

Mechanism of combination membrane and electro-winning process on treatment and remediation of Cu^{2+} polluted water body

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Abstract

Mechanism of treatment and remediation of synthetic Cu^{2+} polluted water body by membrane and electro-winning combination process was investigated. The influences of electrolysis voltage, pH, and electrolysis time on the metal recovery efficiencies were studied. Relationship between trans-membrane pressure drop (ΔP), additions ratio, initial Cu^{2+} concentration on operating efficiency, stability of membrane and the possibility of water reuse were also investigated. The morphology of membrane and electrodes were observed using scanning electron microscopy (SEM), the composition of surface deposits was ascertained using combined energy dispersive X-ray spectroscopy (EDX) and atomic absorption spectrophotometer. The results showed that using low pressure reverse osmosis (LPRO), Cu^{2+} concentration could increase from 20 to 100 mg/L or even higher in concentrated solutions and permeate water conductivity could be less than 20 $\mu\text{S}/\text{cm}$. The addition of sodium dodecyl/sulfate improved Cu^{2+} removal efficiency, while EDTA had little side influence. In electro-reduction process, using plating electrode cell, Cu^{2+} concentration could be further reduced to 5 mg/L, and the average current efficiency ranged from 9% to 40%. Using 3D electrolysis treatment, Cu^{2+} concentration could be reduced to 0.5 mg/L with a current efficiency range 60%–70%.

Key words: heavy metal; water body; membranes; electro-winning ; remediation

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Introduction

Significant quantities of heavy metals have been released into the environment due to rapid industrialization and have created a major global concern. The process of urbanization and industrialization is accompanied by increased automobile and industrial emissions of heavy metals to surrounding water bodies (Castelblanque and Salimbeni, 2004, Chang *et al.*, 2007). Copper, cadmium, zinc, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, pigment manufacture, printing and photographic industries, etc. (Kadirvelu *et al.*, 2001; Williams *et al.*, 1998; Chang *et al.*, 2007; Reeve, 2007).

Unlike organic wastes, heavy metals are non-biodegradable, can subject to bio-magnification and be accumulated in living tissues, causing various diseases and disorders (Kamitani and Kaneko, 2007). For example, copper can cause stomach and intestinal distress, liver and kidney damage, and anemia. As a result, there has been a tightening of the regulations for heavy metals in point source wastewater discharges. The remediation of

heavy metal wastewater to harmless concentrations is an important goal.

Traditional treatment processes (such as ion exchange, activated carbon adsorption, liquid membrane extraction, biosorption) are incapable of reducing metal concentration to the levels regulated by law (such as precipitation processes), prohibitively expensive and difficult to operate (Couillard, 1994; Churchill *et al.*, 1995; Bayhan *et al.*, 2001; Yang *et al.*, 2001; Namasivayam and Senthilkumar, 2002; Wang *et al.*, 2006). Electrochemical method is the most promising processes for heavy metal recovery, however, its low current efficiency and high energy consumption were the main problems, especially for low heavy metal concentration (Chen, 2004).

Membrane separation processes is a powerful process developed to remove various contaminants. It has some advantages, such as continuous operation, low floor space requirement and easy transportation (Ujang and Anderson, 1998; Castelblanque and Salimbeni, 2004; Petrov and Nenov, 2004). Membrane separation processes are gaining widespread acceptance in the treatment of industrial and municipal wastewater, as well as in groundwater remediation. Ozaki *et al.* (2002) studied the removal performance of reverse osmosis membrane for the separation of Cu^{2+} and Ni^{2+} from both synthetic and real plating wastewater.

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Juang and Shiau (2000) studied the removal of Cu²⁺ and Ni²⁺ from synthetic wastewater using chitosan-enhanced membrane filtration.

