

Fate of copper in submerged membrane bioreactors treating synthetic municipal wastewater

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Abstract

This paper assesses the impact of copper on the performance of two membrane bioreactors (MBR) treating municipal wastewater at a hydraulic retention time (HRT) of 4 h, and solids residence times (SRT) of 20 days, at influent copper concentrations of 0.2–8 mg Cu/L. The addition of copper resulted in a significant increase in soluble microbial products (SMPs), and a predominance of >100 kDa molecular weight SMPs. The study showed that in well-buffered wastewaters, complete nitrification was achieved at total copper concentrations as high as 840 mg/L or 10% of the mixed liquor volatile suspended solids. MINTEQ simulation showed that most of the copper (99.8%) in the MBR was in the form of inorganic copper precipitates, with free Cu²⁺ and total soluble copper in the range of 0.0–0.11 and 0.1–0.82 mg/L, respectively.

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1. Introduction

The recent emergence of MBR for small and large-scale wastewater treatment plant applications is primarily attributable to the sharp decline in membrane cost, rendering the technology more cost-competitive with conventional treatment alternatives. The adverse impacts of various heavy metals originating from industrial sources [1] on sludge settleability and effluent quality in conventional activated sludge systems have been established [2,3]. Copper, one of the most prevalent and toxic heavy metals present in municipal wastewaters, resulted in sharp decrease in specific oxygen uptake rate of heterotrophic bacteria [4] at soluble concentrations as low as 0.02–0.9 mg/L. Meanwhile Cabrero et al. [5] reported that a total copper concentration of 10 mg/L caused serious upsets in their activated sludge system. The toxicity of copper to nitrifiers has been observed in batch reactors at soluble copper concentrations as low as 0.08 mg/L [6] and in continuous flow reactors at free copper concentrations of 0.05 mg/L [7].

The inhibitory impact of Ni and Cr⁶⁺ in conventional activated sludge (CAS) was mitigated by operating at SRTs of 20 days [2,3]. It is widely known that heavy metal toxicity is a function of the mass ratio of the toxicant to biomass rather than the concentration of heavy metal only [8]. Furthermore, more recent studies have shown that environmental stress [9], and toxic substances [10] increase the production of SMP, which are retained in MBRs [11]. Despite being a contributor to membrane fouling [12], SMPs may play a role in mitigating metal toxicity due to the chelating capacities of various functional groups [13]. An intricate relationship exists between biomass and SMP primarily due to two reasons namely biomass produces SMP and SMPs are partially biodegradable.

In contrast to CAS where biomass concentrations are relatively low and SMPs breakthrough the system, MBRs ability to retain biomass and SMPs may influence the system's response to heavy metals. Since SMPs accumulation in membrane bioreactors is expected to be cyclical [13], where periods of net accumulation would be followed by net depletion due to the long time required for SMP biodegradation, the heavy metal chelating capacity of the MBR is anticipated to be cyclical. Furthermore the molecular weight distributions of SMPs in MBR will likely differ substantially from CAS since as a result of the

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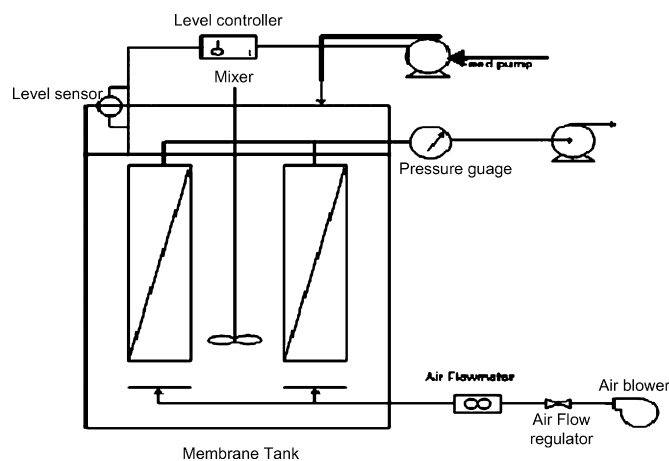


Fig. 1. Reactor schematic.

long SRT, biomass-associated SMPs predominate [14]. The literature on the fate of heavy metals and interaction of the various metal removal mechanisms, i.e. precipitation, biosorption and chelation in MBRs is scant. Unfortunately for submerged MBRs, which represent the majority of wastewater treatment applications, studies only reported overall metal removal efficiencies [15,16].

