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Effects of Cu^{2+} on biological process of wastewater treatment plant (WWTP) in electroplating industrial park

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ABSTRACT

The construction of industrial clusters in China increases the possibility of treating heavy metals containing wastewater by biological treatment process. Those heavy metals which entered wastewater treatment systems will have a toxic impact on the bacteria. The effects of 0–10 mg L^{-1} Cu^{2+} on the performance of an anoxic/oxic—membrane bioreactor (A/O-MBR) process, which simulated the wastewater treatment process in a local surface processing industrial park, in treating electroplating mixed wastewater were investigated in this research. Under the experimental conditions (simulated the real influent scenario), COD removal efficiency and nitrification efficiency of the process were obviously inhibited by 5 and 3 mg L^{-1} Cu^{2+}, respectively, while were severely inhibited by 10 and 5 mg L^{-1} Cu^{2+}, respectively. Above 1 mg L^{-1} of Cu^{2+} would put negative effects on the activities of both autotrophic and heterotrophic bacteria, moreover, autotrophic bacteria were more sensitive to Cu^{2+} than heterotrophic bacteria. The synthesis of the extracellular polymeric substance (EPS) can be stimulated by 1 mg L^{-1} Cu^{2+} while inhibited at higher concentrations. The quantity of EPS was in direct proportion to that of proteins in the experiment indicated that proteins in EPS played a major role in protecting cells from the harm of heavy metals.

Keywords: Electroplating wastewater; Copper; Inhibition concentration; Sludge activity; Extracellular polymers substance (EPS)

1. Introduction

The increasing trend toward constructing industrial clusters in urban development in China increases the possibility of treating metal ions containing wastewater by biological process. For example, the wastewater treatment plant (WWTP) in Jiaonan Electroplating Industrial Park in Shandong province and Xianfeng Electroplating Industrial Park in Fujian province [1]. More than 67 electroplating industrial parks were constructed by the end of 2014 all over China [1]. Comparing with the conventional scattered electroplating factories, wastewater produced during production process is more easily being classified and collected, thus makes electroplating wastewater treatment more targeted and makes it convenient for supervision and management. Based on the electroplating process, effluents can be classified into plating pieces pretreatment wastewater, electroplating rinse wastewater (it can be divided into cyanide containing,

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chromium containing, and comprehensive wastewater), deplating wastewater, and mix-wastewater (the mixture of cleaning wastewater, condensate, and leakage) [2]. The main contaminants in plating pieces pretreatment wastewater are mineral oil, surfactant (such as degreaser), metallic oxide, acid, and alkali. The main contaminants in electroplating rinse wastewater are heavy metals, nitrogen, cyanide, and surfactant (such as leveling agent, brightening agent, and wetting agent). Mix-wastewater contains quite low concentration of contaminants and the compositions are similar to electroplating rinse wastewater. Deplating wastewater takes up a small part of the total electroplating wastewater and the main contaminants are surfactant (such as coordination agent and corrosion inhibitor), nitrogen, and heavy metals.

Adsorption [3], ion exchange [4], chemical precipitation [5], and electrodialysis [6,7] can be used to treat wastewater which contain high concentration of heavy metals, such as electroplating rinse wastewater and mix wastewater. After the removal of heavy metals, wastewater is collected and treated by reverse osmosis (RO) for further reuse. The reuse water should reach the standard for electroplating rinse and it makes up 80% of the total wastewater produced. The RO concentrates are mixed with plating pieces pretreatment wastewater (RP mixture) and wait to be treated (occupies 20% of the total wastewater produced). The main contaminants of the RP mixture are low concentration of organics, nitrogen, and heavy metals. These organic compounds are difficult to be biodegraded. The RP mixture produced in the industrial park is of big quantity, therefore, combination of physicochemical and biological treatment processes would be appropriate for its treatment [8]. After treatment, the effluent is discharged directly, therefore, it should reach the electroplating wastewater discharging standard. Although physicochemical pretreatment process can remove most of heavy metals, low concentration of heavy metals still inevitably flow into the biological treatment unit, which puts an impact on its stable operation. Thus, it is essential to find out the limiting concentrations of heavy metals which will cause obvious influence on the biological treatment system. Biological treatment processes are seldom reported being used for post-treatment of RP mixture. Sochacki et al. [8] had used constructed wetlands to polish electroplating wastewater. The heavy metals (Cu, Ni, Pb, Zn) removal were promoted in the system through precipitation as sulfides mediated by sulfate-reducing bacteria. Liu et al. [9] used a two-stage biological aerated filter for depth processing of electroplating wastewater. These researches proved the feasibility of using biological process for post-treatment of electroplating wastewater.

