

## Effectiveness of ferric salts in removing low levels of dosed copper from NOM-containing natural water

Weixi Zhan, Arumugam Sathasivan, Paul Nolan, Laszlo Koska, Ana Heitz and Cynthia Joll

### ABSTRACT

Water utilities dose copper in drinking water systems to inhibit/kill microorganisms including algae. Under conditions observed in the systems, the majority of dosed copper is reported to be in dissolved forms of Cu-NOM and inorganic compounds. High concentrations (40 mg/L) of ferric salts are reported to be able to remove large amounts of copper. However, the fate of dissolved copper when a small amount of ferric salts (<2 mg/L) is present in natural water or in the distribution pipes when they are released from the corroded iron pipes are not known. The current paper investigates the mechanisms behind the dissolved copper removal in NOM-containing bulk water. When copper was dosed from 250–800  $\mu\text{g-Cu/L}$ , relatively high solubility was demonstrated in Mundaring water, with dissolved copper increased from 250–720  $\mu\text{g-Cu/L}$ . Both ferric chloride and ferric hydroxide were found to have a considerable ability to remove dissolved copper while the former showed higher capacity. Ferric chloride showed a linear relationship with copper removal ( $R^2 = 0.99$ ) and the removal by ferric hydroxide showed excellent agreement with either the Freundlich ( $R^2 = 0.98$ ) or Langmuir ( $R^2 = 0.99$ ) adsorption isotherm.

**Key words** | adsorption, copper, ferric salts, Freundlich isotherm, Langmuir isotherm, NOM

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### INTRODUCTION

Copper is dosed by water utilities to control algal blooms and inhibit microbiological activities. Depending on the intake time for treatment and distribution, source water can contain variable amounts of copper. While the presence of copper may enhance the disinfection capability of disinfectants, accumulation of copper in distribution systems can be a nuisance. Concerns about relatively high copper concentrations in drinking water are mostly related to its acute gastrointestinal effects, which include nausea, vomiting and diarrhoea. Lower levels of copper in drinking water are also under scrutiny (Lagosu *et al.* 1999) and the World Health Organization (WHO) regulations recommend copper concentrations in drinking water to be less than 1 mg/L and to have a maximum of 2 mg/L. In the Goldfields and Agricultural Water Supply System

(G&AWSS) in Western Australia, trial experiments were undertaken in which cupric sulfate was dosed into pipelines to inhibit nitrification and to prevent microbiologically accelerated decay of chloramine. Restrained by the *Guidelines for Drinking-water Quality* (WHO 2008) and authorized by the Department of Public Health (WA), a copper dose varying between 0.25–0.40 mg-Cu/L is implemented in the field. However, some copper loss was observed along the distribution pipe, and the dosed copper did not reach the extremities of the system where it was most required. Fundamental experiments were carried out to elucidate the fate of various copper species in bulk water and the distribution system. Ferric ions or pre-formed ferric flocs are speculated as the most possible precursors leading to copper loss in the iron pipeline

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system. In order to better understand how copper was lost in the water supply system, this research investigated the mechanisms of copper loss when ferric salts appeared in natural bulk water.

Various copper species can dominate in different aquatic environments. In some natural water bodies containing high dissolved organic matter, less than 0.5% of dissolved copper was found to be free cupric ions (Wagemann & Barica 1978). When water is buffered by carbonate (e.g. calcium carbonate) the aqueous copper species can be in equilibrium with  $\text{CuO}_{(s)}$  (tenorite). Under these circumstances, the major forms of dissolved copper species are inorganic copper compounds such as  $\text{CuCO}_3^0$  and  $\text{Cu}(\text{OH})_3^-$  in the pH range of 6.5–9.0 (Snoeyink & Jenkins 1980). In addition, copper has an especially high affinity for complexing with organic matter. Natural organic matter (NOM) is regarded as an important ligand which could bind with copper and form colloidal compounds in natural water bodies (Lehman & Mills 1994). According to Hullebusch *et al.* (2003), Cu was distributed among dissolved and colloidal ligands, roughly in proportion to the dissolved organic carbon (DOC) in each fraction, though the bioavailability of copper bound to specific organic matter is not fully understood. The stability of NOM-Cu complexes is reported to be quite strong at higher pH (8 or above) and weaker at lower pH (Sarathy & Allen 2005). Soluble copper, which has high bioavailability, can also be increased by complexing with either organic matter or chelating agents, e.g. ethylenediaminetetraacetic acid (EDTA) (Ridge & Sedlak 2004).