Thus the overall objective of this paper is to investigate the long term performance of an MBR treating copper laden synthetic municipal wastewater. The study addresses the fate, speciation and distribution of copper in the MBR system as well as the impact of copper on SMP production.

2. Materials and methods

2.1. System description

Two laboratory scale aerobic 6.6 L Plexiglass MBRs (Fig. 1), each employing a submersible 0.04 μm , 0.047 m^2 membrane module (Zenon Environmental Inc., Burlington, ON, Canada) with one operating as a control reactor with trace copper in the feed, were used in this study. Aeration was provided through the membranes to control membrane fouling and to maintain DO of >2 mg/L in the bioreactors. Membranes were cleaned by immersion in a 200 ppm sodium hypochlorite solution overnight once the transmembrane pressure (TMP) reached 10 psig.

2.2. Operational conditions

Table 1 shows the operational conditions of the test and control MBR, which were identical except for copper [17]. Following startup and acclimatization, the systems were operated for 220 days at room temperature, a hydraulic retention time (HRT) of 4 h and sludge retention time (SRT) of 20 days. The control reactor was fed copper at an average influent concentration of 0.2 mg/L in the form of copper sulfate to reflect typical concentrations in municipal wastewaters. The test MBR was operated at average influent copper concentrations of 2.1 and 7.7 mg/L (denoted henceforth as Stages I and II, respectively) to assess the impact of enhanced SMP production on the fate

of copper. SRT was controlled through direct wastage of sludge from the bioreactors on a daily basis.

2.3. Composition of synthetic wastewater

The synthetic feed was prepared with 280 mg/L glucose, in a mineral solution [13]. The average wastewater characteristics were as follows: COD, 300 mg/L; $\text{NH}_3\text{-N}$, 26 mg/L; $\text{NO}_3\text{-N}$, 0.7 mg/L; $\text{NO}_2\text{-N}$, 0.2 mg/L; and $\text{PO}_4\text{-P}$, 5 mg/L.

2.4. Analytical methods

Total suspended solids (TSS) and volatile suspended solids (VSS) were measured using standard methods [18]. Chemical oxygen demand (COD) and ammonia were measured using HACH methods #8000 and #10031, respectively (Handbook, DR/2500, HACH spectrophotometer). Nitrite, nitrate, and phosphate were measured using an ion chromatograph (Dionex Canada, Ontario, Canada). pH was measured using an Orion pH meter model 410A and a pH probe (VWR model Symphony). Total soluble copper and other soluble metals were measured using atomic absorption spectrophotometry (Philips, model PU9100X). Free copper (Cu^{2+}) concentration was measured using a Cu-selective electrode, Thermo-Orion model 9629 combination electrode, and a Thermo-Orion pH/ISE meter model 710Aplus. The total mixed liquor copper and the total non-soluble copper was determined by acid digestion, followed by filtration through 0.45 μm , and atomic absorption for selected samples as described in Arican et al. [19].

2.5. SMP measurement and fractionation

Samples of mixed liquor supernatant obtained by centrifuging reactor mixed liquor at $1250 \times g$ for 10 min, and then by filtering through 0.45 μm were used for fractionation based on pore sizes of 100, 10 and 1 kDa using stirred cell ultrafiltration (UF) membranes (OMEGACELL from PALL Life Sciences, Ontario, Canada). SMP was determined as COD, after accounting for the COD of glucose and all the intermediates of the Krebs cycle, i.e. pyruvic acid, citric acid, succinic acid, fumaric acid, and malic acid, analyzed by the methods detailed elsewhere

