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Application of electrodialysis to remove copper and cyanide from simulated and real gold mine effluents

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Abstract: In this paper, a laboratory-scale electrodialysis (ED) system with an effective area of 88 cm^2 was used to remove copper and cyanide in simulated and real gold mine effluents. The membrane fouling was characterized by FTIR, SEM-EDX, measuring the membrane resistance and static contact angle. The effects of applied voltage, initial concentration, and flux rate on removal rate of copper and cyanide were investigated. The highest copper (99.41 %) and cyanide (99.83 %) removal rates were achieved under following conditions: applied voltage of 25 V, initial concentration of C2 (concentration of copper and cyanide were 47 mg/L and 242 mg/L), and flux rate of 4.17 mL/s. Besides, the lowest concentration of copper (0.44 mg/L), cyanide (0.48 mg/L) and zinc (0.34 mg/L) in the treated effluent were all below the regulatory limits (copper, cyanide $<$0.5 mg/L, zinc $<$2.0 mg/L). The results showed the presences of CuCN, $[Cu(CN)_3]^{2-}$, $Cu(OH)_2$, and $Zn(OH)_2$ in precipitations, and the fouling of anion-exchange membranes(AEMs) can be decreased significantly via pH adjustment. This research provides a new insight into the removal of copper and cyanide from gold mine effluent.

Key words: electrodialysis (ED); copper; cyanide; gold mine effluent; membrane fouling

1 Introduction

Due to the dwindling resources of simple cyanide extractable gold deposits, currently a large proportion of the gold production is recovered from complex gold ores, many of which contain soluble copper minerals [1]. The cyanidation based extraction of gold from its host minerals has remained fundamentally unchanged since its inception over 100 years ago [2]. However, using cyanidation generates a large amount of effluent, which contains copper and cyanide [3]. The discharge of these effluents into environment is strictly controlled. Many countries and environmental protection agencies have imposed limiting standards for the discharge of gold mine effluent [4]. In view of these considerations, the recovery/removal of copper and cyanide is necessary.

In order to achieve the regulated concentration of cyanide and copper in the discharged effluent (<0.5 mg/L) [5], several treatment systems have been developed. The majority of current approaches were based on cyanide destruction by chemical oxidation and/or recovery by acidification [4, 6]. The chemical oxidation is very efficient in detoxifying free cyanide bearing wastes, however it is less-effective in the case of cyanide based metal complex (such as copper) due to slow reaction kinetics [6-7]. Moreover, the toxic intermediates (cyanogen chlorides) produced during the oxidation process would produce additional environmental pollution [8]. On the other hand, the acidification treatment approach has been adopted in gold processing facilities, whereas the high consumption and cost of reagents have significantly limited their application [9]. Other recent emerging treatment methods including Inco SO_2-air process, hydrogen peroxide oxidation, active carbon adsorption, biological degradation, ozone oxidation, electrochemical oxidation and ion-exchange resins have been explored [1, 10-14]. The comparison of all those methods and theirs in terms of advantages and disadvantages has been listed in literature 4.

The Inco SO_2-air process involves the use of SO_2 (or other sulfite source), which reacts together with oxygen and copper cyanide complexes, resulting in cyanide oxidation to cyanate. At the end of the reaction, copper is precipitated out as copper hydroxide. In order to meet stringent environmental regulations, the operational cost increases significantly [1, 4, 15]. As to hydrogen peroxide oxidation, excess reagent is decomposed to water and oxygen, which results in high cost of reagent [9]. Activated carbon adsorption has an affinity for many metal cyanide compounds, including the soluble cyanide species of copper, zinc, nickel and iron. However their low adsorption capability has severely hampered their wide application in practice, which is used only for low concentrations of cyanide [8, 11]. Biological degradation is environmental friendly and relatively inexpensive, but the technology is not well established and it tends to be very site specific with specific evaluation [12]. Ozone oxidation is efficient in cyanide removal, and some regeneration of cyanide is possible. However the reagent and equipment is costly. [10] In electrochemical oxidation process, all cyanide baths can be treated regardless of concentration but it requires post treatment by a number of oxidation methods [13]. Ion-exchange resins is efficient method but the pretreatment is required and it is difficult to find suitable resin, which limited their application [14].

