Catalytic role of iron in the formation of silver nanoparticles in photo-irradiated Ag^+ -dissolved organic matter solution[☆]

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ABSTRACT

Photo-reduction of Ag^+ to silver nanoparticle (AgNPs) by dissolved organic matter (DOM) is a possible source of naturally occurring AgNPs. However, how this photo-reduction process is influenced by ubiquitous metal ions is still not well understood. In addition, in previous studies, the formation of AgNPs in DOM solution was usually monitored by UV-Vis spectroscopy, and there is still lack of quantitative analysis for the formed AgNPs. In the present study, the role of $\text{Fe}^{2+}/\text{Fe}^{3+}$ at environmental concentration level on this photochemical process was investigated, and the enhanced formation of AgNPs by $\text{Fe}^{2+}/\text{Fe}^{3+}$ was probed and quantified by using UV-Vis spectroscopy, transmission electron microscopy, and liquid chromatography-inductively coupled plasma mass spectrometry. It was demonstrated that while Fe^{3+} can oxidize AgNPs to release Ag^+ , Fe^{2+} can reduce Ag^+ into AgNPs. However, the DOM-induced reduction of Fe^{3+} makes iron an effective electron shuttle between DOM and Ag^+ , and both Fe^{2+} and Fe^{3+} enhanced AgNP formation. The impacts of environmentally relevant factors, including DOM concentration and solution pH, on this process were studied comprehensively, which showed that the catalytic role of iron was more significant at higher DOM concentration and lower pH. This iron-enhanced formation of AgNPs in photo-irradiated Ag^+ -DOM solution have great environmental implications on the formation of natural AgNPs and the transformation of engineered AgNPs in acidic surface water with high iron content.

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1. Introduction

The antimicrobial capability of silver nanoparticles (AgNPs) and other conventional forms of silver (e.g., silver metal and silver salt) has been utilized in numerous consumer products and medical devices in recent years (Chernousova and Epple, 2013). In their production, use and disposal, the release of silver ion (Ag^+) and AgNPs from these silver-containing consumer products and medical devices is inevitable (Benn and Westerhoff, 2008; Geranio et al., 2009; Gottschalk and Nowack, 2011; Mitrano et al., 2014). The released AgNPs readily transform in the environment through processes like oxidative dissolution (Dobias and Bernier-Latmani, 2013; Liu and Hurt, 2010; Liu et al., 2010) and sulfidation (Levard

et al., 2011; Liu et al., 2011), which not only modifies their properties, but also have great impacts on their transport, bioavailability, and toxicity (Levard et al., 2012). The oxidative dissolution of AgNPs releases Ag^+ , which increases the toxicity of AgNP significantly (Kittler et al., 2010; Xiu et al., 2012; Yang et al., 2012). However, recently it was also discovered that ubiquitous dissolved organic matter (DOM) can reduce Ag^+ into AgNPs with DOM as both reductant and coating agent (Adegboyega et al., 2013; Akaighe et al., 2011; Hou et al., 2013; Yin et al., 2012, 2014). This reduction process is not only a possible source of naturally occurring AgNPs (Akaighe et al., 2011; Yin et al., 2012), but also has great impacts on the fate and transformation of engineered AgNPs (Yu et al., 2014). Further studies showed that this reduction process is influenced by thermal (Adegboyega et al., 2013; Akaighe et al., 2011) or sunlight irradiation (Hou et al., 2013; Yin et al., 2012), pH (Hou et al., 2013; Yin et al., 2012), source (Akaighe et al., 2011; Yin et al., 2012) and redox states of DOM (Maurer et al., 2012). However, effect of ubiquitous metal ions on this reduction process is still largely

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unknown. In aquatic ecosystems, light-induced redox cycling of $\text{Fe}^{2+}/\text{Fe}^{3+}$ plays important role in numerous chemical processes (Emmenegger et al., 2001; Song et al., 2005), e.g., the catalytic reduction of Cr(VI) (Agrawal et al., 2009; Gaberell et al., 2003). Recently, Adegboyega et al. showed that Fe^{3+} or Fe^{2+} ions in the mixtures of Ag^+ and DOM enhanced the formation of AgNPs under heating (90 °C) (Adegboyega et al., 2014) or UV irradiation (Adegboyega et al., 2016). However, how the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in Ag^+ -DOM system on the formation of AgNPs under other more environment-relevant conditions (e.g., under sunlight irradiation) is still not well understood. In addition, in previous studies, the formation of AgNPs in DOM solution was usually monitored by UV-Vis spectroscopy (Adegboyega et al., 2014, 2016; Yin et al., 2012), and there is still lack of quantitative characterization for the formed AgNPs.