Table 1
MBR operational conditions at steady state

Parameters	Test MBR		Control MBR
	(I)	(II)	
Operation, days	0–120	121–220	0–220
pH in MBR	6.7–7.3	6.7–7.3	6.8–7.3
DO in MBR	2–3	2–3	2–3
Feed Cu	2.1 \pm 0.7 (8)	7.7 \pm 1.1 (8)	0.2 \pm 0.1 (5)
TSS in MBR (g/L)	11.6 \pm 1.2 (7)	13.2 \pm 0.8 (8)	10.5 \pm 1.2 (32)
VSS in MBR (g/L)	10.0 \pm 0.9 (7)	10.5 \pm 1.1 (8)	9.3 \pm 1.0 (32)
Influent $\text{NH}_4\text{-N}$	26.2 \pm 4.3 (10)	26.8 \pm 1.8 (13)	25.3 \pm 2.1 (32)
Effluent $\text{NH}_4\text{-N}$	0.3 \pm 0.2 (10)	0.3 \pm 0.3 (13)	0.3 \pm 0.2 (32)
SMP (mg/L)	121 \pm 32 (10)	128 \pm 33 (13)	56 \pm 18 (30)

All concentrations are in mg/L, unless otherwise specified. Values in parenthesis reflect number of samples.

Table 2
Minteq model input parameters

	Test MBR		Control MBR
	Stage I	Stage II	
Alk.as CaCO ₃ (mg/L)	60	60	60
NO ₃ ⁻ (mmol/L)	1.21	1.36	1.36
NO ₂ ⁻ (mmol/L)	0.02	0.02	0.02
PO ₄ ³⁻ (mmol/L)	0.19	0.11	0.12
SO ₄ ²⁻ (mmol/L)	0.88	0.97	0.97
Cl ⁻ (mmol/L)	0.92	0.92	0.92
Na (mmol/L)	6.1	6.1	6.1
Ca (mmol/L)	0.153	0.153	0.153
Mg (mmol/L)	0.665	0.665	0.665
Fe (mmol/L)	0.07	0.07	0.07
Mn (mmol/L)	7.7 × 10 ⁻⁴	7.7 × 10 ⁻⁴	7.7 × 10 ⁻⁴
Zn (mmol/L)	1.7 × 10 ⁻³	1.7 × 10 ⁻³	1.7 × 10 ⁻³
Cu (mmol/L)	3.32	13.22	0.36
BM (mmol/L)	2.3	2.4	2.1
SMP1 (mmol/L)	5.8	4.2	7.6
SMP2 (mmol/L)	8.8	7.3	12.6
log ^c K for BM	3.6	3.6	3.6
log ^c K for SMP1	8.2	7.8	8.1
log ^c K for SMP2	6.4	5.8	6.4

[13]. Analytical methods for the determination of complexation stability constant (^cK) and complexation capacity (C_c) using titrimetric methods and employing Scatchard model [20] are presented elsewhere [13].

2.6. Copper speciation in the MBR

MINTEQ program [21] was employed to theoretically fractionate copper associated with the solid phase, i.e. adsorbed on biomass (Cu-BM) and precipitated copper (CuP) as well as in the liquid phase, i.e. free (Cu²⁺), hydrolyzed (Cu-H), inorganically bound (Cu-L) and SMP bound (SMP1-Cu and SMP2-Cu). SMPs were modeled as two types of ligands with different affinities: SMP1 and SMP2, respectively. Copper biosorption isotherm studies at room temperature, were conducted by biomass centrifugation-resuspension in distilled water at 1250 × g for 20 min. Various concentrations of copper sulfate (20–200 mg Cu/L) were added to the washed biomass in 50 ml flasks and the pH was adjusted to 5.5 to minimize precipitation in the sorption studies. The 20 mg/L was reflective of the total copper concentrations in the control MBR while the 200 mg/L represented the total copper concentrations in the test MBR in Stage I. Batches and controls (without biomass) were mixed on a rotary shaker for the equilibration time of 4 h established through kinetic sorption studies.

2.7. MINTEQ modeling

The input to the model included concentrations of cations and anions in the system as well as the total mixed liquor copper, while the pertinent output was the various fractions of copper species in the system. Accordingly for routinely-monitored species, i.e. NO₃⁻, NO₂⁻, PO₄²⁻, alkalinity, and total copper, the steady-state averages were used. The input values for

the other sporadically measured species, i.e. SO₄²⁻, Cl⁻, Na⁺, Mg²⁺, Ca²⁺, Fe²⁺, Mn²⁺, and Zn²⁺ were as listed in Table 2. The equivalent ligand concentration of SMP (mmol/L) used in the MINTEQ model was calculated as the product of the complexation capacity of SMP (C_c), and the average SMP concentration.

