effects on the behaviors and fates of NPs and heavy metal ions is rather limited, which is critical to comprehensively understand their environmental risk. In this study, the aggregation, solubility and Cd-adsorption of CuO NPs co-existing with humic acid (HA) and Cd²⁺ upon different solution pH and contact sequences were determined. In the ternary systems of CuO NPs, HA and Cd²⁺, pH was more important than the contact sequence of the components in affecting the NP aggregation, while the contact sequence was a predominant factor in determining the NP solubility. Pre-equilibration of CuO NPs and HA before addition of Cd²⁺ resulted in the highest solubility and lowest aggregation of the NPs, relative to other sequences of addition of the components. The adsorption capacity of CuO NPs for Cd-ions increased with an increasing pH value from 5 to 9. HA significantly enhanced the Cd-adsorption capacity of CuO NPs at pH 7 and 9, while at pH 5 a non-significant effect was observed. The results are helpful to better estimate the behaviors and fates of CuO NPs and Cd²⁺ when they coexisting in natural waters.

1. Introduction

With the continuous growth of the nanotechnology industry, nanoparticles (NPs) have been increasingly manufactured and applied in industrial and commercial products. As one of the five most commonly used NPs (Leitch et al., 2012), CuO NPs are widely used in different products, such as antifouling paints, catalysts, solar cells, cosmetics and wood preservation (Adeleye et al., 2016; Velsankar et al., 2020; Shiny et al., 2021). Consequently, CuO NPs are inevitably released into the environment during the production, transportation, usage, treatment and disposal of CuO NP-containing products (Keller et al., 2017). Major portions of the engineered CuO NPs will eventually enter the natural surface waters through soil runoff/leaching, wastewater treatment plant effluents and accidental discharge (Xu et al., 2021; Razmara et al.,

2020). Much attention has therefore been paid to the potential harm of CuO NPs to aquatic organisms, and a large number of studies have demonstrated the high toxicity of CuO NPs (Wang et al., 2016; Xiao et al., 2015). In order to thoroughly interpret the environmental risk of CuO NPs, there is a need to comprehensively understand their behaviors (e.g., aggregation and dissolution) in the aquatic environment.

Heavy metal pollution is a worldwide problem. Plus, natural organic matter (NOM) is ubiquitous in the environment. Hence, there is a strong potential for heavy metal ions, NPs and NOM to co-exist in the aquatic environment. Following co-exposure, interactions of NPs, heavy metals and NOM are bound to occur. For example, NPs can adsorb metal ions on their surface through both physical and chemical sorption (Wang et al., 2019, 2021). The adsorbed metal ions on the surface of NPs may enhance the NP aggregation by compressing the electrical double-layer

* Corresponding author.

** Corresponding author.

E-mail addresses: xiaoyinlong@sicau.edu.cn (Y. Xiao), yg8813@sicau.edu.cn (G. Yang).

¹ The first two authors contributed equally to this work.

of the NPs (Wang et al., 2019, 2020). The enhanced aggregation of NPs can further decrease the available surface area, which may result in the reduction of the dissolution of the NPs (Arenas-Lago et al., 2019). NOM can interact with NPs through electrostatic attraction and ligand exchange, which can further affect the aggregation and dissolution of the NPs (Jorge de Souza et al., 2019; Xiao et al., 2018). Heavy metal ions have a high potential to complex with the polar groups of NOM, which can complicate the adsorption of heavy metal ions on the surface of NPs (Demangeat et al., 2020; Fan et al., 2016). Meanwhile, heavy metal ions can alter the conformation of NOM and further impact their adsorption on NPs (Cheng et al., 2020; Yang et al., 2011). Therefore, different interaction sequences of NPs, heavy metals and NOM may result in significantly different aggregation, dissolution and metal-adsorption behavior of NPs in the aquatic environment. In addition, solution pH is essential to be considered when assessing the interactions of NPs, heavy metals, and NOM. This is because it can remarkably affect the physicochemical properties of NOM and CuO NPs (e.g., surface chemistries of NOM and NPs), and the species of metal ions (Hortin et al., 2020; Li et al., 2012). Currently, the interaction effects of NOM and electrolyte ions (e.g., Ca^{2+} and Na^+) upon different pH values on the environmental behavior and fate of CuO NPs have been studied (Xiao et al., 2018; Arenas-Lago et al., 2019). However, to the best of our knowledge, the interaction effects of heavy metal ions, NOM, and CuO NPs on the environmental behaviors and fates of the NPs and heavy metal ions have not been studied. This hinders a proper estimation of the behaviors and fates of CuO NPs and heavy metal ions in natural waters and further impedes the interpretation of the combined toxicity of the NPs and heavy metals.