In the present study, we have demonstrated that the catalytic role of $\text{Fe}^{2+}/\text{Fe}^{3+}$ at environmental concentration level on the photo-reduction of Ag^+ by DOM. The formation of AgNPs was demonstrated by using UV-Vis spectroscopy and transmission electron microscopy (TEM), and further quantitative analysis for the formed AgNPs was performed by using the liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS). Environmental factors including the DOM concentration and solution pH, have been studied comprehensively, focusing on the catalytic role of $\text{Fe}^{2+}/\text{Fe}^{3+}$. This $\text{Fe}^{2+}/\text{Fe}^{3+}$ -enhanced formation of AgNPs in photo-irradiated Ag^+ -DOM solution have great environmental implications on the formation of natural AgNPs and the transformation of engineered AgNPs in acidic surface water with high iron content.

2. Experimental section

2.1. Materials

AgClO_4 , $\text{Na}_2\text{B}_4\text{O}_7$, and H_3BO_3 were purchased from Beijing Chemicals (Beijing, China). $\text{Fe}(\text{ClO}_4)_3$ (>98%) and $\text{Fe}(\text{ClO}_4)_2$ (>98%) were from Sigma-Aldrich. HNO_3 (65%) was from Merck (Darmstadt, Germany). Polyvinylpyrrolidone (PVP, molecular weight 58 000) was from Aladdin Chemistry Co. Ltd. (Shanghai, China). Water suspension of PVP-coated AgNPs (Lot number 10122203701) from Shanghai Huzheng Nanotechnology CO., Ltd. (Shanghai, China) was used to probe the oxidation of AgNPs by Fe^{3+} . The size distribution of these commercial AgNPs (24.3 ± 10.1 nm) was estimated by TEM using Nano Measurer 1.2 software and Gaussian fitting (Fig. S1). At least 300 particles were counted for the size distribution. Suwannee River Natural Organic Matter (Lot No. 1R101N) from the International Humic Substance Society (St. Paul, MN) was used as a DOM model. The dissolved organic carbon of the DOM solution was determined with a Phoenix 8000 UV-persulfate total organic carbon analyzer (Tekmar-Dohrmann, Cincinnati, OH). Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) with grades of analytical or better. All the reagents were used as obtained without further purification. Ultrapure water (18.3 M Ω) produced with a Milli Q Gradient system (Millipore, Billerica, MA) was used throughout the experiments.

2.2. Transformation of silver under dark or simulated sunlight

The experiments were performed in 100 mL quartz glass bottles with quartz caps under dark conditions or in a sunlight simulator (TEMI880, Beifang Lihui, Beijing, China) equipped with three wind-refrigerated 2500 W Xe lamp. The total volume of the solution was 100 mL. The intensity of the light was set as 550 W m $^{-2}$. The spectrum of the simulated sunlight was given in our previous study (Yin et al., 2014). During the experiment, the reaction temperature

was maintained at ~35 °C by a water bath. Although phosphate is usually used as buffer to cover a wide range of pH, considering the low solubility of Ag_3PO_4 in water ($K_{\text{sp}}(\text{Ag}_3\text{PO}_4) = 1.46 \times 10^{-16}$) (Fu et al., 2007), phosphate is not a suitable buffer in our study. Therefore, acetic acid-acetate (pH 3.6), 2-(N-morpholino) ethanesulfonic acid (MES)-NaOH (pH 5.5 and 6.3), and borate (pH 7.4 and 8.0) were used as buffers for different pH conditions. The oxidation of AgNPs by Fe^{3+} and reduction of Ag^+ by Fe^{2+} in the absence of DOM were performed at room temperature under dark or simulated irradiation. In the photo-irradiated Ag^+ - $\text{Fe}^{2+}/\text{Fe}^{3+}$ -DOM systems, the parameters, including concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and DOM, and pH of solution, were investigated, focusing on the catalytic role of $\text{Fe}^{2+}/\text{Fe}^{3+}$.