Copper is among the most common polluting metal ions in industrial wastewater and is also associated with toxicity problems [10]. Several studies have been conducted to determine the microbial inhibition potential of Cu^{2+} on activated sludge processes. The processes involved including sulfate reduction, hydrolytic acidification, nitrification, denitrification, methanogenesis, and others [11–14]. Ochoa-Herrera et al. [13] reported that 50% inhibition concentrations (IC_{50}) of copper in fermentative bacteria, aerobic glucose-degrading heterotrophs, and nitrifying bacteria were 3.5, 4.6, and 26.5 mg L^{-1}. However, even for microorganisms in the same trophic group, the inhibition concentrations being reported were quite different [13]. Such as, the IC_{50} of Cu^{2+} to sulfate-reducing bacteria ranging from 0.84 to 200 mg L^{-1} have been observed [11,15]. The significant inhibitory levels for copper were influenced by the experimental conditions.

Although many researches have been carried out to reveal the inhibition of copper ions to bacteria involved in wastewater treatment, due to the complex field water content, it is hard to give a definite value, under which, the concentration of copper ions in the influent should be kept to ensure a stable treatment performance of the WWTP in electroplating industrial park. The objective of this study was to investigate the performance of the treatment system with the inflow containing different concentrations of Cu^{2+} to simulate the situation of the WWTP in a local surface processing industrial park in Harbin, China, with treatment capacity of 1×10^4 t d^{-1}. The biomass activity in the biological reactor was investigated to determine inhibition level due to heavy metal accumulation. The effects of Cu^{2+} on extracellular polymeric substance (EPS) production and component of activated sludge were also investigated.

2. Materials and methods

2.1. Experimental methods

A laboratory-scale anoxic/oxic-membrane bioreactor (A/O-MBR), which simulates the biological wastewater treatment process in a local surface processing industrial park in Harbin, was used in this study. The schematic diagram of the A/O-MBR system is shown in Fig. 1. The reactor has a working volume of 9.45 L and the volumetric ratio of the anoxic and aerobic tank is 1:2.86. A hollow fiber polyvinylidene fluoride (PVDF) membrane module (with a mean pore size of 0.2 μm and effective surface area of

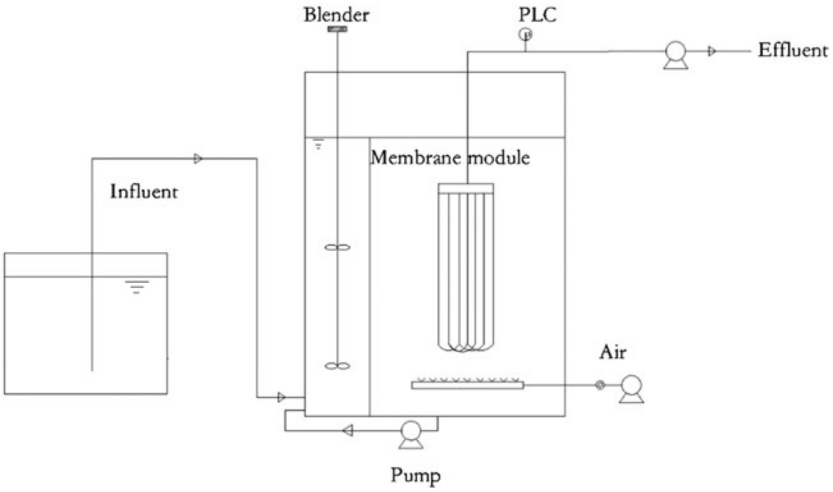

Fig. 1. Schematic diagram of the A/O-MBR.

$0.2\ m^2$) (Motian Membrane Technology Co. Ltd™, China) was submerged in the aerobic tank. The trans-membrane pressure (TMP) was monitored using a pressure gauge. When the TMP exceeded −30 kPa, the membrane module was taken out for physical and chemical cleaning. The membrane flux was $5.93\ L\ m^{-2}\ h^{-1}$.