Among all the heavy metals, cadmium (Cd) is a serious toxicant of major environmental and occupational concern. In the aquatic ecosystems, Cd contamination can significantly affect the biogeochemistry of nutrients and the ecosystem structure and function (Hayes et al., 2018). Moreover, it is non-biodegradable and can be put in the food chain threatening human health. Therefore, the objectives of this study were to determine the interaction effects of CuO NPs, NOM and Cd-ions upon varying pH values (1) on the aggregation and solubility of the CuO NPs, and (2) on the removal profiles of free Cd-ions from the aqueous phase.

2. Materials and methods

2.1. Chemicals

CuO NPs (nominal size: 40 nm; purity: $\geq 99\%$; shape: sphere; surface area: 30–50 m^2/g) used in this study were purchased from the Aladdin Reagent Company (Shanghai, China). Humic acid (HA, containing $>90\%$ fulvic acid) obtained from the Aladdin Reagent Company (Shanghai, China) was used as a surrogate for natural dissolved organic matter (DOC). Other chemicals used in this study including cadmium chloride ($\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$), concentrated nitric acid, sodium hydroxide, and hydrochloric acid were all at analytic grade quality and were provided by Sinopharm Chemical Reagent Co., China.

2.2. Preparation of aqueous media

The water samples containing CuO NPs, NOM and Cd^{2+} at different pH were prepared individually. Specifically, the stock HA solution was prepared by dissolving a specific amount of HA powder in MilliQ water. The pH value of the HA stock solution was adjusted to 8.5 with 0.1 M NaOH solution and afterwards the HA stock solution was stirred

overnight and then filtered through a 0.45 μm cellulose acetate membrane. The HA stock solution was stored at 4 °C in the dark before use. The total organic carbon (TOC) concentration in the prepared HA stock solution was measured using a TOC analyzer (TOC-VCPH, Shimadzu, Japan). A stock suspension of CuO NPs was freshly prepared in MilliQ water, and it was sonicated in a water bath sonicator for 20 min prior to use. In order to acquire the final exposure concentration (10 mg/L) of HA, CuO NPs and Cd^{2+} , precomputed amounts of stock solutions of HA, CuO NPs and CdCl_2 were mixed in MilliQ water. In the binary systems (CuO NPs and HA; CuO NPs and Cd^{2+}), the stock solutions of each component were mixed in a 50 mL conical tube and then the tube was filled up to 30 mL with milliQ water. The desired pH values (i.e., 5, 7 and 9) were obtained by adding small volumes of 0.1 M of NaOH and/or HCl. The testing of the synthetic solution with the same treatment was conducted in triplicate. Then these tubes were placed on an orbital shaker with a speed of 140 rpm at room temperature (approximately 20 °C) for 24 h to ensure sufficient equilibration. Furthermore, the behavior of CuO NPs in the ternary systems (CuO NPs, HA and Cd^{2+}) was determined. In order to gain insight into the CuO NP behavior upon different component contact sequences, three ternary systems were simulated: (1) CuO NPs and HA were pre-equilibrated for 24 h on an orbital shaker (140 rpm) before the addition of Cd^{2+} (denoted as (CuO NPs-HA) + Cd^{2+} hereafter); (2) CuO NPs and Cd^{2+} were pre-equilibrated for 24 h on an orbital shaker (140 rpm) before the addition of HA (denoted as (CuO NPs- Cd^{2+}) + HA hereafter); (3) HA and Cd^{2+} were pre-equilibrated for 24 h on an orbital shaker (140 rpm) before the addition of CuO NPs (denoted as (Cd^{2+} -HA) + CuO NPs hereafter).

2.3. Aggregation of CuO NPs

Hydrodynamic diameters of the CuO NP suspensions upon different treatments after 24 h of equilibration were determined by dynamic light scattering (DLS) analysis (Malvern, Instruments, Ltd., UK). Meanwhile, the zeta-potential of each synthetic solution was determined by Zeta-PALS software based on the Smoluchowski equation.