2.3. Characterizations and quantification of the species of silver

2.3.1. UV-vis spectrometry

UV-vis spectra were recorded on a Shimadzu UV-vis-NIR Spectrophotometer (UV-3600, Japan). The wavelength scanning was performed from 200 to 800 nm at 0.5 nm wavelength interval.

2.3.2. Transmission electron microscopy

TEM analysis was performed on a Hitachi H-7500 (Hitachi, Japan) or JEOL 2011 (Herts, England) transmission electron microscope. TEM samples were prepared by placing 5 μL aliquots of the aqueous sample onto an ultrathin carbon-coated copper grid and drying at room temperature.

2.3.3. Quantification of Ag^+ and AgNPs

The Ag^+ in irradiated sample was quantified by LC-ICP-MS according to our previous study (Zhou et al., 2014). An amino column with the 500 Å pore size (Venusil Durashell-NH $_2$, 5 μm particle size, 250×4.6 mm) purchased from Bonna-Agela Technologies Inc. (Tianjin, China) was used for the separation of Ag^+ and AgNPs. The mobile phase was 0.1% (v/v) FL-70 (mixture of nonionic and anionic surfactants from Fisher Scientific, Fair Lawn, NJ) and 2 mmol L $^{-1}$ $\text{Na}_2\text{S}_2\text{O}_3$. The column temperature and flow rate of mobile phase were set as 20 °C and 0.7 mL min $^{-1}$, respectively. The injection volume was 100 μL . Into 1 mL sample was added 20 μL 1 mol L $^{-1}$ $\text{Na}_2\text{S}_2\text{O}_3$, and then the sample was injected for LC-ICP-MS measurement. Due to the complexation of Ag^+ with $\text{S}_2\text{O}_3^{2-}$ in sample and mobile phase, the adsorbed Ag^+ can well desorbed from AgNPs and DOM, and then be separated effectively from AgNPs. Under the above conditions, AgNPs and Ag^+ in the sample can be well separated in 5 min. Then the Ag^+ in sample was quantified according to Ag^+ standard and the concentration of AgNPs was obtained by subtracting the Ag^+ from the total Ag, which was determined directly by ICP-MS after digestion (Zhou et al., 2014). The spiked recovery of Ag^+ in 30 mg L $^{-1}$ DOM solution of this LC-ICP-MS method was $98.7 \pm 0.6\%$.

3. Results and discussion

3.1. Reduction of Ag^+ by Fe^{2+}

To probe the possible reduction of Ag^+ by Fe^{2+} , the reaction of Ag^+ and Fe^{2+} under simulated irradiation was monitored by UV-vis spectroscopy. As shown in Fig. 1A, a small absorption peak was evident at about 410 nm at 0.5 h, which was ascribed to the surface plasmon resonance (SPR) of AgNPs (Chinnapongse et al., 2011). The SPR peak enhanced over time from 0.5 to 2 h, indicating the further formation of AgNPs. However, the SPR peaks further broaden and shift to longer wavelength at 4 h–8 h, which was ascribed to the formation of AgNP aggregates (Yin et al., 2012) due to the absence of capping agent. Considering the relatively lower concentration of

Fig. 1. UV-visible spectra (A and C) and TEM images (B and D) of AgNPs formed in Fe^{2+} - Ag^+ (A and B) and Fe^{2+} - Ag^+ -PVP (C and D) solution. Conditions: $1 \text{ mmol L}^{-1} \text{ AgClO}_4$, $5 \text{ } \mu\text{mol L}^{-1} \text{ Fe}(\text{ClO}_4)_2$, pH 6.3, simulated sunlight for A and B; $1 \text{ mmol L}^{-1} \text{ AgClO}_4$, $5 \text{ } \mu\text{mol L}^{-1} \text{ Fe}(\text{ClO}_4)_2$, $5 \text{ } \mu\text{mol L}^{-1} \text{ PVP}$, pH 6.3, simulated sunlight for C and D. The time for simulated sunlight was 6 h for B and D.