The influent continuously fed into the A/O-MBR in this research was synthesized according to the water quality of wastewater samples collected from the local surface processing industrial park (summarized in Table 1), at the same time considering the shock concentration caused by industrial accident. The synthesized influent consisted of 1/3 municipal wastewater and 2/3 synthetic wastewater. The final simulated wastewater contained (mg L^{-1}): sucrose (166.67), sodium dodecyl sulfonate (25.00), polyethylene glycol 6,000 (10.00), saccharin sodium (35.00), NH_4Cl (42.00), KH_2PO_4 (8.8), $NaHCO_3$ (66.67), $CaCl_2$ (7.53), and $MgSO_4{\cdot}7H_2O$ (36.67). 1 mL trace element solution was added into 1 L of simulated electroplating wastewater, the trace elements solution contained 5.00 g L^{-1} EDTA, 3.00 g L^{-1} $FeCl_3{\cdot}6H_2O$, 2.36 g L^{-1} KI, 0.30 g L^{-1} H_3BO_3, 0.24 g L^{-1} $MnCl_2{\cdot}4H_2O$, 0.24 g L^{-1} ZnSO4·$7H_2O$, and 0.03 g L^{-1} $Na_2MoO_4{\cdot}2H_2O$. $CuSO_4{\cdot}5H_2O$ stock solutions (10 g Cu^{2+} L^{-1}) were added to simulated wastewater as experiment design.

Table 1
The characteristics of real RP mixture

Parameter	Variation	Mean value
COD (mg L^{-1})	186.44–372.61	293.19
BOD_5 (mg L^{-1})	48.16–110.67	81.27
pH	6.1–8.7	6.6
Ni (mg L^{-1})	0.65–2.41	0.76
Cu (mg L^{-1})	0.34–7.50	4.33
Zn (mg L^{-1})	0.02–5.01	1.92
Cr (mg L^{-1})	0.02–1.36	0.31
TP (mg L^{-1})	0.05–5.70	3.22
NH_4^+-N (mg L^{-1})	14.34–38.25	28.43

2.2. Analytical methods

The mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solid (MLVSS), sludge volume index (SVI), COD, and NH_4^+-N concentrations were analyzed according to Standard Methods [16]. pH was measured using a pH meter (HANNA, Italy). The ammonia uptake rate (AUR) and oxygen uptake rate (OUR) of the biomass were monitored to characterize the activities of autotrophic and heterotrophic microbes according to Katsou et al. [17]. The OUR and AUR were normalized with the volatile suspended solid (VSS) of the mixture. The inhibition rate of Cu^{2+} on microbial activity was determined according to Eq. (1):

$$\mathrm{IR} = (R_0 - R)/R_0 \times 100\% \tag{1}$$

where IR is inhibition rate (%), R_0 and R are OUR (mg O_2 g^{-1} VSS h^{-1}) or AUR (mg NO_3^--N g^{-1} VSS h^{-1}) of biomass prior and after the introduction of Cu^{2+}, respectively. In this study, obvious inhibition refers to a more than 10% inhibition rate of the COD and ammonia nitrogen removal, and serious inhibition refers to a more than 20% inhibition rate. The extraction of EPS was carried out according to the method descripted by Chang and Lee [18] at beginning and end of each running operation. The extracted EPS was analyzed for total proteins and polysaccharides. The measurement of polysaccharides and proteins referred to the phenol–sulfuric acid method [19] and the modified Lowry method [20], respectively. A scanning electron microscope (SEM) image of the sludge was obtained using a Hitachi S-4800 SEM to get a visual idea of the appearance. All the measurements were performed in triplicate, the mean and standard deviation of the results are reported. The analysis of variance method was used to test the statistical significance of the results, and *p* values less than 0.05 was considered to be statistically significant.

2.3. Wastewater and system operating characteristics

The reactor was inoculated with 4.50 g L^{-1} activated sludge which was obtained from a local WWTP treating municipal wastewater (Harbin, China). The sludge retention time was 15 d and the hydraulic retention time was 8 h. The nitrification liquid recycle ratio was 200%. The dissolved oxygen in the anoxic and aerobic tank was kept at 0.2–0.5 mg L^{-1} and 2.0–4.0 mg L^{-1}, respectively. The activated sludge was acclimated with simulated wastewater and the process for 20 d. When the COD and NH_4^+-N removal efficiencies stably exceed 90%, the experimental process began.