2.4. Solubility of CuO NPs and removal of free Cd-ions

After 24 h of equilibration, samples taken from three independent CuO NP suspensions with the same water chemistry as triplicates were used to analyze the concentrations of dissolved Cu-ions. The samples were centrifuged at 16,089 g for 30 min and then the supernatants were filtered through 0.02 μm syringe filters (Anotop 25, Whatman). Subsequently, concentrated nitric acid (65%) was used to digest the filtrates and the Cu concentrations (i.e., the amount of dissolved Cu-ions shedding from CuO NPs) in the filtrates were analyzed by inductive coupled plasma optical emission spectrometry (ICP-OES, iCAP 6300 DUO, Thermo, USA). The quantification limits of ICP-OES for Cd and Cu were 0.001 and 0.005 mg/L, respectively. For quality assurance/control of the ICP analysis, every 25 samples a blank and the standard solutions of Cu (GSB04-1725-2004, China) and Cd (GSB04-1721-2004, China) were measured. The recoveries of Cu and Cd were 98–102% and 97–104%, respectively. In the meantime, the Cd concentrations in the filtrates were also quantified by ICP-OES, and the mass difference with the concentration of free Cd in the solution with the addition of the Cd-ions alone was defined as the removal of free Cd^{2+} from the aqueous phase. The removal efficiency for Cd-ions was calculated using the following equation:

$$\text{Removal efficiency (\%)} = \frac{(\text{Total free Cd Conc.} - \text{Cd Conc. in the filtrates})}{\text{Total free Cd Conc.}} \times 100$$

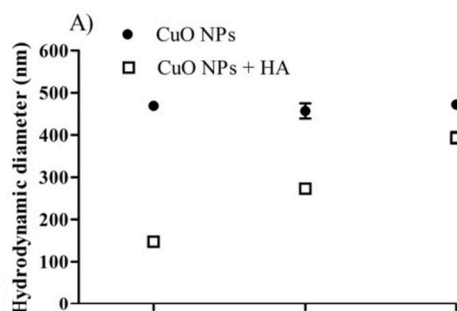
In addition, standard solutions were used to check the recoveries of Cu and Cd after the filtration step, and the recoveries of Cu and Cd were respectively in the ranges of 96–101% and 94–104%, confirming that there was no loss of Cu and Cd after passing through the syringe filter.

2.5. Characterization of the test substances

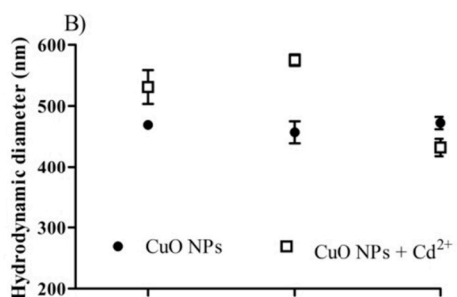
The pristine morphology and size of the CuO NPs were determined by both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Fig. S1). In addition, after 24 h of equilibration the solid fractions in the systems with the HA alone, with the CuO NPs and HA, and with the (CuO NPs-HA) + Cd²⁺ were isolated following the method of Huang et al. (2017). Surface functional groups on the solid fractions were analyzed by Fourier transform infrared spectroscopy (FTIR, NICOTCT 6700, Thermo Nicolet Corporation, USA) within the range of 500–4000 cm⁻¹ in transmission mode.

2.6. Statistical analysis

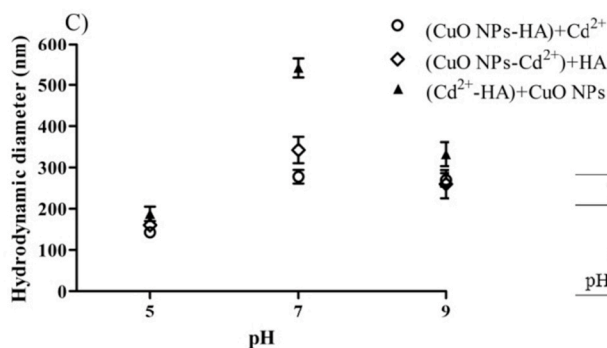
Statistical analysis was performed with the SPSS 19.0 package for windows (SPSS, Chicago, IL, USA). Two-way analysis of variance (ANOVA) was used to analyze the combined effects of pH and HA addition, pH value and Cd²⁺ addition, as well as pH value and component addition sequence on the aggregation and solubility of the CuO NPs. Two-way ANOVA was also used to test the combined effects of pH and CuO NPs addition and pH and addition sequence of HA/CuO NPs/Cd²⁺ on the removal of free Cd-ions from the aqueous phase. One-way ANOVA followed by an independent *t*-test was used to compare the significance between groups. Before conducting ANOVA, both the normality and homogeneity of variance of the data were checked. The significance level in all analysis was set at $\alpha = 0.05$. All the data in this study were expressed as mean values \pm standard deviation (SD).