3. Results and discussion

3.1. General performance

The detailed COD, TSS, and total phosphorous (TP) removals have been presented elsewhere [13,17]. The steady state permeate COD, TSS, NH₄-N, NO₃-N, and TP generally averaged around 5–8, <1, 0.4, 16 and 2.7–3.0 mg/L, respectively, for both MBRs at the various operational conditions. As apparent from Table 1, the test MBR achieved good ammonia removal efficiency. It is noteworthy that complete nitrification in the test MBR was sustained at the 7.7 mg/L influent copper concentration which resulted in a steady-state total mixed liquor copper concentration of 840 mg/L.

3.2. Copper fractionation

3.2.1. Overall copper balance

Fig. 2(a) and (b) shows the cumulative copper in the feed, effluent, wasted (by sludge removal) and accumulated in the

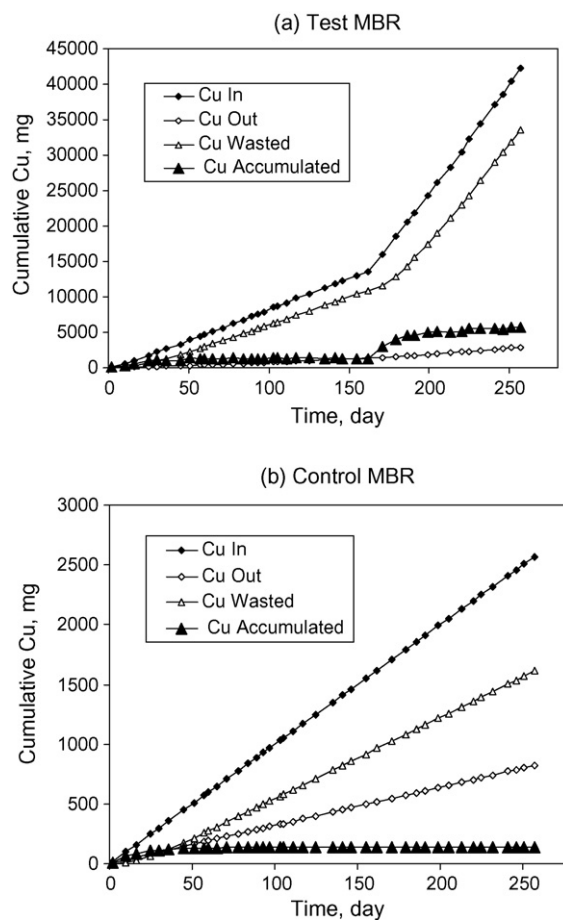


Fig. 2. Cumulative copper mass balance in test and control MBR.

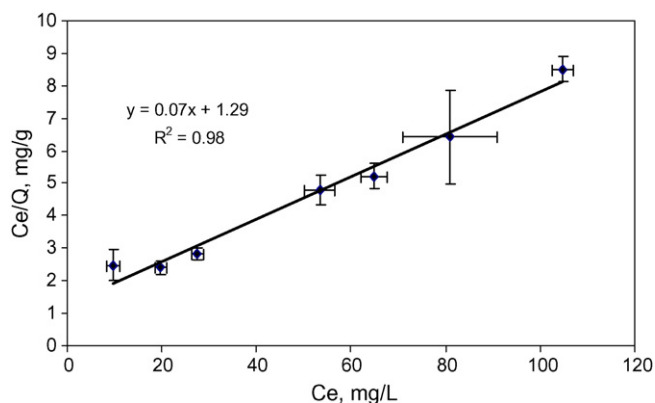


Fig. 3. Linearized Langmuir isotherm of Cu adsorption by activated sludge.

test and control MBR, respectively. The calculated final accumulated copper in the reactor derived from the cumulative mass balance of copper closed well within 8% of the steady state measured values of 230 mg/L (or a total accumulated copper of 1518 mg in the reactor) and 840 mg/L (or a total accumulated copper of 5544 mg) at feed copper concentrations of 2.1 and 7.7 mg/L, respectively. Similarly for the control MBR, the steady-state mixed liquor copper concentration of 21 mg/L compared very well with the experimental measurement of 24 mg/L.