Five experimental runs were conducted in this research, each run lasted for 15 d. Copper was continuously added into the reactor in each experimental run. The concentration of Cu^{2+} in the influent were 0, 1, 3, 5, and 10 mg L^{-1}, respectively. Between each of the two runs, no Cu^{2+} was added to recover the microbial activity. Each recover operation lasted for at least one sludge age, and when COD and NH_4^+-N removal efficiencies reached more than 90% in two successive days, the microbial activity recovery was regarded finished. Except for a 20 d recovery period between Run IV and V, the microbial activity could be recovered within one sludge age.

3. Results and discussion

3.1. Effects of Cu^{2+} on A/O-MBR biological performance

COD and ammonium nitrogen removal performance of the A/O-MBR were evaluated as well as biomass activity, including autotrophic and heterotrophic biomass activity, under different Cu^{2+} concentrations. The EPS production of the activated sludge and EPS component were analyzed. The operating conditions of the reactor during the entire experimental period are summarized in Table 2.

3.1.1. Effects of Cu^{2+} on COD removal

The profiles of COD removal efficiencies in different experimental runs are shown in Fig. 2. The COD removal performance in Run I (without Cu^{2+} addition) was used as the control. The A/O-MBR system exhibited an excellent performance in terms of COD removal in electroplating wastewater treatment. The average COD removal efficiency in Run I was 89.4 ± 2.6% with the average effluent COD concentration 35.37 ± 8.09 mg L^{-1}. The COD removal efficiency fluctuated at the beginning of the operation in Run II and Run III due the impact of copper on the metabolic activity of the activated sludge. The COD removal efficiency decreased from 85.0 to 70.2% in the initial 5 d in Run II and decreased from 90.1 to 75.3% in the initial 7 d in Run III. However, by the end of each run, the COD removal got recovered due to the acclimation of the activity sludge. The average COD removal efficiencies were 85.1 ± 6.2% and 82.1 ± 6.1%, respectively, and the average COD removal inhibition rate reached to 4.8 ± 6.9% and 8.2 ± 6.8%, respectively in Run II and Run III. This indicated that Cu^{2+} concentration below 3 mg L^{-1} partially inhibited the heterotrophic biomass and made COD removal efficiency satisfactory but a little bit lower than that without Cu^{2+}. Stasinakis et al. [21] proved that the heavy metals resistant capacity of bacteria can be improved by a proper acclimation. When the concentration of Cu^{2+} increased to 5 mg L^{-1} in Run IV, the organic removal capacity deteriorated. The COD removal efficiency decreased by 12.2% in the whole run and the average COD removal efficiency was 77.7 ± 3.7%. The average COD removal inhibition rate reached 13.1 ± 4.1%, which is an obvious inhibition level. In Run V, the COD removal efficiency decreased from 76.6% on the third day to 64.1% in the end and the average COD removal efficiency was 71.8 ± 14.4%. The average inhibition rate of 10 mg L^{-1} Cu^{2+} was 19.8 ± 16.1%, it was very close to the serious inhibition level. The COD removal efficiency decreased continuously throughout Run V, indicating that part of the sludge were dead and the microbes could not withstand the toxicity of 10 mg L^{-1} Cu^{2+}.

3.1.2. Effects of Cu^{2+} on nitrification

The A/O-MBR showed a good nitrification performance when Cu^{2+} was absent. When the ammonium

Table 2
Operational conditions of A/O-MBR during the different periods

Parameter		Run I	Run II	Run III	Run IV	Run V
COD (mg L^{-1})	Influent	337.22 ± 32.05	281.72 ± 49.58	333.93 ± 47.90	325.08 ± 30.08	305.02 ± 50.42
	Effluent	35.37 ± 8.09	39.85 ± 8.95	59.50 ± 21.18	72.25 ± 12.38	84.93 ± 43.72
	Removal efficiency	89.4 ± 2.6%	85.1 ± 6.2%	82.1 ± 6.1%	77.7 ± 3.7%	71.8 ± 14.4%
NH_4^+-N (mg L^{-1})	Influent	24.21 ± 5.95	26.37 ± 2.69	26.21 ± 2.21	26.65 ± 2.49	27.09 ± 5.40
	Effluent	1.86 ± 1.71	3.91 ± 1.84	5.28 ± 1.61	8.11 ± 2.39	15.44 ± 9.18
	Removal efficiency	92.3 ± 6.2%	85.4 ± 6.7%	80.0 ± 5.3%	69.9 ± 7.9%	44.4 ± 32.8%
pH	Influent	6.2 ± 0.1	6.3 ± 0.3	6.4 ± 0.2	6.2 ± 0.2	6.4 ± 0.2
MLSS (g L^{-1})		4.34 ± 0.15	4.18 ± 0.21	4.08 ± 0.29	3.93 ± 0.37	3.62 ± 0.41
Cu (mg L^{-1})	Influent	0.0	1.0	3.0	5.0	10.0