Two-way ANOVA	<i>p</i> -value	Percentage Contribution (%)
pH	<0.001	17.8
HA	<0.001	64.9
pH × HA	<0.001	16.9



Two-way ANOVA	<i>p</i> -value	Percentage Contribution (%)
pH	<0.001	29.1
Cd	<0.001	21.7
pH × Cd	<0.001	42.4



Two-way ANOVA	<i>p</i> -value	Percentage Contribution (%)
pH	<0.001	62.6
Addition sequence	<0.001	21.5
pH × Addition sequence	<0.001	13.4

Fig. 1. Hydrodynamic diameters of 10 mg/L CuO NPs after 24 h incubation upon different treatments. A) represents the combined effects of pH and HA (10 mg/L) on the hydrodynamic diameter of CuO NPs; B) indicates the combined effects of pH and Cd²⁺ (10 mg/L) on the hydrodynamic diameter of CuO NPs; C) presents the combined effects of pH and addition sequence of Cd²⁺, CuO NPs and HA on the hydrodynamic diameter of the NPs. The data are presented as mean \pm SD (*n* = 3). Two-way ANOVA is reported in the tables shown on the right hand side of the graphs.

Table 1

Zeta-potentials of 10 mg/L suspensions of CuO NPs after 24 h of exposure upon different treatments.

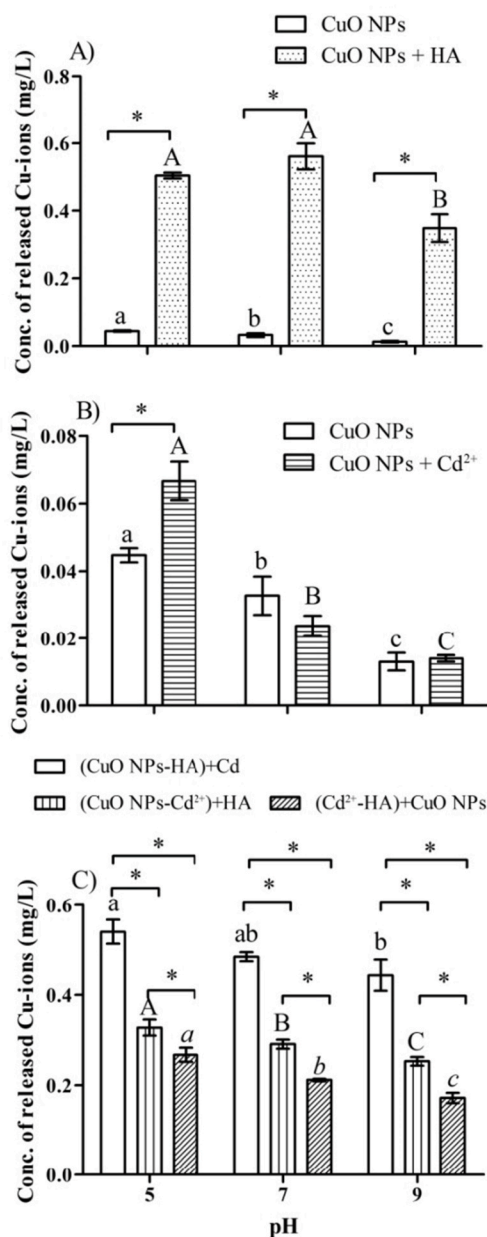
Treatment	Zeta-potential (mV) ^a		
	pH 5	pH 7	pH 9
CuO NPs	12 ± 1	2 ± 1	-9 ± 1
CuO NPs + HA	-22 ± 1	-20 ± 2	-17 ± 0
CuO NPs + Cd ²⁺	-2 ± 0	-10 ± 0	-17 ± 1
(CuO NPs-HA) + Cd ²⁺	-8 ± 0	-18 ± 1	-25 ± 0
(CuO NPs-Cd ²⁺) + HA	-14 ± 1	-17 ± 1	-19 ± 2
(Cd ²⁺ -HA) + CuO NPs	-12 ± 0	-21 ± 2	-18 ± 1

^a Zeta-potentials are expressed as mean ± SD (n = 3).