Depending on different ambient circumstances, for instance, open or closed (or partially closed) to the atmosphere (defined as the partial pressure of carbon dioxide on the water surface) and contents of NOM, the solubility of copper in bulk water could be controlled by equilibria between the soluble copper complexes and the metastable solid phase such as cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ) (Broo *et al.* 1999), tenorite ( $\text{CuO}$ ), etc. The size of  $\text{Cu}(\text{OH})_2$  particles varies with pH. At pH 8, which was the normal pH of the water source studied in this research (Mundaring), the size of  $\text{Cu}(\text{OH})_2$  particulates was reported to be about 400 nm (Sun & Skold 2001), increasing with increasing pH. Our laboratory experiments proved that pre-formed Cu-containing particles/aggregates could be removed by

0.2  $\mu\text{m}$  membrane filters, which therefore were chosen to filter particulate copper formed in bulk water in this research (Zhan & Sathasivan 2007).

Ferric salts (e.g. ferric chloride, iron oxide) are reported to promote the removal of dissolved copper compounds by several mechanisms. Ferric chloride addition (up to 40 mg-Fe/L) was reported to enhance copper removal from wastewaters in which ethylenediaminetetraacetic acid (EDTA) was present, by forming  $\text{FeEDTA}^-$  and reducing the EDTA available for copper binding (Ridge & Sedlak 2004). Further, removal of free metal ions (including  $\text{Cu}^{2+}$ ) by iron oxide filtration or amorphous ferric oxyhydroxide adsorption has been reported (Benjamin & Leckie 1981). Lai & Chen (2001) reported the removal of copper bound with humic acid by adsorption and chemical bonding when iron oxide was employed in sand filtration. The presence of humic acid was reported to increase copper removal by adsorption and filtration. Benjamin & Leckie (1981) investigated the adsorption mechanisms occurring between heavy metals (including Cu) and amorphous iron oxyhydroxide. It was suggested that the adsorbent surface was composed of different binding sites, and that the strength of different binding sites varied considerably. Adsorption was also found to be a function of the concentration of metal ions, the concentration of the adsorbent and pH. At small adsorbent densities, the adsorption can be described by the Langmuir isotherm. It is generally believed that adsorption is the major mechanism governing the removal of heavy metal ions by pre-formed Fe flocs (e.g. iron oxide). In addition, Hankins *et al.* (2006) reported that metal ion removal occurs through a combination of charge neutralization and enmeshment when hydrolysed ferric salts are dosed. Although these studies, which investigated the mechanisms governing the removal of cupric ions by ferric salts, can be used to broadly interpret the findings in our study, Mundaring water contains higher concentrations of NOM and lower concentrations of copper (less than 400  $\mu\text{g/L}$ ) and ferric ions than those typically reported in the literature.