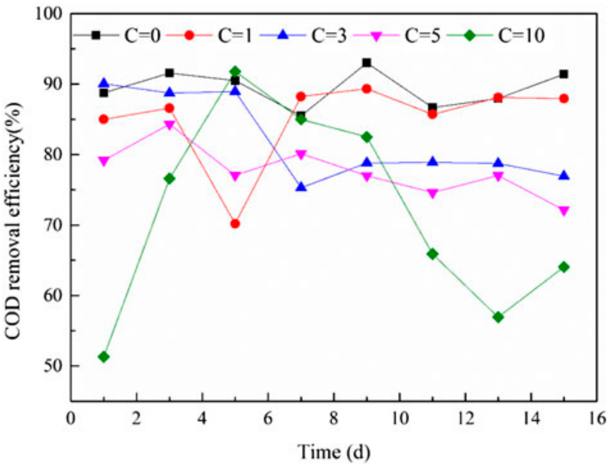

Fig. 2. Variations in COD removal efficiency in the experiment.

nitrogen concentration in the influent ranged from 14.17 to 29.69 mg L^{-1}, the average ammonium nitrogen concentration in the effluent was 1.86 ± 1.71 mg L^{-1}, the average ammonium nitrogen removal efficiency was 92.3 ± 6.2%. The ammonium nitrogen removal efficiency increased in the initial 9 d in Run II. For Cu is an essential element for all aerobic organisms as the redox potential of the Cu^{1+}/Cu^{2+} transformation is utilized by a number of enzymes [22]. However, when cellular Cu levels are too high, it can become very toxic. In the final 6 d, the ammonium nitrogen removal efficiency decreased continuously. The average ammonium nitrogen removal efficiency was 85.4 ± 6.7%. This also indicated that the effects of Cu^{2+} on bacterial activities depend both on concentration and on exposure time. In Run III, the ammonium nitrogen removal efficiency decreased from 87.9% on the third day to 72.5% on the 11th day. The average ammonium nitrogen removal efficiency was 80.0 ± 5.3%. The average inhibition rate for nitrification was 13.3 ± 5.7% and reached an obvious inhibition level. As showed in Fig. 3, the ammonium nitrogen removal efficiency decreased from 87.3 to 61.7% when 5 mg L^{-1} Cu^{2+} was added. The effluent ammonium nitrogen concentration increased from 2.92 mg L^{-1} at the beginning of Run IV to 11.47 mg L^{-1} by the end. The average nitrification inhibition rate was 24.3 ± 8.6%, which reached a serious inhibition level. When the influent Cu^{2+} concentration increased to 10 mg L^{-1}, the activity of the ammonia-oxidizing bacteria was seriously inhibited and the ammonium nitrogen removal efficiency decreased to 13.3% by the end of Run V. These results showed that the inhibition of copper on nitrification

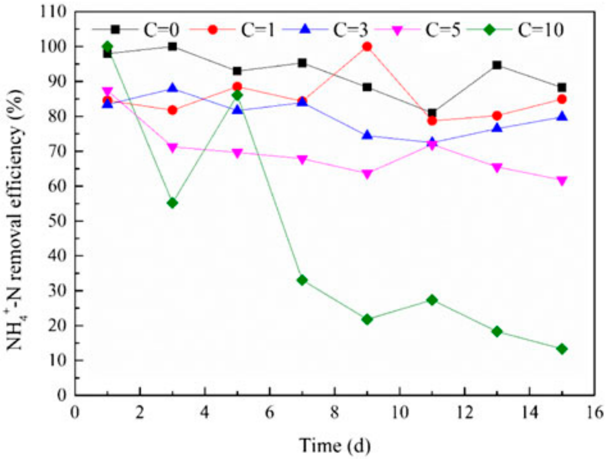

Fig. 3. Variations in NH_4^+-N removal efficiency in the experiment.

was much stronger than on COD removal. Therefore, Cu^{2+} concentration in the influent of an electroplating WWTP should be strictly monitored to avoid the inhibition on nitrification. According to the result in this research, the influent Cu^{2+} concentration should be kept below 5 mg L^{-1}.