3. Results

3.1. Aggregation of CuO NPs

The hydrodynamic diameters and zeta-potentials of the CuO NPs upon different exposure treatments after 24 h were determined (Fig. 1 and Table 1). In the suspension with the CuO NPs alone, the hydrodynamic diameters of the CuO NPs at different pH values (i.e., 5, 7 and 9) were similar (approximately 460 nm) (Fig. 1A), while the zeta-potentials of the CuO NP suspensions at different pH values were different (Table 1). At pH 5, 7, and 9, the zeta-potentials of the suspensions with the CuO NPs alone were 12, 2, and -9 mV, respectively. In the binary



Two-way ANOVA	p-value	Percentage Contribution(%)
pH	<0.001	4.7
HA	<0.001	91.5
pH × HA	<0.001	3.0

Two-way ANOVA	p-value	Percentage Contribution (%)
pH	<0.001	71.4
Cd	<0.05	1.4
pH × Cd	<0.001	14.3

Two-way ANOVA	p-value	Percentage Contribution (%)
pH	<0.001	9.0
Addition sequence	<0.001	89.3
pH × Addition sequence	0.783	0.2

Fig. 2. Concentrations of dissolved Cu-ions released from the CuO NPs at 10 mg/L upon various treatments. A) presents the combined effects of pH and HA (10 mg/L) on the concentrations of dissolved Cu-ions shedding from the CuO NPs; B) shows the combined effects of pH and Cd²⁺ (10 mg/L) on the concentrations of Cu-ions shedding from the CuO NPs; C) represents the combined effects of pH and addition sequence of CuO NPs, HA and Cd²⁺ on the concentrations of dissolved Cu-ions shedding from the CuO NPs. The data are presented as mean ± SD (n = 3). Different lowercase, capital, and italic letters on the bars represent statistical differences as determined by means of one-way ANOVA among different pH values from 5 to 9 upon the same component treatment (P < 0.05). The asterisk (*) denotes a statistical difference determined by t-test between different treatments at the same pH value (P < 0.05). Two-way ANOVA is reported in the tables on the right hand side of the graphs.

system of CuO NPs and HA, the pH value and HA as well as their interactions significantly affected the hydrodynamic diameter of the CuO NPs ($P < 0.05$) (Fig. 1A). HA significantly inhibited the NP aggregation, with 148, 273 and 394 nm at pH 5, 7 and 9, respectively, after 24 h of co-exposure (Fig. 1A). In the binary system of CuO NPs and Cd^{2+} , Cd^{2+} induced 13% and 26% higher aggregation of the NPs at pH 5 and 7, respectively, while at pH 9 the hydrodynamic diameter of the NPs after co-exposure with Cd^{2+} was even slightly smaller as compared to the case in which no Cd^{2+} was added (Fig. 1B).

In the ternary systems (CuO NPs, Cd^{2+} and HA), the hydrodynamic diameter of the CuO NPs peaked at pH 7 (Fig. 1C). Two-way ANOVA showed that 63% of the size variation of the CuO NPs in the ternary systems was attributed to the change of pH (Fig. 1C). Besides the suspension pH, the sequence of addition of the components in the ternary systems also significantly affected the hydrodynamic diameter of the CuO NPs ($P < 0.05$), contributing to 22% of the size variation of the CuO NPs (Fig. 1C). Generally, aggregation of the CuO NPs in the ternary systems followed the tendency: $(\text{Cd}^{2+}\text{-HA}) + \text{CuO NPs} > (\text{CuO NPs-Cd}^{2+}) + \text{HA} > (\text{CuO NPs-HA}) + \text{Cd}^{2+}$.

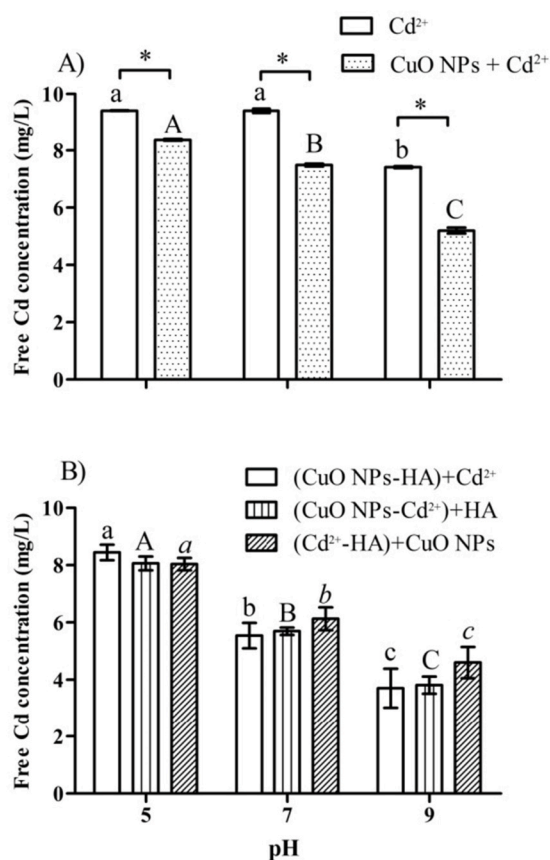
3.2. Solubility of CuO NPs

The solubility profiles of the CuO NPs upon different exposure treatments are presented in Fig. 2. There were less than 1% of Cu-ions shedding from the CuO NPs after 24 h of exposure in MilliQ water (Fig. 2A). HA significantly increased the dissolution degree of the CuO NPs ($P < 0.05$). To be specific, after 24 h of co-exposure of the CuO NPs