In the application of treatment and remediation of heavy metal wastewater, membrane process can also increase the concentration of heavy metal content in the retentate water, making it easy for electro-deposition recovery of heavy metals. Combination of these two techniques can treat heavy metals polluted waters efficiently, at the same time, recovery of heavy metals and implementation of reuse of the polluted water can be achieved. Figure 1 shows a typical flow sheet of electro-membrane combination treatment process.

In this article, synthetic wastewater containing Cu²⁺ was treated with low pressure reverse osmosis (LPRO) and ultrafiltration (UF) membrane combining with electro-winning devices (plane and 3D electrodes). The mechanism of treatment and remediation of Cu²⁺ polluted water was investigated, and the variables such as pressure, operation time, temperature, additions ratio and current density were also studied. The possibility of water reuse in ultra low pressure RO membrane separation process was evaluated.

1 Materials and methods

1.1 Water samples

Water samples were obtained from water body near a print circuit board (PCB) factory in Shenzhen, South China. The water quality was: pH 7–8, COD 100 mg/L, concentration of Cu²⁺ 10–50 mg/L. Synthetic water samples were prepared by adding different amounts of copper sulfates (AR, Merck, German) and other additions (such as EDTA, PPG, and sodium dodecyl sulfate) into distilled water to simulate the real polluted water. The composition of synthetic raw polluted water is shown in Table 1.

1.2 Ultrafiltration and low pressure reverse osmosis membrane

The filtration equipment was manufactured by SAIBO Industry (Wuxi, China). This laboratory scale membrane filtration unit was used to carry out the experiments. It consisted of a module containing two disk membranes arranged in parallel. The system was fed by a plunger

Table 1 Composition of synthetic water

Parameter	Range	Mean
pH	7–8	–
Cu ²⁺ (mg/L)	10–100	20
Ni (mg/L)	1–2	1
COD* (mg/L)	50–120	100
EDTA (mg/L)	5–20	10
Polypropylene glycol (mg/L)	20–60	40

* Caused by EDTA, PPG, and sodium dodecyl sulfate; – usually around 7.0.

pump, which provided the high pressure needed. Solution samples were filtered with disk membranes (Φ76) manufactured by GE-Osmonics (USA), in which a polyamide selective layer is supported on polysulfone layers.

The performance of the RO and UF processes were evaluated by measuring Cu²⁺ concentration, COD, conductivity of the influent and effluent to the units, and trans-membrance pressure drop (Δ*P*). To improve the removal efficiency of metal ions, the effects of additions anionic surfactant sodium dodecyl sulfate (SDS) and EDTA (AR, Merck, German) were also tested.

1.3 Electro-winning devices

The electro-winning cell reactor was made of acrylics with dimension of 6 cm × 5 cm × 5 cm and the total system volume of 120 cm³. Cell was packed with a pair of electrodes (graphite and stainless steel plates employed as cathode and anode, respectively). Size of each electrode was 4 cm × 4 cm dipped inside the reactor with the effective area of 16 cm². A DC power supply (DH1716-7A, Matrix, China) was operated at a fixed current mode and the output voltage was recorded. To enhance the mass transfer of Cu²⁺ onto the cathode, special active carbon particles were packed between the electrodes (Fig. 2).

The effects of electrolysis voltage, surfactant-to-metal molar ratio, pH, and electrolysis time on the metal and surfactant recovery efficiencies were investigated. Cu²⁺ concentration used in the electro-winning experiments ranged from 25 to 1000 mg/L.

1.4 Instruments and methods

Metallic ions were determined using atomic absorption spectrophotometer (AAS, Vario 6, Germany). Conductivity and salinity of water were measured using conduct-