3.2.2. Biosorption of copper

The equilibrium relationship between adsorbed copper and total soluble copper at room temperature fitted the Langmuir model well as shown in Fig. 3. The coefficients of the Langmuir model (Q_{\max} , the maximum metal sorption per g of biomass and b , constant related to the affinity) were found to be 14.3 mg Cu/g TSS and 0.05 L/mg, respectively. Since the Scatchard model is based on a Langmuir model, copper binding capacity was also evaluated using the Scatchard model which revealed a log stability constant ($\log^{\circ}K$) of 3.6 L/mol. The equivalent binding capacity was found to be 0.242 mmol Cu/g biomass (15.2 mg Cu/g VSS), which is comparable to the 14.3 mg Cu/g biomass obtained from the Langmuir model.

3.2.3. SMP production

Fig. 4 illustrates the diurnal variation of SMPs in the test and control MBRs. The cyclical nature of the SMPs in both systems has been elaborated upon elsewhere [17]. It is conspicuous that the high copper concentrations in the test MBR affected a significant increase in SMPs from the 25–75 mg/L,

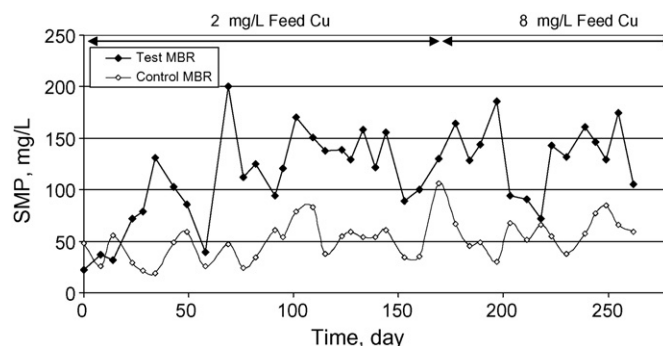


Fig. 4. Temporal variation of SMP in test and control MBRs.

observed in the control MBR, to the 100–150 mg/L in the test MBR at the 7.7 mg Cu/L feed. The average net accumulated SMP in the test MBR at the 20-d SRT during the last 70 days of steady state operation was 121 ± 32 mg COD/L (10 samples) at a feed copper of 2.1 mg/L, i.e. about twice the concentration of SMP in the control MBR (56 ± 18 (30 samples)). However, the concentration of SMP in the MBR remained relatively constant at 128 ± 33 mg COD/L (13 samples) afterwards despite an increase in the feed copper to 8 mg/L. Table 3 illustrates the fractionation of SMPs in the control and test MBRs. It should be noted that the fraction of SMP >100 kDa increased from about 33% of the total SMP in the control MBR to as high as 87% at 8 mg/L feed copper concentration while all other fractions diminished with increasing feed copper concentrations. Thus not only are the total SMP influenced by copper addition but also the molecular weight distribution.

3.2.4. Copper complexation capacity and MW distribution of SMP

As shown in Table 2, SMP in the test and control MBR were found to have heterogeneous sites, with $\log^{\circ}K$ of 7.8–8.2 and 5.8–6.4 mol^{-1} , both of which are considered weak stability constants relative to EDTA with a $\log^{\circ}K$ for copper of 19 [22]. As shown in Table 1, the average net accumulated SMP in the test MBR at the 20-d SRT and a feed copper of 2.1 mg/L was 121 ± 32 mg COD/L, i.e. about twice the concentration of SMP in the control MBR. Interestingly, despite higher SMP concentration in the test MBR, the equivalent ligand concentration of SMP (determined as the product of SMP complexation capacity and SMP concentration) decreased by 45% and 42% for the moderate and weak SMP, respectively. The increase in SMP >100 kDa in the presence of copper along with the fact that SMP > 100 kDa has the lowest complexation capacity [13]

Table 3
Chelating properties of SMP in the control and test MBR

	Control MBR	Test MBR at 2.1 mg/L of feed Cu	Test MBR at 7.7 mg/L of feed Cu
%MW > 100 KD	33.0 ± 6.0 (4)	76.6 ± 8.0 (5)	87.2 ± 3.3 (4)
%MW 10–100 KD	26.3 ± 5.3 (4)	11.5 ± 2.7 (5)	7.6 ± 1.3 (4)
%MW 1–10 KD	33.7 ± 4.7 (4)	7.3 ± 4.7 (5)	3.2 ± 2.0 (4)
%MW < 1 KD	7.0 ± 2.3 (4)	4.7 ± 1.2 (5)	2.1 ± 0.9 (4)

Values in parenthesis reflect number of samples.