with HA in the water at pH 5, 7 and 9, there were respectively 0.50, 0.56 and 0.35 mg/L of soluble Cu-ions. Two-way ANOVA showed that 92% of the variation of the CuO NP solubility after co-exposure with HA at pH ranging from 5 to 9 was attributed to the presence of HA (Fig. 2A). In the binary system of CuO NPs and Cd^{2+} , Cd^{2+} significantly increased the concentration of dissolved Cu-ions in the acidic water ($P < 0.05$), resulting in a 49% increase of the amount of dissolved Cu-ions in comparison with the amount of dissolved Cu-ions in the suspension with solely CuO NPs (Fig. 2B). However, Cd^{2+} did not significantly affect the CuO NP solubility at pH 7 and 9. In the ternary systems (CuO NPs, Cd^{2+} and HA), the sequence of addition of these components significantly affected the dissolution of the CuO NPs ($P < 0.05$). Two-way ANOVA showed that the variation in solubility of the CuO NPs in the ternary systems at different pH was predominantly determined by the sequence of addition of the components (Fig. 2C). Specifically, in the system of $(\text{CuO NPs-HA}) + \text{Cd}^{2+}$, the concentrations of Cu-ions were 0.54, 0.48 and 0.44 mg/L after 24 h of incubation at pH 5, 7 and 9, respectively. The NP dissolution degrees in the system of $(\text{CuO NPs-HA}) + \text{Cd}^{2+}$ were around 1.5–1.9 and 2.0–2.6 folds higher than the dissolution degrees determined in the suspensions of $(\text{CuO NPs-Cd}^{2+}) + \text{HA}$ and $(\text{Cd}^{2+}\text{-HA}) + \text{CuO NPs}$, respectively (Fig. 2C).

3.3. Removal of Cd-ions from the aqueous phase

In the water to which only Cd^{2+} was added, the concentration of free Cd-ions at pH 9 was 7.4 mg/L after 24 h, which was significantly lower than the concentrations determined at pH 5 and 7 (Fig. 3A). In the



Two-way ANOVA	p-value	Percentage Contribution (%)
pH	<0.001	61.1
CuO NPs	<0.001	35.8
pH × CuO NPs	<0.001	2.9

Two-way ANOVA	p-value	Percentage Contribution (%)
pH	<0.001	93.8
Addition sequence	0.088	1.1
pH × Addition sequence	0.097	1.7

Fig. 3. Concentrations of Cd-ions determined in the aqueous phase after 24 h of exposure upon various treatments. A) represents the combined effects of pH and CuO NPs on the concentration of free Cd in the water column after 24 h of co-exposure; B) presents the combined effects of pH and addition sequence of Cd^{2+} , CuO NPs and HA on the concentration of free Cd determined in the water column after 24 h of co-exposure. The data are presented as mean \pm SD ($n = 3$). For the same component treatment, different lowercase, capital, and italic letters on the bars stand for a statistical difference by one-way ANOVA among different pH values from 5 to 9 ($P < 0.05$). The asterisk (*) denotes a statistical difference by *t*-test between different treatments at the same pH value ($P < 0.05$). Two-way ANOVA is reported in the tables on the right hand side of the graphs.