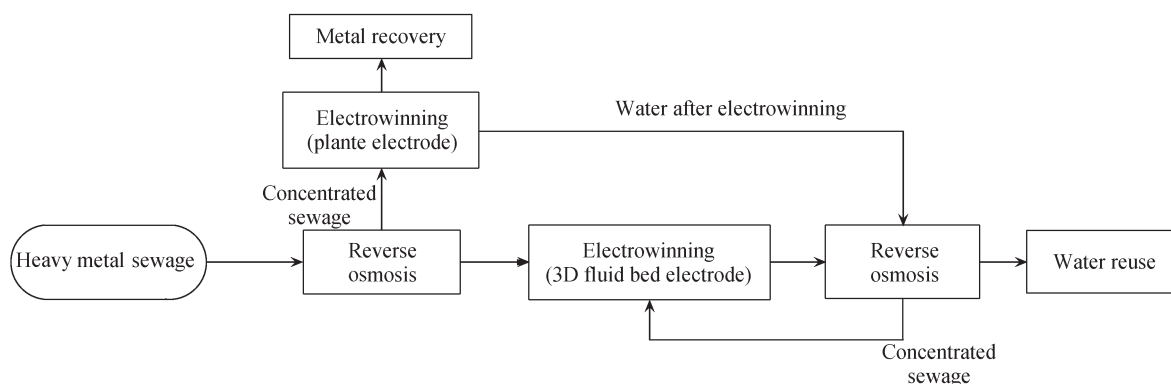


Fig. 1 Simplified flow sheet of electro-membrane combination process.

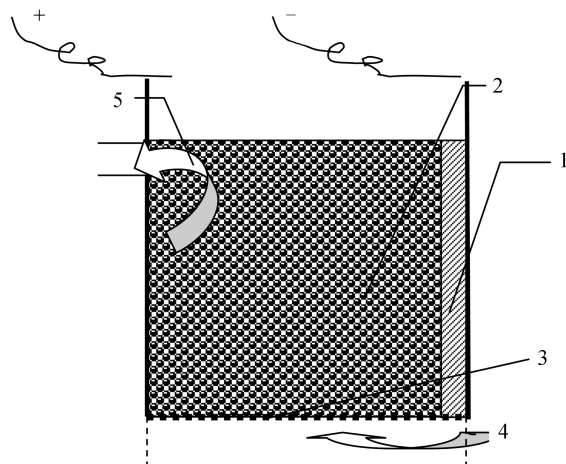


Fig. 2 Schematic of 3D pack electrode cell. (1) separate membrane; (2) packed active carbon particles; (3) porous supporter; (4) solution inlet; (5) wastewater outlet.

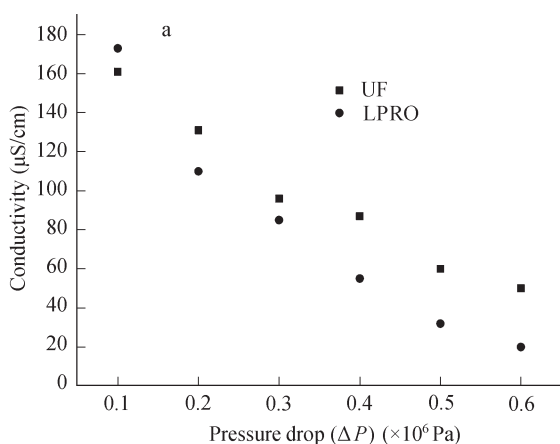
meter (EC215, Hanna Instrument, Germany). Morphology of membranes and electro rods were observed using Quanta 200 environmental scanning electron microscopy (ESEM) (FEI Company, Holland), elements composition were ascertained by energy dispersive X-ray spectroscopy (EDX) (EDAX, USA).

2 Results and discussion

2.1 Effect of copper removal and concentration in LPRO and UF processes

The purpose of evaluating the effects of various parameters was to explore the suitable conditions for the maximum retention of metal with the highest possible permeate flux. Thus the retention of metal and the permeate flux were the main criteria for the evaluation of performance of membrane processes. After metal ion concentrations of permeate and feed solutions were measured, retention values (R) were calculated according to following Eqs. (1) and (2).