As mentioned above, some of above-mentioned methods have been hindered due to either high consumption of reagents or technical obstacles, others require special equipment or further treatment, and others are not well established yet. Thus, there is an urgent need for the development of an alternative treatment process, which is capable of achieving high removal efficiency at low reagent consumption without secondary pollution[16-17]. Electrodialysis (ED) could not only lower the concentrations of the targeted pollutant, but also concentrate the useful ingredients in wastewater for further reuse [18]., It has proven to be an efficient technology for industrial applications, which includes brackish water desalination, boiler feed and process water, demineralization of food products, table salt production, waste treatment, etc. [19-20]. The investment cost and operating cost (energy consumption) of ED are becoming more acceptable in these applications, and the cost of this method can be further reduced because of space saving, chemicals saving and the recovery of useful ingredients [21-23].

More recently, the ED technology has attracted increasing attention in galvanic industries effluent treatment because of its inherent advantages including less reagent consumption, convenient operation, environmental friendly, compact and durable equipment, etc. [18, 24-25]. However, there is only a few works on the application of ED to remove the toxic substances and reuse ionized species in gold mine effluent [26-27]. The satisfactory removal of cyanide and metals is necessary to be achieved in order to meet the discharge limits. On the other hand, Ion-exchange membranes fouling is one of the major problems that affects the ED process, which can reduce the flux, increase membrane resistance and energy consumption, and even destroy the membranes [18]. Although there are some studied about ion-exchange membranes fouling in the treatment of other effluents such as cadmium electroplating wastewater, seawater, polymer-flooding produced wastewater and so on [24, 28-30]. To the best of our knowledge, the Ion-exchange membrane fouling has rarely been investigated in the treatment of gold mine effluent.

In this research, the feasibility of using ED technology to treat both real and simulated gold mine effluents was investigated to remove cyanide and copper, and the operational parameters were optimized to improve the removal efficiency. In addition, the membrane fouling was studied to understand the fouling behavior during the gold mine effluent treatment process.

2 Experimental

2.1 Solutions

The gold mine effluent was provided by Zhaoyuan gold smelter plant (Shandong, China) and the main compositions of effluent are shown in Table 1. The simulated solutions were made up from CuCN (A R Grade, Aladdin) and NaCN (A R Grade, Aladdin) by referring to the mole ratio of cyanide and copper in the effluent. The concentrations of cyanide and copper in simulated solutions are presented in Table 2. Sodium hydroxide solution was added to adjust the pH of the simulated solution to 9.5. In this work, with the copper/or zinc and cyanide mole relationship used in the solutions, copper and cyanide were predominately present under the $[Cu(CN)_4]^{3-}$, $[Cu(CN)_3]^{2-}$and CN^- forms [2, 31-34], zinc and cyanide were mainly present in the forms of $[Zn(CN)_4]^{3-}$ [35].

Table 1 The main compositions in gold mine effluent

Parameter	Concentration (mg/L)
sodium	275
copper	47
zinc	31.2
potassium	6.3
iron	0.59
aluminum	0.06
gold	0.02
cyanide	242
chloride	159

Table 2 The concentrations of total copper and cyanide in simulated solutions

Concentration	Cyanide ($mg.L^{-1}$)	Copper ($mg.L^{-1}$)
C1	121	23.5
C2	242	47
C3	363	70.5

C4	484	94

2.2 Apparatus

The experimental set-up was consisted of three separated circuits, and each one included a centrifugal pump (CXB-30 Wenzhou Erle Pump Co., Ltd.), a rotameter (0-25 L/h) and a 5 L tank (Fig.1.a). The direct current was supplied by a CV/CC regulated power supply (WYL1702, Hangzhou Siling Electrical Instrument Ltd.). The ED stack was composed of two electrodes made of a titanium plate coated with ruthenium, five anion exchange membranes (AEM) and six cation exchange membranes (CEM). Ionic species transportation in the ED stack was shown in Fig.1.b

Ion-exchange membranes can be considered as ion-exchange resins in film form. There are two different types of ion-exchange membranes: (1) CEMs which contain negatively charged groups (typically $–SO_3^-$, $–COO^-$, $–PO_3^{2-}$, $–PO_3H^-$ and $C_6H_4O^-$) fixed to the polymer matrix, and (2) AEMs which contain positively charged groups (typically $–NH_3^+$, $–NRH_2^+$, $–NR_2H^+$ and $–NR_3^+$) fixed to a polymer matrix. In a CEM the fixed anions are in electrical equilibrium with mobile cations in the interstices of the polymer. The mobile cations in solution are referred to as counter-ions. The mobile anions are called co-ions and are more or less completely excluded from the membrane matrix because of their electrical charge which is identical to that of the fixed ions. Due to the exclusion of the co-ions, a CEM is preferentially permeable to cations. AEMs carry positive charges fixed on the polymer matrix. They therefore exclude cations and are preferentially permeable to anions [19, 36].