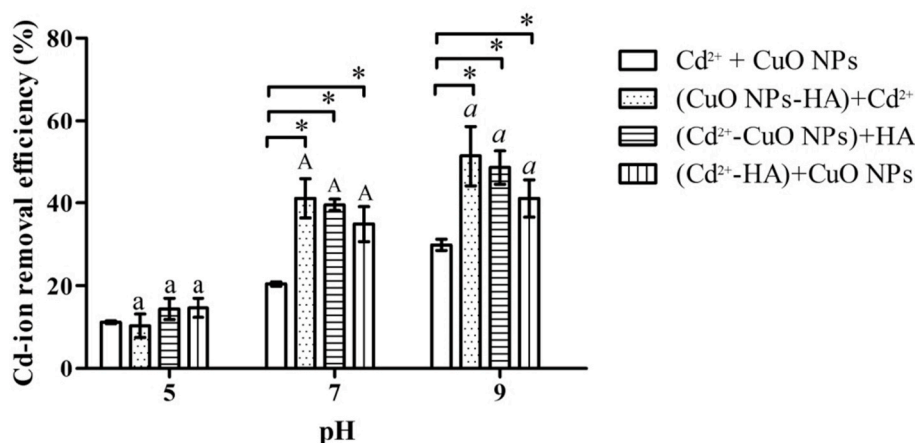


Fig. 4. Removal efficiency of Cd-ions after 24 h of exposure upon various treatments. The same lower-case, capital and italic letters on the bars at pH 5, 7 and 9, respectively, indicate that non-significant difference of the Cd-ion removal efficiency was obtained upon a different sequence of addition of the components, as based on one-way ANOVA ($P > 0.05$). The asterisk (*) denotes a statistical difference as obtained by the *t*-test between the treatments in the presence and absence of HA ($P < 0.05$). The data are presented as mean \pm SD ($n = 3$).

binary system of CuO NPs and Cd²⁺, the removal efficiencies of CuO NPs for Cd-ions were 11, 20 and 30% at pH 5, 7 and 9, respectively (Figs. 3A and 4). In the ternary systems (CuO NPs, Cd²⁺ and HA), the sequence of addition of the components did not significantly affect the removal efficiency of free Cd from the aqueous phase ($P > 0.05$) (Figs. 3B and 4). The removal efficiencies of Cd-ions in the ternary systems were in the ranges of 35–41% at pH 7 and 41–51% at pH 9, which were significantly higher than the removal efficiencies of Cd-ions in the binary system of Cd²⁺ and CuO NPs ($P < 0.05$) (Fig. 4). On the other hand, at pH 5 the removal efficiencies for free Cd-ions in the ternary systems were not significantly different from the removal efficiency obtained in the binary system of Cd²⁺ and CuO NPs ($P > 0.05$) (Fig. 4).

4. Discussion

In the binary system of HA and CuO NPs, the inhibition effect of HA on the NP aggregation was decreased with an increase of pH (Fig. 1A). This phenomenon might be due to the fact that at pH 5, the surface charge of the CuO NPs was positive (Table 1), thus favoring the adsorption of HA with a negative surface charge. However, at pH 7 and 9, the surface charges of the CuO NPs were less positive and even negative (Table 1), leading to harder adsorption of HA on the NPs and a reduction of the stabilizing effect of HA on the CuO NPs. In addition, it has been reported that NOM tends to own a more linear or stretched structure at a higher pH value (Demangeat et al., 2020; Grillo et al., 2015). This might also contribute to the larger size of the CuO NPs-HA complexes at the higher pH.

The effects of exposure sequence on the NP aggregation behavior might result from different interaction modes among the components (Fig. 1C). In the (CuO NPs-HA) + Cd²⁺ system, the direct contact between the CuO NPs and HA could facilitate the adsorption of HA on the CuO NPs. This could result in an enhancement of stability of the NPs due to the electrostatic and steric repulsions induced by the adsorbed HA. In the (CuO NPs-Cd²⁺) + HA system, the adsorption of Cd²⁺ on the CuO NPs could increase the number of complexation sites on the surface of the CuO NPs (Wang et al., 2019; Liu et al., 2011). Therefore, metal-bridged ternary complexes (CuO NPs-Cu²⁺-HA) were more likely to form, leading to an enlargement of the contact radius of the suspended CuO NPs (Wang et al., 2019; Mak and Lo, 2011). In the (Cd²⁺-HA) + CuO NPs system, the complexes of HA-Cd²⁺ had a potential to bridge with each other to form clusters which could then bind with the CuO NPs to form aggregates (Wang et al., 2019; Tang et al., 2014).

It was found that NOM was far more important than pH in affecting the solubility of CuO NPs (Fig. 2A). In fact, Gao et al. (2019) concluded that the content of organic matter determined the solubility of CuO NPs and pH mainly affected their dissolution rate (Gao et al., 2019). It was found that Cd²⁺ at pH 5 significantly increased the dissolution of CuO

NPs, while at pH 7 and 9 non-significant effects were observed (Fig. 2B). Similarly, Xu et al. (2021) found that Mn²⁺ and Al³⁺ only in an acidic soil solution significantly facilitated the dissolution of CuO NPs (Xu et al., 2021). The authors attributed the different effects of the two metal ions on the solubility of CuO NPs upon varying pH conditions to the fact that the hydrolytic reactions of Mn²⁺ and Al³⁺ occurred more easily in acidic conditions. This could yield a higher amount of H⁺ and consequently improved the dissolution degree of the CuO NPs.