Major copper species in natural waters are likely to exist as inorganic compounds, organic complexes and particulate forms rather than free cupric ions. Those soluble copper complexes are expected to be transported with water while particulate copper could settle down or accumulate on the

surface of pipes. We have shown in separate studies that copper dosed at low concentrations into Mundaring water exists mainly as soluble forms including Cu-NOM complexes and inorganic compounds. Under these conditions copper is expected to pass through the treatment processes into distribution systems, especially when conventional coagulation/sedimentation is not practised, such as in GWDS, the system of focus in this study. However, depending on pH values, various ferric species at low concentrations can be present in natural water bodies or released from iron pipelines. For instance, free ferric ions could prevail in low pH waters, while  $\text{Fe}(\text{OH})_3$  or  $\text{Fe}_2\text{O}_3$  are the major forms in modestly high pH or slightly alkaline solutions (Benjamin *et al.* 1996) such as those that exist in distribution systems. The impacts of the presence of low level ferric salts on dosed copper are not yet clear. This research focuses on the mechanisms and the capacities of various dissolved copper removal by ferric salts (ferric ions and ferric hydroxide flocs) in NOM-containing bulk water (Mundaring water). Further, the behaviour of ferric salts at  $<2\text{ mg/L}$  to remove various soluble copper species in Mundaring water is discussed.

## WATER SAMPLING AND METHODOLOGY

### Water source and sample collection

All raw water samples were collected from the outlet of the Mundaring reservoir, which is the source water for GWDS. Containers were pre-cleaned using sodium hypochlorite (12.5%) to remove dissolved organic carbon (DOC) which might remain in the containers. Afterwards, Milli-Q water (18 M $\Omega$ ,  $<70\text{ ppb-C/L}$ ) was used to wash all the containers. All containers were rinsed using Mundaring raw water (MRW) three times during sample collection. Analysis of MRW for bulk water quality characteristics was undertaken immediately after sample collection. MRW was preserved in a refrigerator at 4°C. The characteristics of Mundaring raw

water are shown in Table 1. These characteristics varied only slightly when sampled at different times of the year.

### Experimental protocol

The removal of dissolved copper was investigated by varying copper and ferric dosages in an NOM-containing MRW. Four experiments were conducted. In the first experiment, copper dosage was fixed at  $250\text{ }\mu\text{g-Cu/L}$ . A jar tester was used to stir the bulk water during dosing of both cupric sulfate and ferric hydroxide. Stirring lasted for 2 min during copper dosing. In order to determine the dissolved copper content of the copper-dosed solution, an aliquot (50 ml) was filtered through a  $0.2\text{ }\mu\text{m}$  polycarbonate membrane and the copper concentration in the filtrate was measured. The ferric hydroxide concentration was varied as follows: 0.2, 0.5, 1.0 and  $2.0\text{ mg-Fe/L}$ . The stirring speed was set at 200 rpm for the initial 2 min after ferric hydroxide dosing to make sure that ferric hydroxide was mixing well and that a reasonably well-controlled floc size formed. About 20 rpm was applied for another 20 min afterwards. After completing the ferric dosage, samples were left intact at room temperature (20–30°C) for pH maintenance. During this time, the pH of each sample was monitored and adjusted to maintain pH within 7.8–8.2.  $\text{H}_2\text{SO}_4$  (1 N) and NaOH (1 N) were used to modify pH values if necessary. Samples were filtered through a  $0.2\text{ }\mu\text{m}$  polycarbonate membrane after ferric dose. By measuring the copper concentration remaining in the filtrate, copper removal by ferric salts was calculated by the difference between dissolved copper in bulk water before and after treatment with ferric ions.

In the second experiment, various copper dosages of 250, 400, 600 and  $800\text{ }\mu\text{g-Cu/L}$  and constant ferric hydroxide dosage ( $1\text{ mg-Fe/L}$ ) were applied. In the first experiment it was noted that  $250\text{ }\mu\text{g-Cu/L}$  could remain soluble in Mundaring water, i.e. all of the  $250\text{ }\mu\text{g/L}$  of dosed copper could be measured in filtered water. However, increased copper doses resulted in the formation of particulate copper

**Table 1** | Water quality characteristics of Mundaring raw water

pH	UV abs 254 nm	DOC (mg-C/L)	Alkalinity (mg/L $\text{CaCO}_3$ )	Fe (mg/L)	Mn (mg/L)	P (mg/L)	S (mg/L)	Ca (mg/L)
7.6–8.1	0.04–0.05	2.8–3.1	8.9–9.5	$<0.02$	$<0.005$	$<0.05$	8.8	18