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (1)$$



where, C_p and C_f are the concentration of metal ion in the permeate and in the feed solution, respectively.

$$\text{SF} = \frac{J}{\Delta p} = \frac{1}{\mu R_t} \quad (2)$$

where, SF is membrane specific flux; J is membrane flux; Δp is pressure difference between high and low pressure sides of the membrane; μ is viscosity of permeate solution; R_t is total resistance in membrane filtration process.

Table 2 shows the permeability of low pressure RO and ultra-filtration membranes. The resistance in membrane filtration process R_t in LPRO process was quite stable in the whole Δp range studied, while in UF process R_t increased with the increasing pressure.

The efficiency of LPRO and UF processes in removing Cu^{2+} from wastewater is presented in Fig. 3. Conductivity was reduced more than 80% and 90% after UF and LPRO process, respectively. As shown in Fig. 3b, Cu^{2+} was removed fairly well from the wastewater by LPRO. The concentration of Cu^{2+} in the product water (permeate) from LPRO process was reduced to an average value of 1 mg/L in two level series LPRO process for an initial feed concentration range 10–100 mg/L. Each step has an Cu^{2+} removal efficiency of 85%. On the other hand, the removal efficiency of Cu^{2+} by UF ranged from 65% to 80%.

Cu^{2+} concentration of retentive flux increased as the feed raw water Cu^{2+} concentration increase. When feed Cu^{2+} concentration is less than 50 mg/L, LPRO Cu^{2+} concentration on permeated water always had concentrations below 5 mg/L. As feed Cu^{2+} concentration increased, Cu^{2+} concentration of the permeated water increased slowly,

Table 2 Permeability of low pressure reverse osmosis and ultrafiltration membranes

ΔP (MPa)		0.1	0.2	0.3	0.4	0.5	0.6
J ($\text{L}/(\text{m}^2 \cdot \text{h})$)	UF	6	8	10	12	16	18
	RO	2	4	6	8	10	14
SF ($\text{L}/(\text{m}^2 \cdot \text{h} \cdot \text{MPa})$)	UF	60	40	33	30	32	30
	RO	20	20	20	20	20	22
R_t (10^{14} m^{-1})	UF	0.5	0.75	0.96	1.0	0.98	0.98
	RO	1.5	1.5	1.5	1.5	1.5	1.5

UF: ultrafiltration; RO: reverse osmosis.

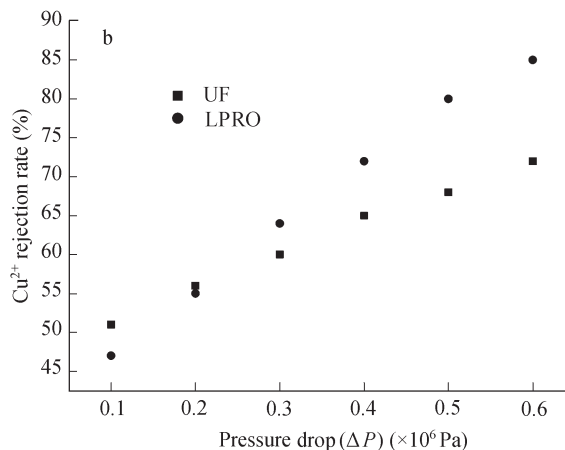


Fig. 3 Relationship between permeated water conductivity (a) and Cu^{2+} rejection ratio (b) with ΔP after 48 h filter reaction at 298 K. Initial Cu^{2+} concentration: 100 mg/L, pH: 6.0. UF: ultrafiltration; LPRO: low pressure reverse osmosis.

but not more than 15 mg/L. Considering the shorter membrane filtering time and distance, the result of the removal efficiency results were quite good. In contrast, as the feed Cu²⁺ concentration increased, Cu²⁺ concentration of retentive flux increased gradually. Effect of feed Cu²⁺ concentration on permeate, retentive flux Cu²⁺ concentration and rejection ratio are summarized in Table 3, where the trans-membrane pressure was fixed at 0.6 MPa. There was little difference between RO and UF retentive flux Cu²⁺ concentration, but the Cu²⁺ concentrations in RO and UF permeate flux were quite different. Figure 4 shows SEM and elements analysis of low pressure membrane surface. The EDX analysis results of Fig. 4 are summarized in Table 4.