In the ternary systems of CuO NPs, Cd²⁺ and HA, the contact sequence of the components was found to be a determined factor in influencing the dissolution of the CuO NPs (Fig. 2C). In the (CuO NPs-HA) + Cd²⁺ system, the initial interaction of HA with CuO NPs made HA readily accessible to complex with CuO NPs and consequently resulted in more Cu-ions shedding from the surface of the CuO NPs, as compared to the solubility of the CuO NPs in the suspensions of (CuO NPs-Cd²⁺) + HA and (Cd²⁺-HA) + CuO NPs. In addition, as mentioned above, the hydrodynamic diameter of the CuO NPs in the (CuO NPs-HA) + Cd²⁺ system was the smallest, as compared to other ternary systems (Fig. 1C). These relatively small size fractions might foster the contact probability between the CuO NPs and HA and consequently increased the amount of Cu-ions shedding from the CuO NPs (Demangeat et al., 2020; Zhao et al., 2017). In the suspensions of (CuO NPs-Cd²⁺) + HA and (Cd²⁺-HA) + CuO NPs, besides the aggregate size effects on the solubility, the initial binding of Cd²⁺ with CuO NPs or HA might partly limit the complexation reactions of CuO NPs with HA ligands (Demangeat et al., 2020; Fan et al., 2016), and consequently reduced the solubility of CuO NPs.

When the solution pH is higher than 8, Cd(OH)₂ is formed (Kataria and Garg, 2018). Therefore, it was found that the concentration of free Cd-ions was significantly reduced at pH 9 (Fig. 3A). It is interesting to find that at pH 7 and 9, HA increased the capacity of CuO NPs for removing free Cd-ions (Fig. 4). Relative to the suspensions with the solely CuO NPs at pH 7 and 9, the combination of HA and CuO NPs resulted in more negative surface charges (Table 1), which could increase the Cd²⁺ adsorption on the CuO NPs-HA complexes through electrostatic attraction. Furthermore, the combination of HA and CuO NPs potentially introduced more sorption sites (e.g., oxygen-containing functional groups) (Demangeat et al., 2020; Tian et al., 2012; Chen et al., 2012), which could increase the Cd²⁺ sorption through chemical complexation and also contributed to the higher removal efficiency for Cd-ions in the ternary systems. The FTIR spectrum verified that more functional groups (O-H, C=O, C-O and C-H) were present after co-exposure of the CuO NPs with HA (Fig. S2), which also indicated that the adsorption of HA onto the CuO NPs indeed occurred. On the other hand, at pH 5 there was non-significant effect of HA on the capacity of CuO NPs for removing free Cd-ions (Fig. 4). This might be due to an increasing competition between free Cd-ions and hydronium ions for binding with HA and CuO NPs.

5. Conclusions

In this study, the interaction effects of CuO NPs, HA, and Cd²⁺ upon different pH on the aggregation, solubility and Cd-adsorption of the CuO NPs were determined. In the ternary systems of CuO NPs, HA and Cd²⁺, pH was more important than the contact sequence of the components in influencing the NP aggregation, while the contact sequence was a predominant factor in determining the NP solubility. The removal efficiency of CuO NPs for free Cd-ions from the aqueous phase was higher at a higher solution pH value. At pH 7 and 9, HA significantly enhanced the adsorption capacity of CuO NPs for Cd-ions, while at pH 5 a non-significant effect of HA on the Cd-ion adsorption capacity of CuO NPs was observed. These results are helpful to properly estimate the environmental behaviors and fates of CuO NPs and Cd²⁺ when they co-existing in natural waters.

Credit author statement

Yinlong Xiao: Conceptualization, Methodology, Data curation, Formal analysis, Supervision, Writing, Funding acquisition; **Wei Tang:** Investigation, Writing – original draft; **Willie J. G. M. Peijnenburg:** Writing – review & editing; **Xiaohong Zhang:** Resources; **Jun Wu:** Methodology, Formal analysis, Resources; **Min Xu:** Methodology, Writing – review & editing; **Hong Xiao:** Methodology, Writing – review & editing; **Yan He:** Methodology, Software; **Ling Luo:** Writing-Review, Editing; **Gang Yang:** Supervision, Resources, Funding acquisition. **Chao Chen:** Writing – review & editing; **Lihua Tu:** Conceptualization, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was funded by the National Natural Science Foundation of China (Grant No. 21906109) and by the Power Construction Corporation of China (Grant No. DJ-ZDXM-2019-42).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2022.114770>.

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