Note: Mundaring water sample was collected at different times during the year: only little change (varying qualities are shown as ranges of related parameters in the table) was found in water quality. Similarity of MRW qualities from different seasons were also found by Dryer *et al.* (2008). Cu concentration measured in the raw water was found to be less than  $10\text{ }\mu\text{g-Cu/L}$ .

in the bulk water, i.e.  $\text{Cu}(\text{OH})_2$ . In these experiments particulate and dissolved copper in bulk water was always measured before ferric dosing. Similar to the procedure above, 1 mg-Fe/L of  $\text{Fe}(\text{OH})_3$  was dosed into samples containing different copper concentrations. The same preservation conditions and filtration processes were used.

As discussed in the introduction, depending on pH values and pipe conditions, free ferrous ions could also be released instantly from leaking pipes. These free ions remove copper via various mechanisms different from those employed by pre-formed ferric hydroxide flocs. Therefore, ferric chloride instead of ferric hydroxide was used in the third and fourth experiments which were conducted by following the same procedures as in the first and second experiments, respectively.

#### The preparation of standard solutions: copper sulfate, ferric chloride and ferric hydroxide

Standard copper sulfate solution (0.25 g/L as Cu) was prepared by mixing  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  into Milli-Q ultrapure water. The pH of the standard solution was maintained at 5.6 so that copper could be maintained as cupric ions. The volume of bulk water samples in all experiments ranged from 1.0–1.5 L, and consequently a 1.0–1.5 mL standard solution was dosed using volumetric pipettes (20–1,000  $\mu\text{L}$ ) to achieve a target concentration of 0.25 mg-Cu/L. The relative change of sample volume was therefore within 0.1%.

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (crystal) and Milli-Q water were used to make ferric salt solutions. Both  $\text{FeCl}_3$  and  $\text{Fe}(\text{OH})_3$  standard solutions were made at the concentration of 1 g-Fe/L. The  $\text{FeCl}_3$  solution was maintained at pH  $3 \pm 0.2$  to maintain free ferric ions. NaOH (1 N) was used to increase the pH of the  $\text{FeCl}_3$  solution to  $5.3 \pm 0.1$  to form ferric hydroxide flocs. During the course of ferric dosing, the solution was stirred using a magnetic stirrer, with the stirring speed set at 200 rpm to maintain consistent floc size.

#### Copper measurement method

The copper concentration was analysed using a spectrophotometer (Hach DR2800 2005). The bicinchoninate

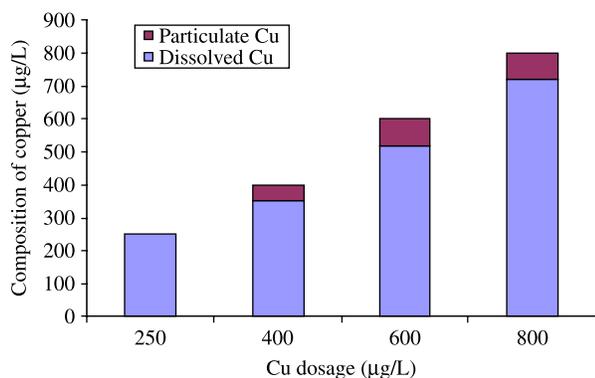
method (Hach method 8506) and porphyrin methods (Hach method 8143) were used in the laboratory. The measuring ranges of the two methods are 0.04–5 mg/L (Hach method 8506) and 1–210  $\mu\text{g}/\text{L}$  (Hach method 8143), respectively. Samples were digested using nitric acid (1:1) to pH 4–6 for total copper measurement. Potable pH meters (Hach30d) with temperature compensation were used to measure pH values. For measuring dissolved copper concentration, samples were filtered through a 0.2  $\mu\text{m}$  PC (polycarbonate) membrane. In order to minimize interaction between the sample and membrane and to prevent speciation changes, the volume of the filtrate was chosen to represent approximately 50% of the volume of the raw sample (Hoffmann *et al.* 1981). For instance, to obtain 50 mL filtrate, 100 mL sample water was added and 50 mL out of it was filtered through the filter paper.