The homogeneous anion exchange membranes and the cation exchange membranes were purchased from Qianqiu Environmental Protection & Water Treatment Corporation (China) and their main characteristics are listed in Table 3. The effective areas of membrane and electrode were both 88cm^2. The whole experimental set-up was fixed by brackets in stainless steel, which was purchased from Shandong Tianwei Membrane Technology Co., Ltd (Shandong, China) [28].

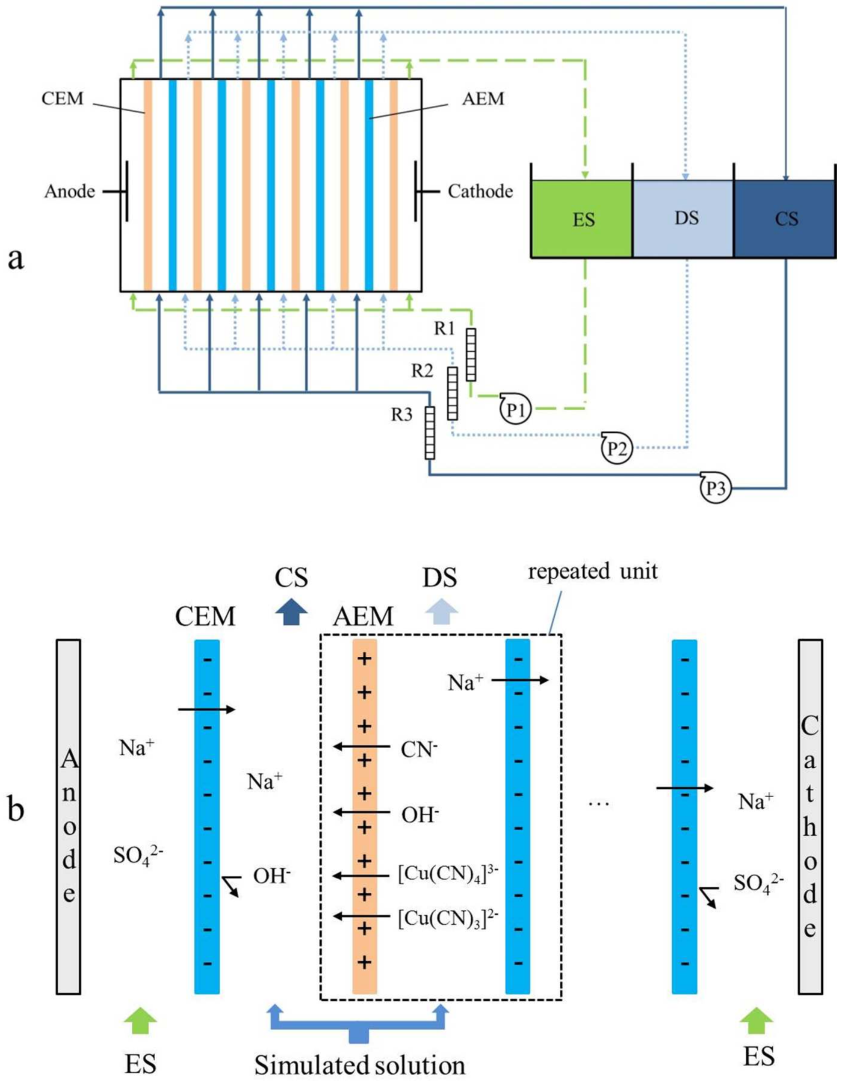

Fig. 1 Flow diagram of the experimental setup (a) and ionic species transport in the ED stack with the simulated solution (b) (AEM, anion exchange membrane; CEM, cation exchange membrane; DS, diluted solution; CS, concentrated solution; ES, electrode solution; P1—pump for ES, P2—pump for DS, P3—pump for CS; R1—rotameter for ES, R2—rotameter for DS, R3—rotameter for CS.)