Table 4
Simulated and measured Cu in MBRs (all concentrations are in mg/L, except pH)

SRT	Test MBR		Control MBR
	20 d	20 d	20 d
Feed Cu	2.1 ± 0.7	7.7 ± 1.1	0.1 ± 0.06
Reactor pH	6.8–7.3	6.8–7.3	7.0–7.5
Simulated free Cu ²⁺	0.01–0.10	0.01–0.09	0.01–0.06
Measured free Cu ²⁺	0.02–0.09	0.02–0.11	0.00–0.05
Simulated total soluble Cu	0.52–0.84	0.51–0.72	0.26–0.46
Average measured total soluble Cu	0.63 ± 0.13	0.67 ± 0.11	0.33 ± 0.22

explains the decrease in the equivalent molar concentration of SMP in the test MBR.

3.3. Fate of copper

3.3.1. MINTEQ model

The input to the MINTEQ model included predominantly the feed water chemistry, the concentrations of SMP and biomass in the reactor, the total copper concentration in the reactor, as well as the complexation and biosorption equilibrium data, as illustrated in Table 2. The equivalent ligand concentration of SMP used in the MINTEQ model was calculated as the product of the complexation capacity of SMP (C_c), and the average SMP concentration. Table 4 compares the simulated and free copper concentrations at the ambient MBR pH. It is evident that the simulated concentrations of free copper at the operating pH are comparable to the measured values for both the test and control MBRs. Similarly, the simulated and the measured total soluble copper compared well. MINTEQ simulation revealed that at both levels of mixed liquor copper in the test MBR, approximately 99.8% of the total copper was precipitated at the operating pH (6.8–7.3) of the reactor, thus rationalizing the excellent system performance at the high copper content of sludges. Similarly, in the control MBR about 96.2% of the total copper was precipitated at the ambient pH of 6.8–7.3.

3.3.2. Copper fractionation at ambient pH

Fig. 5 presents the fractionation of soluble copper derived from the MINTEQ model simulations at the 20-d SRT for both the control MBR and the test MBR in Stage II. Simulation of the MBR at Stage II, at influent copper concentration of 7.7 mg/L, and pH of 6.8, showed that Cu²⁺, Cu-SMP, and Cu-L + Cu-H, constituted 15%, 73%, and 12% of the total soluble copper. However simulation at pH of 7.3 showed the concentration of Cu²⁺ decreased from 15% of the total soluble copper to 2%, while the concentration of Cu-SMP and Cu-L + Cu-H increased to 82%, and 16%, respectively. In the control MBR at an influent copper concentration of 0.2 mg/L, i.e. approximately one-tenth of the influent copper concentration of Stage I, Cu²⁺ constituted 21% and 4% of the total soluble copper at pH 6.8 and 7.3, respectively, while Cu-SMP was 43% and 35% of the total soluble copper, respectively. It must be emphasized that the absolute concentrations of free copper in the control MBR were generally lower than the test MBR in Stages I and II. By comparison of the frac-