AgNPs formed, the solution was concentrated by ultrafiltration with Amicon Ultra-15 centrifugal filter (with 3 kDa nominal molecular weight cut-off) before TEM characterization. It should be noted that the ultrafiltration and TEM sample preparation could possibly induce the aggregation of AgNPs, however, which should not influence the formation of AgNPs. As shown in Fig. 1B, AgNPs with size ranged from several nm to over 100 nm were observed and the lattice planes observed in high resolution TEM image (Fig. S2) can be indexed to face-centered cubic (fcc) silver metal. These results demonstrated that dissolved Fe^{2+} can reduce Ag^+ into AgNPs according to reaction 1.

Previous study also showed that adsorbed Fe^{2+} in mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ hydroxides (green rusts) can reduce Ag^+ to submicron-sized particles of Ag^0 under dark conditions (O'Loughlin et al., 2003). These results suggested that Fe^{2+} should play important role in the formation of naturally occurring AgNPs.

To further validate the formation of AgNPs by Fe^{2+} in the presence of capping agent, PVP was added into the mixture of Fe^{2+} and Ag^+ before simulated irradiation. The results (Fig. 1C) showed a significant absorption between 350 nm and 700 nm, indicating a polydispersed distribution of AgNPs. The TEM (Fig. 1D) showed that the size of AgNPs ranged from several nm to about 50 nm. Compared with AgNPs in the absence of PVP, the AgNPs formed in PVP solution is more dispersed in aqueous solution, which was ascribed to the stabilization effect of PVP as capping agent. This result also suggested that DOM in solution should also have similar stabilization effect to the Fe^{2+} -reduced AgNPs.

3.2. Oxidation of AgNPs by Fe^{3+}

The possible oxidation of AgNPs by Fe^{3+} under dark conditions was investigated under various pH. As shown in Fig. 2A, in the absence of Fe^{3+} , the absorption intensity of AgNPs located at about 400 nm decreased with solution pH, suggesting oxidative

Fig. 2. The oxidation of AgNPs by Fe^{3+} at different pH as monitoring by (A) UV-visible spectroscopy, and (B) LC-ICP-MS. Conditions: 10 mg L^{-1} AgNPs, in the presence or absence of $50 \text{ } \mu\text{mol L}^{-1}$ $\text{Fe}(\text{ClO}_4)_3$, reaction time 10 h.

dissolution of AgNPs is favorable at lower pH (Liu and Hurt, 2010). This result was further validated by measuring of dissolved Ag^+ in AgNPs solution by LC-ICP-MS. As shown in Fig. 2B, with the decreasing of solution pH, the concentration of dissolved Ag^+ increased accordingly. Superoxide and hydrogen peroxide are possibly involved in the accelerated-oxidative dissolution of AgNPs at lower pH (reaction 2–4) (Jones et al., 2011).