2.2 Effect of copper removal and recovery in 3D electro-winning processes

The electrolysis process liberates metal ions from the solution metal complexes by electrodepositing metals onto the cathode. In order to maximize the removal ratio of met-

Table 3 Effect of feed Cu²⁺ concentration on permeated and retentive flux, rejection ratio (pH 6.0, ΔP 0.6 MPa)

Cu ²⁺ in feed (mg/L)		10	25	50	75	100
Cu ²⁺ in permeated water (mg/L)	UF	5	10	22	26	30
	RO	1.0	2.5	5	8	15
Cu ²⁺ in retentive flux (mg/L)	UF	25	53	95	141	150
	RO	37	61	96	140	150
Cu ²⁺ rejection ratio (%)	UF	45	55	60	65	70
	RO	90	84	84	85	85

Table 4 Energy dispersive X-ray spectroscopy (EDX) analysis result from Fig. 4

Element (at.%)	Blank	48 h
CK	81.08	89.37
OK	12.82	07.70
SiK	–	00.79
SK	04.87	00.22
CaK	–	00.17
FeK	00.78	00.18
CuK	–	00.84

–: Elements were not detected in the sample by EDX.

al ions from the membrane concentrate and the possibility for copper recovery, the solutions were treated by electro-winning process where graphite was used as anode and stainless as cathode. To enhance the mass transfer of copper ions onto the cathode, special activated carbon particles were packed between the electrodes, which formed a 3D packet electro-winning cell.

The comparison of the average Cu²⁺ removal efficiency and current efficiency for the electrolysis process under various current densities is shown in Fig. 5. The current efficiency η is defined in the Eq. (3).

$$\eta = \frac{A_{\text{actual}}}{A_{\text{theoretical}}} \times 100\% \tag{3}$$

where, A_{actual} is actual amount of Cu²⁺ removal and $A_{\text{theoretical}}$ is theoretical amount of Cu²⁺ removal.

As seen from Fig. 5, about 60% Cu²⁺ was recovered at 20 A/m² in the 3D packages bed cell in 60 min, while the other electrolysis parameters were constant, and current efficiency reached 62%. It is apparent from Fig. 6 that using plante electrode cell Cu²⁺ concentration can be reduced to 5 mg/L, but it can be less than 0.5 mg/L using 3D cell. Increase of current density caused an increase in power consumption. At lower current density, less power is consumed, but to obtain a higher recovery rate requires a longer electrolysis time. Therefore, in practice, low current density may not be used.

When the concentration of heavy metals in solution declined, current efficiency in electro-winning decreased too. In order to get a higher current efficiency in heavy metals recovery, it is necessary to determine the appropriate electro-deposition time and the minimum final concentration of heavy metals. During electro-deposition process, concentration of electrolyte solution decrease steadily, but the decline was more pronounced in first 30 min, then decreased slowly. Therefore, 60 min electrolysis is suitable. It is apparent from Fig. 6 that the reaction rate changes after the second-hour of the experimental run at 10 A/m². Figure 6 shows that the copper removal efficiencies are all higher than 90% at pH 6.0, current density 10 A/m², and hydraulic residence time (HRT) 60 min. Increasing