## RESULTS AND DISCUSSIONS

### Impact of increased copper dose on concentrations of dissolved and particulate copper

Dryer *et al.* (2008) proved that, although MRW is capable of maintaining considerable dissolved copper, its NOM is a lack of hydrophobic fraction, which is mainly composed of phenolic chromophores. Since Mundaring water has limited capacity to maintain dissolved copper in MRW, it was anticipated that, as the copper dose was increased, more particulates ( $>0.2 \mu\text{m}$ ) would be observed. It was necessary to determine the extent of particulate formation and the dissolved copper concentration in bulk water before adding ferric salts. To understand how dissolved copper varied with copper dosage in NOM containing Mundaring raw water, copper dosage was varied from 250  $\mu\text{g-Cu}/\text{L}$  to 800  $\mu\text{g-Cu}/\text{L}$  and particulate and dissolved forms were measured (Figure 1).

At 250  $\mu\text{g-Cu}/\text{L}$ , all Cu species in Mundaring raw water were soluble, with particulate copper forming at concentrations of 400  $\mu\text{g-Cu}/\text{L}$  or more. Soluble copper may be present in inorganic forms ( $\text{CuCO}_3^0$ ,  $\text{Cu}(\text{OH})_3^-$ ) or Cu-NOM compounds. Particulate copper concentration (defined as non-filterable copper) was increased from 50  $\mu\text{g-Cu}/\text{L}$  at 400  $\mu\text{g-Cu}/\text{L}$  to 80  $\mu\text{g-Cu}/\text{L}$  at 800  $\mu\text{g-Cu}/\text{L}$ . Nevertheless,



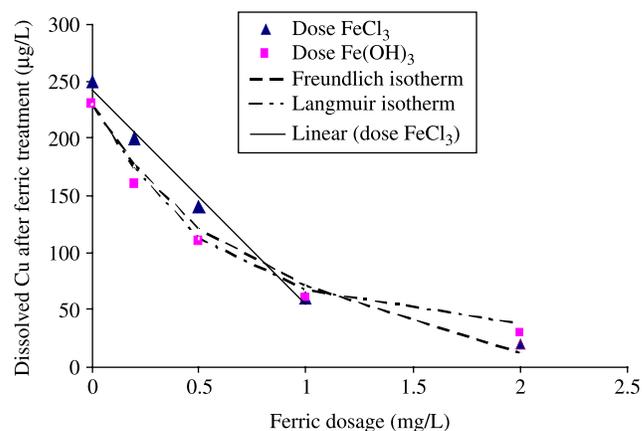
**Figure 1** | Particulate and soluble fractions of total copper contained in bulk water samples after addition of various amounts of copper.

the increased dissolved copper concentration was observed which could be due to the spare binding capacity of NOM (UV abs. 0.05/cm, DOC 3.1 mg-C/L) in Mundaring water. The increasing copper dose continued binding with organic matter in Mundaring water and formed more Cu-NOM complexes.

### Copper removal by ferric salts: impact of varying ferric dose and dissolved copper concentrations

In the first experiment in this series ferric salts were added to solutions of copper in which the concentration was fixed at 250 µg-Cu/L. Before the ferric dose, particulate and dissolved copper in bulk water were measured by filtering an aliquot of the sample (50 ml) through a filter membrane (0.2 µm pore size). The concentration of copper measured in the filtrate was 230–250 µg-Cu/L, indicating that almost all of the Cu species were present in dissolved forms at this concentration. The dissolved copper concentration remaining in the filtrate decreased as the concentration of added ferric salts increased, as plotted in Figure 2.