3.2. *Effects of Cu^{2+} on sludge activity*

Sludge activity was generally used as the indicator as it can influence the system performance [23]. In this study, OUR and AUR were measured to characterize the activities of heterotrophic and autotrophic biomass. Variations in sludge activity caused by the presence of Cu^{2+} are shown in Fig. 4. In Run I, OUR and AUR were 18.02 mg O_2 g^{-1} VSS h^{-1} and 0.88 mg NO_3^--N g^{-1} VSS h^{-1}, respectively. The values decreased with the increase in Cu^{2+} concentration in the influent. The inhibition rate on heterotrophic biomass activity were 15.9, 51.0, 72.8, 89.1%, respectively in Run II to Run V, when Cu^{2+} concentration in the influent increased from 1 to 10 mg L^{-1}. While, the inhibition rate on autotrophic biomass activity were 40.6, 75.4, 89.7, 100.0%, respectively. Full inhibition on autotrophic biomass activity occurred when Cu^{2+} concentration exceeded 5 mg L^{-1}.

The variations in biomass activity were proportional to the changes in COD and ammonium-nitrogen removal. Nitrifying micro-organisms are, particularly, vulnerable to the presence of Cu^{2+} compared to carbon oxidation micro-organisms. These findings are consistent with the results from Feng et al. [12] and Vaiopoulou and Gikas [23], who found that nitrifiers were more sensitive than aerobic heterotrophic micro-organisms when they were exposed to Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cr^{6+}. This is due to the slow intrinsic growth rate of nitrifying bacteria and their high sensitivity to external factor [24]. It was worth noting that the activities of both heterotrophic and autotrophic biomass by the end of each Run were lower than those in the control system, illustrating that Cu^{2+} concentration over 1 mg L^{-1} will have negative effects on activated sludge.

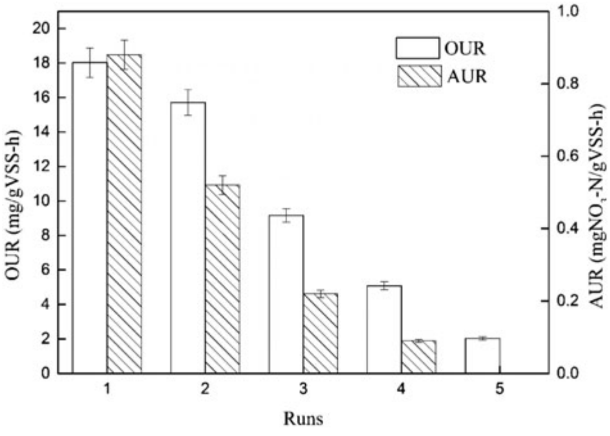

Fig. 4. Variations in OUR and AUR in the experiment.

3.3. *Effects of Cu^{2+} on sludge characteristics*

3.3.1. *MLSS, MLVSS, SVI, and sludge morphology*

The MLSS, MLVSS, and SVI of the activated sludge on day 1 and day 15 in each Run are shown in Table 3. The MLVSS/MLSS ratio decreased by 4% from Run I to Run V, suggesting the deposit of non-volatile inorganic solids within the activated sludge [25]. Growth inhibition existed during the whole Cu^{2+} addition periods and MLSS decreased with the increase in Cu^{2+}. When activated sludge was exposed to 1 mg L^{-1} Cu^{2+}, the SVI increased from 170.79 to 226.31 mL g^{-1}. A more stable suspension may cause by the predominant repulsive forces between the metal ions [25]. With the increase in Cu^{2+} in the influent, more Cu accumulated in the activated sludge, resulted in the decrease in SVI due to the death of bacteria. By the end of Run V, the SVI was only 76.94 mL g^{-1}. Morphology of the activated sludge in Run V before and after 10 mg L^{-1} Cu^{2+} addition were recorded by SEM (Fig. 5). The photos showed that flocs before Cu^{2+} addition had a relatively compact structure with plumb and smooth cells. However, by the end of Run V, the structure of the activated flocs became loose with numerous small aggregates of wizened and ruptured bacterial cells scattered on the surface. This indicated that 10 mg L^{-1} Cu^{2+} is fatal to microbes.