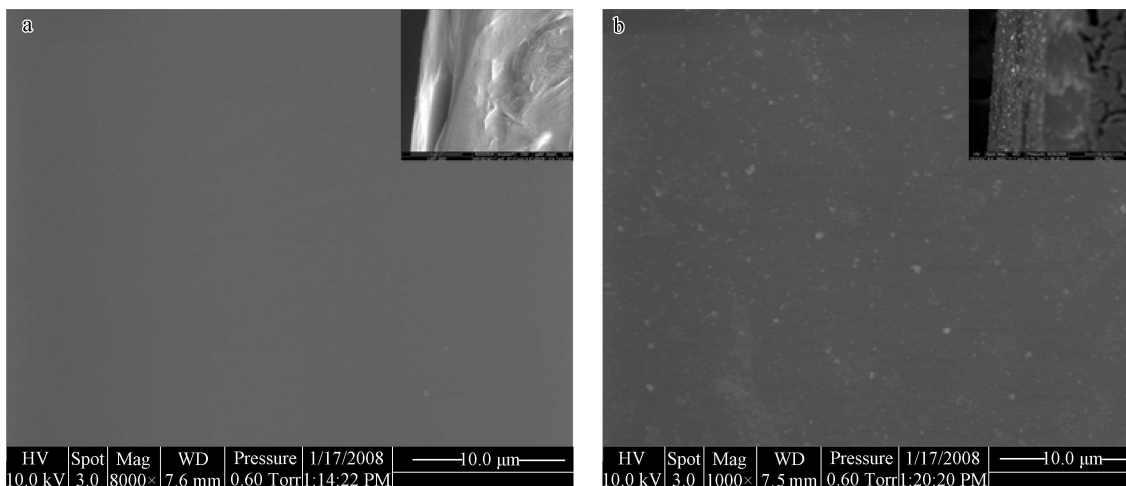


Fig. 4 Scanning electron microscopy (SEM) and elements analysis of low pressure RO membrane. (a) original LPRO (blank) membrane; (b) after 48 h filter reaction.

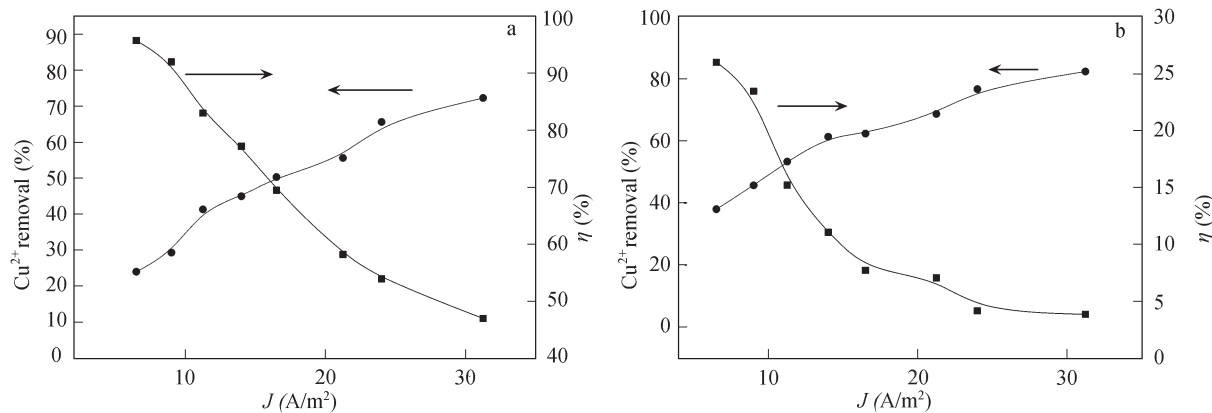


Fig. 5 Cu^{2+} removal efficiency in electro-winning process using 3D electrode cell (a) and plante electrode cell (b). Condition: initial pH 6.0, 298 K, initial Cu^{2+} concentration 100 mg/L.