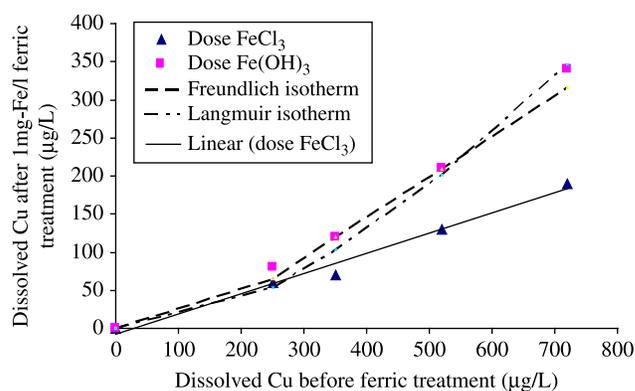
In a subsequent experiment the concentrations of ferric salts were fixed at 1 mg-Fe/L, while the amount of copper added varied from 250 to 800 µg-Cu/L, to reach different dissolved copper concentrations in bulk water. Following the same procedure described in the previous experiment, particulate and dissolved copper in bulk water were measured before the ferric dose. The results of dissolved bulk Cu before Fe treatment are shown in Figure 1. Figure 3 demonstrated the results of dissolved copper remaining



**Figure 2** | The results of ferric dosage vs Cu remaining after ferric dosage plotted against Freundlich and Langmuir adsorption isotherms.

in the filtrate after ferric salt treatment, against dissolved copper before the treatment.

Both ferric chloride and ferric hydroxide showed considerable capacity to remove copper at low concentration levels. Within the range tested, ferric chloride showed a linear relationship for copper remaining, irrespective of whether ferric was dosed into a copper solution (Figure 2) or whether copper was dosed into a ferric solution (Figure 3). Only one point (2 mg-Fe/L FeCl<sub>3</sub>) was excluded from the linear relationship (Figure 2) because the concentration of Cu approached the method's limit of detection (20 µg/L). On the other hand, Figures 2 and 3 showed an exponential and a power curve, respectively, when copper was being removed by Fe(OH)<sub>3</sub>, ranging from 0.2–2 mg-Fe/L.



**Figure 3** | The results of dissolved copper before ferric treatment vs copper remaining after ferric treatment plotted against Freundlich and Langmuir adsorption isotherms.

**Table 2** | Parameters applied in adsorption isotherms

Variables and constants (unit)	Cu removal/ $\mu\text{g Fe(OH)}_3$ ( $\mu\text{g}/\mu\text{g}$ )	$K_F$	[Cu] ( $\mu\text{g}/\text{L}$ )	$n$	$a$ ( $\mu\text{g}/\text{L}$ )	$Y_m$ ( $\mu\text{g}/\mu\text{g}$ )	$R^2$
Freundlich	$Y = ([\text{Cu}_0] - [\text{Cu}])/\text{ferric dosage}$	0.017	$C$	1.856			0.98
Langmuir	$Y = ([\text{Cu}_0] - [\text{Cu}])/\text{ferric dosage}$		$C$		131.1	0.517	0.99

Note:  $[\text{Cu}_0]$ : dissolved bulk copper concentration before ferric dose.  $C$ : dissolved copper concentration after Fe treatment. Freundlich isotherm:  $Y = K_F C^{1/n}$ ; Langmuir isotherm:  $C/Y = (a + C)/Y_m$ ;  $R^2$ : coefficient of determination.

The results indicated that the capacities and possible mechanisms controlling Cu removal from solution by  $\text{FeCl}_3$  and  $\text{Fe(OH)}_3$  may be different. The observed linear relationship for  $\text{FeCl}_3$  showed that adsorption was not the only mechanism involved in copper precipitation for this ferric salt. However, when pre-formed  $\text{Fe(OH)}_3$  was added, Cu removal in Figures 2 and 3 showed a saturation trend. This indicates that, for  $\text{Fe(OH)}_3$ , the mechanism of copper removal from solution involves adsorption between dissolved copper species and pre-formed  $\text{Fe(OH)}_3$  flocs. The linear trend observed with  $\text{FeCl}_3$  may be due to a combination of mechanisms, including the neutralization of negatively charged copper compounds ( $\text{Cu(OH)}_3^-$ , Cu-NOM) by positively charged ferric ions, adsorption and induced aggregation.