3.3.2. *EPS production and its component*

EPS, which acts as a gel-like matrix that binds cells together to form sludge flocs, are the main components of activated sludge [26,27]. EPS plays important roles in regulating the physicochemical properties of activated sludge and the performance of wastewater treatment systems [28]. The changes in EPS content and component can reveal the response and resistance of activated sludge to toxicants at high concentrations [28].

The profiles of EPS production during the experiment are shown in Fig. 6(a). Its quantity decreased in one run period except in Run I and Run II. The EPS quantity varied slightly in Run I, while in Run II, the EPS production increased from 250.68 mg g^{-1} VSS at the beginning to 286.52 mg g^{-1} VSS by the end,

Table 3
Variations in MLSS, MLVSS, and SVI in different runs

	Run I		Run II		Run III		Run IV		Run V	
Parameter	D 1	D 15	D 1	D 15	D 1	D 15	D 1	D 15	D 1	D 15
MLSS (g L^{-1})	4.31	4.40	4.41	4.02	4.34	3.75	4.28	3.59	3.98	3.23
MLVSS (g L^{-1})	3.71	3.78	3.79	3.46	3.73	3.19	3.64	3.02	3.34	2.65
SVI (ml g^{-1})	154.42	160.37	170.79	226.31	203.55	142.61	98.04	90.37	88.38	76.94

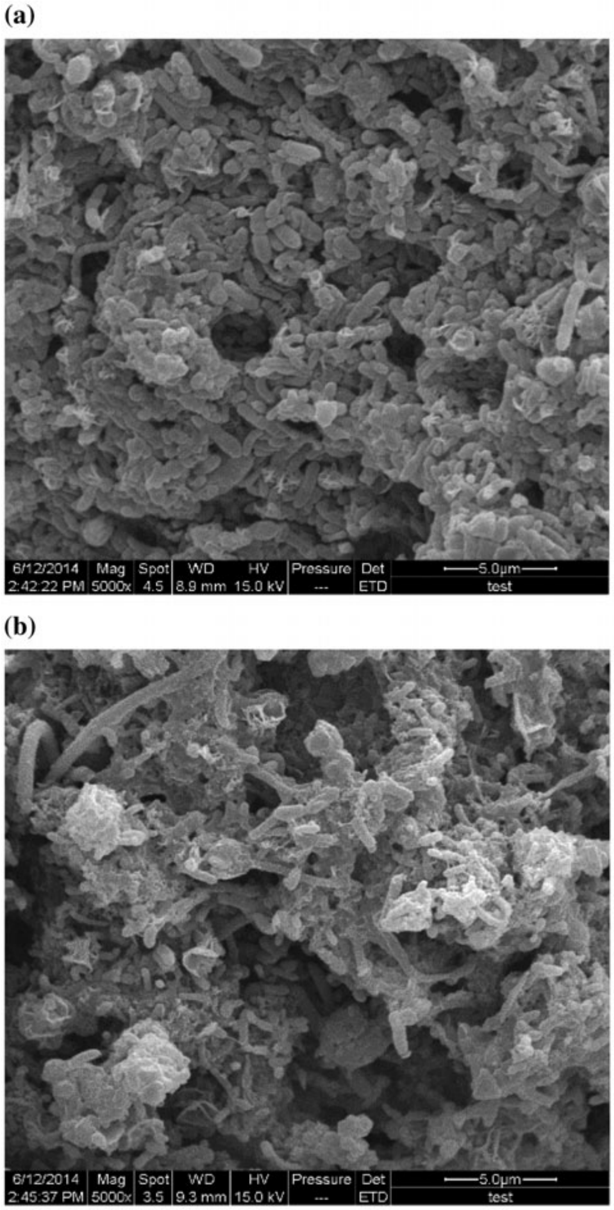

Fig. 5. SEM observations of the activated sludge in Run V ((a) initial stage and (b) final stage).