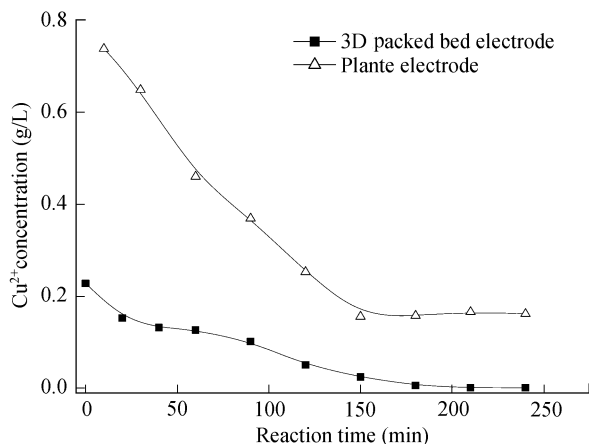


Fig. 6 Copper ion removal efficiency in different electrode cells (10 A/m^2) with initial pH 6.0.

permeate flux enlarges the amount of fouling materials transported to the membrane surface, resulting in more sever irreversible membrane fouling.

2.3 Effect of the addition of sodium dodecyl sulfate and EDTA on Cu^{2+} removal and recovery process

To improve the removal of metal ions in these processes, the effect of the addition of anionic surfactant sodium dodecyl sulfate (SDS) and EDTA were studied. With SDS employed to retain metals inside the reactor, the removal efficiency of Cu^{2+} can reach 90%–99% for UF or RO process. EDTA can also increases removal efficiency of Cu^{2+} in UF process, however, had little influence on LPRO process.

In the process, the appropriate surfactant was added and its concentration was adjusted so that micelles formed.

The permeate water will contain very little, if any, of the feed surfactant components in UF process and even less residual surfactant in RO process, while the retentate will contain most of the surfactant and the solutes. The selective rejection of metal ions having the same electrical charge as the surfactant ion cannot be expected, since the main binding force is due to an electrostatic attraction between metal and surfactant.

Subsequently, the metal-free surfactants were able to retain more metal ions entering the reactor afterward. Thus, the proposed hybrid system can be operated as a continuous adsorption and regeneration (by electrolysis) process. Since Cu^{2+} entering the reactor are retained by membrane, the average residence time of Cu^{2+} is not affected by the HRT. Ideally, by varying the HRT one can achieve higher concentration of Cu^{2+} retained inside the reactor. As shown in Table 5, it can be concluded that EDTA and SDS have little side influence on electro-reduction process.

3 Conclusions

With the use of 3D electrode cell electro-reduction technology, the average copper removal efficiency can reach from 70% to 95% with an average current efficiency ranging from 59% to 75%, respectively. Using plante electrode cell Cu^{2+} concentration can be reduced to 5 mg/L, with average current efficiency ranging from 9% to 40%. The Cu^{2+} concentration can be less than 0.5 mg/L while using 3D electrode cell. The addition of EDTA and SDS had little side influence on electro-reduction process.

The average Cu^{2+} removal efficiency in LPRO process is 85%. On the other hand, the removal efficiency of Cu^{2+}

Table 5 Effect of SDS and EDTA on Cu^{2+} removal and recovery

	ΔP (MPa)	Copper recovery rate in 3D cell (%)	Rejection rate (%)		J ($\text{L}/(\text{m}^2\cdot\text{h})$)		Permeated water conductivity ($\mu\text{S}/\text{cm}$)	
			UF	RO	UF	RO	UF	RO
Blank 0	0.6	87	68	85	17	14	60	20
EDTA (20 mg/L)	0.6	76	75	82	18	12	120	100
EDTA (60 mg/L)	0.6	72	76	83	20	12	200	100
SDS (60 mg/L)	0.6	93	86	92	16	10	180	80
SDS (600 mg/L)	0.6	86	99	99.5	15	8	360	106

* Initial Cu^{2+} concentration 100 mg/L.

by UF ranged from 50% to 70%. The addition of SDS can improve the Cu²⁺ removal efficiency which can reach as high as 90%. The addition of EDTA had little side influence on the membrane filter performance especially in LPRO process.

Conductivity of permeate from LPRO can be less than 100 µS/cm, with low heavy metals concentrations. Thus heavy metals in wastewater can be treated effectively by this hybrid process with recovery of heavy metals and at the same time implementation of water reuse.

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