In the presence of $50 \text{ } \mu\text{mol L}^{-1}$ Fe^{3+} , at pH 3.6, the UV-vis absorption of AgNPs decreased significantly when compared with that in the absence of Fe^{3+} , indicating the Fe^{3+} -enhanced oxidative dissolution of AgNPs (Fig. 2A). However, at pH 5.5, the impact of Fe^{3+} on the dissolution is not significant. At pH 7.4, in the presence of Fe^{3+} , the UV-vis absorption of AgNPs decreased and the SPR peak shifted to the longer wavelength, indicating the Fe^{3+} -induced aggregation of AgNPs. However, at pH 8.0, the variation of SPR peak was not significant, possibly due to the fast precipitation of Fe^{3+} as $\text{Fe}(\text{OH})_3$ at alkaline pH. According to a previous study (Pham et al., 2006), the formation rate of $\text{Fe}(\text{OH})_3$ precipitation is the fastest at pH 8.0 in the range of 6.0–9.5, which may result in a fast Fe^{3+} depletion and inhibit the Fe^{3+} -induced dissolution or aggregation of AgNPs. As the UV-vis absorption of AgNPs is influenced not only by the concentration of AgNPs, but also the size and aggregation of AgNPs, the oxidative dissolution of AgNPs in the presence of Fe^{3+} at various pH was further probed by LC-ICP-MS, as shown in Fig. 2B. The result clearly showed that the Fe^{3+} -enhanced oxidative dissolution of AgNPs was more significant at lower pH (pH 3.6 and 5.5) ($P < 0.05$). For example, the dissolution ratio of AgNPs at pH 3.5 increased from 24.8% to 46.6% after addition of Fe^{3+} . However, the presence of Fe^{3+} have no influence on the dissolution at pH 7.4 and 8.0, possibly due to the lower concentration of dissolved Fe^{3+} at alkaline pH and the aggregation-inhibited dissolution. The above results demonstrated that at lower pH, Fe^{3+} facilitates the oxidative dissolution of AgNPs, according to reaction 5:

3.3. Catalytic role of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the formation of AgNPs in photo-irradiated Ag^+ -DOM solution

In previous studies, it has been observed that iron can accelerate the photo-reduction of $\text{Cr}(\text{VI})$ by DOM (Gaberell et al., 2003). Considering the similar $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox cycling in photo-irradiated Ag^+ -Fe-DOM system, it is reasonable that $\text{Fe}^{2+}/\text{Fe}^{3+}$ could also accelerate the photo-reductive formation of AgNPs in DOM solution. Therefore, the effect of concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and DOM, as well as pH was investigated in the photo-reductive formation of AgNPs in DOM solution, with emphasizing on the catalytic role of $\text{Fe}^{2+}/\text{Fe}^{3+}$.

3.3.1. Concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$

Considering the concentration of filtered iron (including both dissolved and particulate iron that pass through filters) in environmental waters can be up to $12.34 \text{ } \mu\text{mol L}^{-1}$ (Lofts et al., 2008),

Fig. 3. The formation of AgNPs in the absence or presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ photo-irradiated Ag^+ -DOM solution. Conditions: 30 mg L^{-1} DOM, 1 mmol L^{-1} AgClO_4 , 5 or $10 \text{ } \mu\text{mol L}^{-1}$ $\text{Fe}(\text{ClO}_4)_2$ or $\text{Fe}(\text{ClO}_4)_3$, pH 6.3, 8 h light irradiation.

the concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$ on the reduction of Ag^+ was investigated at the environmental concentration level ($0\text{--}10\ \mu\text{mol L}^{-1}$). At 0.5 h, the SPR intensity of AgNPs increased with $\text{Fe}^{2+}/\text{Fe}^{3+}$ concentration from 2 to $7\ \mu\text{mol L}^{-1}$, and the SPR peak of AgNPs broaden at $10\ \mu\text{mol L}^{-1}\ \text{Fe}^{2+}/\text{Fe}^{3+}$ (Fig. S3A and B), possibly due to the formation of AgNP aggregates or larger AgNPs. At 8 h, the SPR peak of AgNPs further broaden and shifted to longer wavelength, with the increasing the concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$ (Fig. S3C and D). The result of LC-ICP-MS (Fig. 3) demonstrated that the presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ at environmental concentration level enhanced the reductive formation of AgNPs. As shown in Fig. 3, in the presence of 5 or $10\ \mu\text{mol L}^{-1}\ \text{Fe}^{2+}$, the AgNP concentration increased by ~50%. Similarly, the AgNP concentration increased by 18% in the presence of $5\ \mu\text{mol L}^{-1}\ \text{Fe}^{3+}$, and then increased by 52% when further increased Fe^{3+} concentration to $10\ \mu\text{mol L}^{-1}$. The catalytic role of Fe^{3+} for the AgNPs formation was ascribed to the redox cycling of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the presence of DOM under light irradiation (as shown in reaction 1, 6 and 7) (Emmenegger et al., 2001), in which $\text{Fe}^{2+}/\text{Fe}^{3+}$ serve as electron shuttle to enhance the transfer of electron from DOM to Ag^+ (Adegboyega et al., 2014).