tionation of soluble copper in both the control and test MBR, it is evident that the primary impact of SMP is increased complexation of copper, thus affecting a reduction in free Cu²⁺ on a percentage basis. The impact of pH on soluble copper fractionation, illustrated in Fig. 5, is important. For both the control and test MBR, the fractional contribution of free Cu²⁺ to the total soluble copper increased sharply with decreasing pH from only 4% in the control MBR at pH 7.3 to 21% at pH 6.8. Similarly in the test MBR, free copper ranged from 2% of total soluble copper at pH 7.3 to 15% at pH 6.8. The copper complexed by SMP was a significant component of the total soluble copper in the operating pH range of 6.8–7.3, constituting 35–43% in the control MBR and 73–82% in the test MBR. In fact, in the control MBR at neutral pH, the SMP-complexed copper was about 1.14 mg/L, more than three times the biosorbed copper of 0.37 mg/L despite the high biomass concentration in the MBR. It is thus evident that SMPs play a significant role in copper complexation even at the low influent copper concentrations typical of most municipal wastewaters. It is conspicuous that in copper-laden wastes, the increased production of SMPs tends to mitigate free copper toxicity. Although inorganic copper precipitates dominated the particulate copper at pH > 6, SMPs were the predominant form of soluble copper. This implies that although SMPs contributed to the bioavailability of copper, they helped mitigate the toxicity of the free Cu²⁺. In fact, model simulation has revealed that at the 2.1 mg/L copper feed concentration and neutral pH, Cu²⁺ increases from 0.05 mg/L in the presence of SMPs to 0.08 mg/L in the absence of SMPs. It is intriguing, however, that the contribution of SMPs to copper complexation in the control MBR increased from 35% to 43%, as pH decreased from 7.3 to 6.8, but decreased in the test MBR from 82% to 73%. Conversely, the

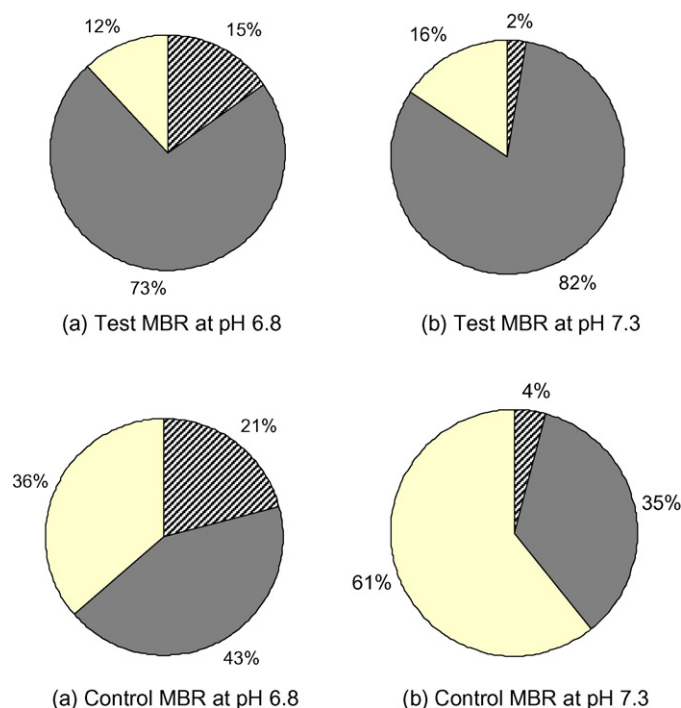


Fig. 5. Equilibrium fractionation of soluble Cu in control MBR and test MBR in Stage II (●) Cu²⁺ (▨) Cu-SMP (■) Cu-L + Cu-H.

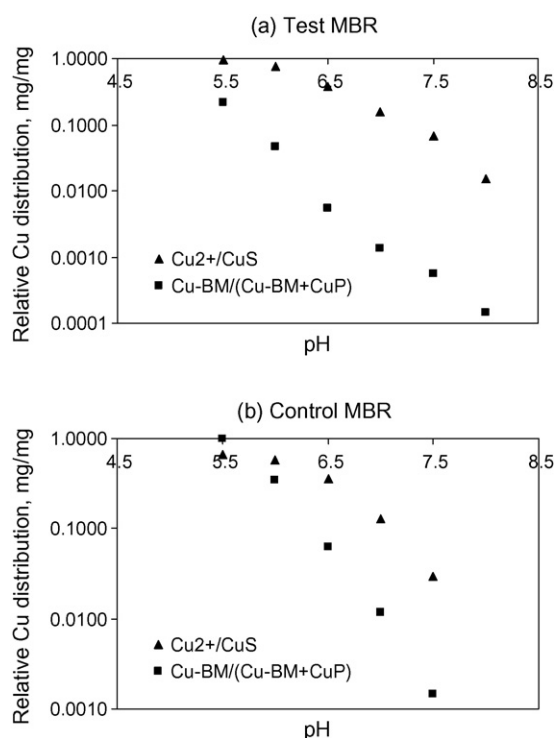


Fig. 6. (a and b) Simulated relative distribution of copper in the solid and liquid phases.

contribution of other ligands to copper complexation decreased much more significantly in the control MBR than in the test MBR.