Benjamin & Leckie (1981) suggested that an adsorption phenomenon occurred between cupric ions and amorphous iron oxyhydroxide and they used the Langmuir isotherm to explain the adsorption mechanism at small adsorption densities. In the present research, the relationship between amorphous ferric hydroxide flocs and various copper compounds (both Cu-NOM complexes and inorganic copper compounds) was investigated. In terms of the laboratory experiments in which ferric hydroxide was used, it was thought that the major mechanism controlling copper removal might involve adsorption. Therefore, the laboratory results were compared with typical adsorption isotherms, such as Freundlich, Langmuir and BET. By employing these adsorption isotherms, copper removal was calculated and was used to predict the amount of dissolved copper remaining after ferric hydroxide treatment. These theoretically predicted results were compared with the laboratory data. Parameters applied to the calculation of isotherms are shown in Table 2.

Based on different types of adsorption isotherms, theoretically predicted curves were plotted against

laboratory data in Figures 2 and 3. The BET isotherm was excluded due to poor fitting with experimental data. However, both the Freundlich and Langmuir isotherms were found to be capable of explaining the removal of copper. Of these two, Langmuir performed better. From the formula of the Langmuir isotherm, it predicted that the maximum dissolved Cu absorbed or removed by 1 g ferric hydroxide in Mundaring water was 0.517 g.

During the dissolved copper removal by ferric salts, pre-formed Cu-containing particles were left in the bulk water. For instance, 80  $\mu\text{g}/\text{L}$  particles were left in the bulk water after 800  $\mu\text{g}/\text{L}$  Cu was dosed. However, the minor heterogeneous Cu species (particles) showed little effect on the trend of dissolved copper removal. Figure 3 shows that the experimental data from 400, 600 and 800  $\mu\text{g}/\text{L}$  Cu doses when particulate Cu was used still fitted the adsorption isotherms curves well. Nonetheless, the effect from increasing Cu-containing particles needs yet further study.

## CONCLUSIONS

Limited by drinking water regulations, low concentrations of copper (250–800  $\mu\text{g-Cu}/\text{L}$ ) are widely used to control algae and micro-organisms in water facilities and distribution systems. In natural water bodies, like Mundaring water, the majority of Cu species are believed to exist in the form of Cu-NOM compounds, although various inorganic Cu compounds may also be present. The fate of dosed copper can be attributed to such factors as pH, alkalinity, hardness, metal ions and NOM. This research investigated the impacts of ferric salts, which are likely to be present naturally in distribution systems in low concentrations, on the loss of copper into particulate forms in NOM-containing water bodies.

Due to NOM content (DOC is about 3 mg/L), Mundaring water showed a considerable capacity to maintain

soluble copper when the copper dosage was gradually increased up to 800  $\mu\text{g-Cu/L}$ , though a smaller portion of particulate copper was noted. Despite the presence of high dissolved copper content, ferric salts added to copper-containing samples showed a strong ability to remove dissolved copper. Removal by ferric hydroxide followed the Freundlich and Langmuir adsorption isotherms, indicating that the major removal mechanism is adsorption. In particular, the good fit with the Langmuir isotherm further indicated that the principle of dissolved copper removal by ferric hydroxide may correspond to a single-layer adsorption mechanism. The presence of the small amount of pre-formed particulate copper did not affect the fate of dissolved copper, though further research is necessary to find out if this effect can still remain negligible when particulate copper increased. In contrast, the removal by ferric chloride showed a linear relationship with respect to the dose. This may be due to a combination of mechanisms involved in Cu removal by ferric ions, including charge neutralization, coagulation and flocculation.

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