The AgNPs in photo-irradiated Ag^+ -DOM systems with or without $\text{Fe}^{2+}/\text{Fe}^{3+}$ were characterized by TEM. In Ag^+ -DOM system without $\text{Fe}^{2+}/\text{Fe}^{3+}$, the AgNPs were spherical and well dispersed in solution (Fig. 4A and B). However, in the presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$,

AgNPs with irregular morphology were evident (Fig. 4C–F), which was ascribed to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ -induced aggregation and subsequent aggregation-induced fusion of AgNPs (Yin et al., 2014).

3.3.2. Concentration of DOM

To investigate the role of DOM in reduction, different concentration of DOM was added into the mixture of Ag^+ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ to a final concentration of 5, 10, 20 and $30\ \text{mg L}^{-1}$ dissolved organic carbon, respectively. After simulated sunlight irradiation, the UV-vis spectra were recorded, as shown in Fig. S4. In the absence of $\text{Fe}^{2+}/\text{Fe}^{3+}$, the SPR intensity of AgNPs significantly increased with DOM concentration, which is consistent with our previous study (Yin et al., 2012). In the presence of Fe^{2+} or Fe^{3+} , the SPR peak of AgNPs broaden and shift to the longer wavelength, suggesting the formation of larger AgNPs or aggregates of AgNPs. The aggregation of AgNPs induced by multivalent metal ion can reduce the distance between AgNPs and consequently fuse small AgNPs to form “new” larger AgNPs (Yin et al., 2014). However, with the increasing concentration of DOM, the red-shift and peak-broaden were partially inhibited, suggesting DOM improved the dispersion of AgNPs (Yin et al., 2014). The quantitative measurement of AgNPs at different DOM concentration was shown in Fig. 5. In the absence or presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$, the AgNP concentration significantly increased with the increase of DOM concentration. More importantly, at all investigated DOM concentration, $\text{Fe}^{2+}/\text{Fe}^{3+}$ enhanced the formation of AgNPs. Comparably, the catalytic role on formation of AgNPs is more significant for Fe^{2+} than Fe^{3+} , and the increase of DOM concentration facilitates the catalytic role of $\text{Fe}^{2+}/\text{Fe}^{3+}$. As DOM serving as electron donor in the photo-reduction process, higher

Fig. 4. TEM images of AgNPs in the absence or presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ in photo-irradiated Ag^+ -DOM solution. (A and B), without $\text{Fe}^{2+}/\text{Fe}^{3+}$; (C and D), $10\ \mu\text{mol L}^{-1}\ \text{Fe}(\text{ClO}_4)_2$; (E and F), $10\ \mu\text{mol L}^{-1}\ \text{Fe}(\text{ClO}_4)_3$. Other conditions: $30\ \text{mg L}^{-1}$ DOM, $1\ \text{mmol L}^{-1}\ \text{AgClO}_4$, pH 6.3, 8 h light irradiation.

Fig. 5. The formation of AgNPs in photo-irradiated Ag⁺-Fe²⁺/Fe³⁺-DOM solution with different DOM concentrations. Conditions: 1 mmol L⁻¹ AgClO₄, 5 μmol L⁻¹ Fe(ClO₄)₂ or Fe(ClO₄)₃, pH 6.3, 8 h light irradiation.

concentration of DOM can promote the reduction of Fe³⁺ (Chen et al., 2003; Fukushima and Tatsumi, 1999), and thus the catalytic role of Fe²⁺/Fe³⁺.