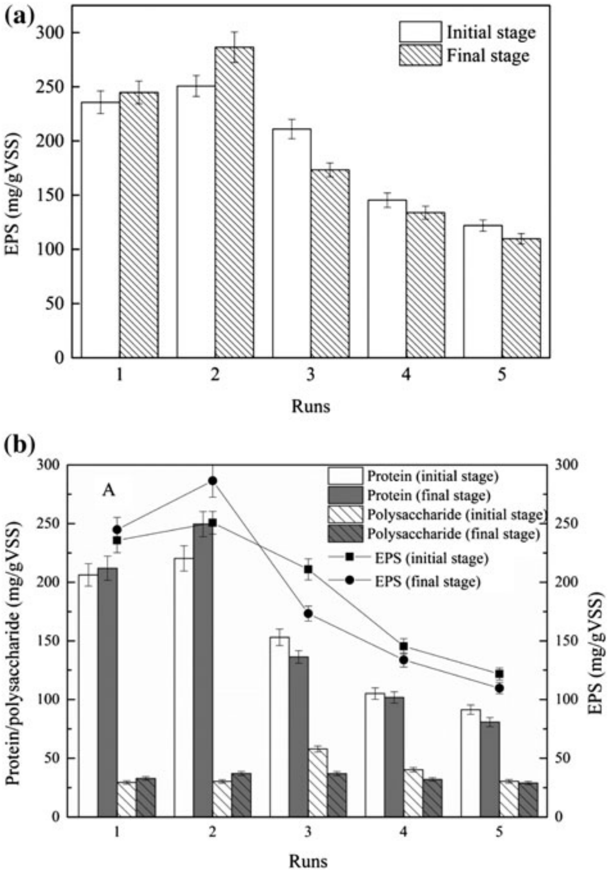

Fig. 6. (a) EPS quantity in each experimental runs and (b) effects of Cu^{2+} on the components of EPS.

indicating that 1 mg L^{-1} Cu^{2+} could stimulate the micro-organisms to excrete more EPS to chelate heavy metal ions. This presumably is a defense mechanism against toxicity. EPS serves as charged functional groups and has the ability to bind other charged particles or molecules [29,30]. Heavy metal ions could be adsorbed by EPS before they enter cells, thus reduces the potential toxicity caused by heavy metals to functional bacteria in activated sludge [31]. Harrison et al. [32] also reported that EPS can build up a protective barrier for the microbes against the harsh external environment. In Run III, EPS concentration did not further increase, but decreased instead by 37.66 mg g^{-1} VSS in the run period. This indicated that 3 mg L^{-1} Cu^{2+} inhibited the bacterial metabolism activity and reduced the production of EPS. The decrease in EPS could be attributed to its biodegradation to sustain the vital metabolic processes [33]. Wang et al. [31] also reported that once Cu^{2+} additions reached 3 mg L^{-1}, EPS quantity decreased markedly due to the higher accumulation of copper ions in the denitrifying phosphorus removal sludge. In the following experimental Runs (IV to V), EPS production decreased continuously, but the reduction reduced slightly. This may be attributed to that copper can destroy the cell membrane integrity and part of cells ruptured and released some proteins and polysaccharides [34].

The compositions of EPS include proteins, polysaccharides, humic substances, lipids, nucleic acids, uronic acids, and some inorganic components [26]. Generally, polysaccharides and proteins are recognized as the major components of EPS. The components of EPS in our research is profiled in Fig. 6(b). Protein was the main component of EPS and it occupied 72.3–87.9% of the total EPS. In the experiment, the quantities of EPS and proteins were in direct proportion. However, no obvious correlation was found between the quantities of polysaccharide and EPS. This indicated that high concentration of Cu^{2+} disturbed the synthesis of EPS, especially proteins, because proteins bond with multivalent cations more easily than polysaccharide [35,36]. Han et al. [37] also pointed that protein can remit the toxicity of heavy metals through binding and mitigating of metals through enzymatic detoxification. Thus, proteins in EPS play a major role in protecting cells from any harm caused by heavy metals.

4. Conclusion

The effects of 0–10 mg L^{-1} Cu^{2+} on activated sludge in an A/O-MBR system treating simulated electroplating wastewater were investigated. It was observed that 3–5 mg L^{-1} of Cu^{2+} would obviously impact the COD removal and nitrification, while above 5 mg L^{-1} of Cu^{2+} caused a serious inhibition. OUR and AUR profiles showed that even 1 mg L^{-1} of Cu^{2+} had negative effects on the activities of both autotrophic and heterotrophic bacteria, although the COD removal and nitrification performance did not show much difference under this concentration. Nitrifying micro-organisms are more sensitive to the presence of Cu^{2+} compared to carbon oxidation micro-organisms. Low concentration of Cu^{2+} stimulated the synthesis of EPS, while above 3 mg L^{-1} of Cu^{2+} caused the decrease in EPS production. From an economic point of view, activated sludge can be used for post-treatment of electroplating wastewater. However, the concentration of metal ions should be carefully controlled to keep a good treatment performance.

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