Fig. 6(a) and (b) depicts the impact of pH on the relative distribution of free copper and biosorbed copper in the control and test MBR (Stage b). As apparent from Fig. 6(a), the biosorbed copper at the 7.7 mg Cu/L feed level accounted for only 5% of the total particulate copper at pH 6, but 22% at pH 5.5. Similarly for the 2 mg Cu/L influent, biosorbed copper was 15% and 38% of total particulate copper at pH 6, and 5.5, respectively. On the other hand, at $\text{pH} > 7$, biosorbed copper was negligible and essentially all the copper was in precipitate form. In the control MBR, however, at the 0.2 mg Cu/L influent, biosorbed copper was about 60% of the total particulate at pH 6, decreasing to around 2% at neutral pH. Since the customary discharge pH criterion is 6–9, for municipal nitrifying systems, the contribution of biosorption to copper removal in municipal wastewaters can therefore be significant in wastewaters with low buffering capacity. It is also interesting to note that as pH decreases, the fraction of soluble copper existing as free Cu^{2+} increased in both the control and test MBRs, translating to higher biosorption capacities in accordance with the equilibrium model. By comparing the relative fraction of soluble copper existing as Cu^{2+} in the test and control MBRs, it is quite conspicuous that this fraction is higher in the test MBR than the control. For example at pH 6, in the test MBR (Fig. 6a), 90% of the soluble copper is Cu^{2+} compared with only 43% in the control MBR. This clearly emphasizes that despite higher SMP production in the test MBRs, the SMP reach their ultimate complexation capacities, which still were insufficient to offset the impact of the high influent copper.

4. Summary and conclusions

In MBRs, as a result of operating at long SRTs, macromolecular biomass associated products (BAP), would dominate the SMP accumulation, effectively reducing overall SMP biodegradability. Thus, in the context of the heavy metal chelation in MBRs, the incorporation of a membrane filter may enhance chelation and complexation of heavy metals. Since copper toxicity to nitrifiers and heterotrophs in accordance with the free ion model is primarily due to the free Cu^{2+} species, the accumulation of high molecular weight (>100 kDa) SMPs for long periods of time will tend to mitigate copper toxicity. In fact model simulation has revealed that at the 2 mg/L copper feed concentration and neutral pH, Cu^{2+} increases from 0.05 mg/L in the presence of SMPs to 0.08 mg/L in the absence of SMPs. Furthermore at neutral pH, the amount of copper chelated by SMP during the 8 mg Cu/L feed, was equal to that adsorbed on the biomass. Since MBRs operate at higher biomass concentrations relative to CAS, the amount of copper adsorbed on biomass will increase proportionately with increasing MLSS concentration.

Despite the aforementioned advantages of MBR in heavy metal removal as a consequence of higher biomass concentration and SMP retention, most of the copper retained in the MBR is in the form of precipitated copper compounds such as copper hydroxides, phosphates and carbonates. In the context of industrial copper-laden wastewaters, although the system could be successfully operated at total copper concentrations as high as 840 mg Cu/L, with complete COD removal and nitrification at pH 6.8–7.3, model simulations indicated that Cu^{2+} increased from 0.05 mg/L at neutral pH to 4.1 mg/L at pH 6, a level toxic to nitrifiers. In such a case which represents nitrification of low alkalinity high-strength wastewaters, it is evident that operation at long SRTs and accumulation of precipitated copper in the MBR is indeed detrimental to system performance. Since nitrification consumes alkalinity, for wastewaters with low buffering capacities the deleterious impact of copper on system performance would be more pronounced for an MBR than a CAS process. Meanwhile in the case of well-buffered wastewaters, the MBR system is advantageous for withstanding heavy metal toxicity vis-à-vis the CAS due to higher biomass and SMP retention capacities. For typical municipal wastewater employing MBR, the retention of SMPs as well as the high biomass concentrations combine to effectively reduce the free Cu^{2+} below inhibition levels for nitrifiers even at low pHs (about 6) and/or low alkalinity wastewaters.

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