3.3.3. Effect of pH

The effect of pH on the reduction formation of AgNPs was investigated in the range from 5.5 to 8.0, covering the pH range of most surface waters (Lofts et al., 2008). As shown in Fig. 6A and B, the presence of Fe²⁺ or Fe³⁺ enhanced the SPR intensity of AgNPs at pH 5.5 and 6.3, but reduced the SPR intensity of AgNPs at pH 8.0 (Fig. 6C). The formation of AgNPs at pH 5.5 and 8.0 was further quantified by LC-ICP-MS. As shown in Fig. 6D, at pH 5.5, the presence of Fe²⁺ or Fe³⁺ enhanced the formation of AgNPs by 37.0% and 27.3%, respectively. Comparably, the enhancement of AgNPs formation was more significant in the presence of Fe²⁺ than that of Fe³⁺. At pH 8.0, however, the formation of AgNPs in the presence of Fe²⁺/Fe³⁺ was even lower than that in the absence of Fe²⁺/Fe³⁺ (by ~13%). These results suggested that the catalytic role of Fe²⁺/Fe³⁺ was distinct at acidic pH, but was inhibited at alkaline environment. Similar pH-dependent photo-reduction of Cr(VI) was also observed in the presence of low-molecular-weight organic acids and Fe²⁺/Fe³⁺ (Hug et al., 1997; Sun et al., 2009), in which the pH-dependent photo-reduction was ascribed to the following two possible reasons: (i) The pH-dependent reduction of Fe³⁺ to Fe²⁺; and (ii) the pH-dependent reduction of Cr(VI) by Fe²⁺. However, it has been demonstrated that the reduction of Cr(VI) by Fe²⁺ in the absence of low-molecular-weight organic acids enhanced with the increased pH (5.0–9.0) (Buerge and Hug, 1997; Pettine et al., 1998). Therefore, this pH-dependent photo-reduction in the presence of organic

Fig. 6. UV-visible spectra (A, pH 5.5; B, pH 6.3; C, pH 8.0) and LC-ICP-MS quantification (D) of AgNPs in photo-irradiated Ag⁺-Fe²⁺/Fe³⁺-DOM solution at different pH. Other conditions: 30 mg L⁻¹ DOM, 1 mmol L⁻¹ AgClO₄, 5 μmol L⁻¹ Fe(ClO₄)₂ or Fe(ClO₄)₃, 6 h light irradiation.

matter and $\text{Fe}^{2+}/\text{Fe}^{3+}$ should be ascribed to the pH-dependent reduction of Fe^{3+} to Fe^{2+} by DOM. It is well known that the reductive potential of DOM decreased with increased pH (Yin et al., 2012), which is favorable for the reduction of metal ions. However, the photo-reductive formation of Fe^{2+} in the presence of DOM would also decreased with increasing pH (Emmenegger et al., 2001), possibly due to the formation of ferric hydroxide (reaction 5). Thus, the decreased concentration of Fe^{2+} at higher pH subsequently decreased the reduction of Ag^+ to AgNPs.

4. Environmental implications

This study demonstrated that in the presence of DOM, dissolved iron can enhance the reductive formation of AgNPs under simulated sunlight. Considering the concentration of iron and pH conditions investigated in this study is environment-relevant (Lofts et al., 2008), our study, combined with the previous study by Adegboyega et al. (2016, 2014), have great environmental implications for the formation of naturally occurring AgNPs and the transformation and cycling of engineered AgNPs. Previous studies also showed that adsorbed iron or iron-containing minerals can mediate the reductive transformation of metals (Cr(VI), Tc(VII), U(VI), Pu(IV), and Np(V)) (Lloyd et al., 2000, 2002; VanEngelen et al., 2008) in the presence of microorganisms. It is also well known that Ag^+ can be reduced to AgNPs by microorganism and plant (Yin et al., 2015). Therefore, the reduction of Ag^+ into AgNPs could also potentially be accelerated by iron-containing minerals or clays due to the redox cycling of $\text{Fe}^{2+}/\text{Fe}^{3+}$ mediated by organisms (Byrne et al., 2015; Dong et al., 2003; Fredrickson et al., 1998; Roden and Urrutia, 2002). Besides iron, it is reported that other transition metals (e.g., Cu (Maithreepala and Doong, 2008) and Mn (Lovley et al., 2004)) and even biochar (Kappler et al., 2014) can serve as electron shuttles for the reduction of metal and organic pollutants. Therefore, it is reasonable these electron shuttles could also enhance the reductive formation of AgNPs in chemical or biological processes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2017.03.048>.

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