Table 3 The main characteristics of the ion-exchange membranes

Membrane	Thickness (mm)	Exchange capacity (meqg^{-1})	Area resistance (Ω cm^2)	Selectivity (%)	Heat stability (≤℃)
AEM	0.16-0.23	1.8-2.0	5-9	90-95	40
CEM	0.16-0.23	1.8-2.2	2-5	95-99	40

2.3 Experimental procedure

Laboratory-scale tests were mainly performed to investigate the technological parameters of the ED process. 5% Sodium sulfate solutions was added to the electrode compartment, the diluted compartment and concentrated compartment were fed with effluents. Each tank contained 2 L solution and all the solutions had an alkaline pH in order to avoid HCN formation. The experiments were performed under room temperature. All experiments were conducted in potentiostatic mode.

The effects of applied voltage, initial concentration and flux rate on the removal rate, current efficiency and energy consumption were investigated with simulated solution. After the treatment of the simulated solution, the real gold mine effluent was treated by ED with the optimized operational parameters. The total time of each experimental run was 100 or 140 min. During each run, current was recorded and the concentrations of copper and cyanide were measured in the diluted sample.

The measurement of pH was made with a pH-meter (DELTA 320, Mettle–Toledo international incorporated company) using a combined glass electrode. The contents of copper and zinc in the solution were determined through the AA320N atomic absorption spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.). The content of cyanide (total cyanide) was analyzed by distillation and the content of free cyanide (CN^-) was analyzed by titration with silver nitrate [7]. It is worth mentioning that three replicates of each experiment were performed and then their average value was reported in order to minimize the experimental errors. The ion removal rate, current efficiency and energy consumption were calculated accordingly.

2.4 Data analysis

The ion removal rate (η) is calculated as equation (1):

$$\eta = \frac{C_0 - C_t}{C_0} \qquad (1)$$

where η is the ion removal rate (%), C_0 and C_t are the concentration of cyanide (or copper) in dilute compartment at time 0 and t(s) (mol/L), respectively.

The current efficiency (ce %) is given by equation (2):

$$ce = \frac{(C_0 - C_t)ZVF}{NIt} \qquad (2)$$

where C_t and C_0 are the concentration of free cyanide (CN^-) in the diluted compartment at time t (s) and 0 (mol/L), respectively. Z is the ion's absolute valence (Z=1), and V is the circulated volume of solution in the salt cycle (L). I is the current (A), F is the Faraday constant (96,485 A s/mol), and N is the number of stack triplets (N=5), and t is the operation time (s). Since the volume change in each compartment is negligible during the whole operation, V was fixed at 2 L.

The energy consumption (E, kwh/m^3) (not including the energy consumption used in driving solution circulation in the different compartments) can be defined by equation (3):

$$E = \int_0^t \frac{UI}{V}\,dt \qquad (3)$$

where U is the potential (V), I is the current (A), V is the circulated volume of in the salt cycle (0.002 m^3), and t is the operation time (h).

2.5 Membrane fouling analysis

According to the methods in the literature [35], fouling of ion-exchange membrane could be characterized by measuring the membrane resistance and static contact angle, using scanning electron microscopy and surface elemental analysis. To measure the electrical resistance of ion-exchange membranes, a six compartment cell with a four-electrode arrangement was used. The measuring set-up was made from plexiglass and consisted of six separate compartments with a solution volume of 2 dm^3 [37]. The measurement of static contact angle was performed by the sessile drop method (DSA100, Germany KRUSS) at 298.15 K with a relative humidity of (30 ± 2)%. The SEM (scanning electron microscopy) images and elemental analyses were performed with a scanning electron microscopy (S-4800, Hitachi High-Technologies Corporation, Japan) and an X-ray energy dispersive spectrometer (EDX) (EMAX 7593H, Horiba, Japan), respectively. FTIR (Tensor 27, BRUKER OPTIK GmbH) was employed and the spectra were recorded in the range of 400-4000 cm^{-1}.

3 Results and discussion

3.1 Current density of ED process on potentiostatic operation mode

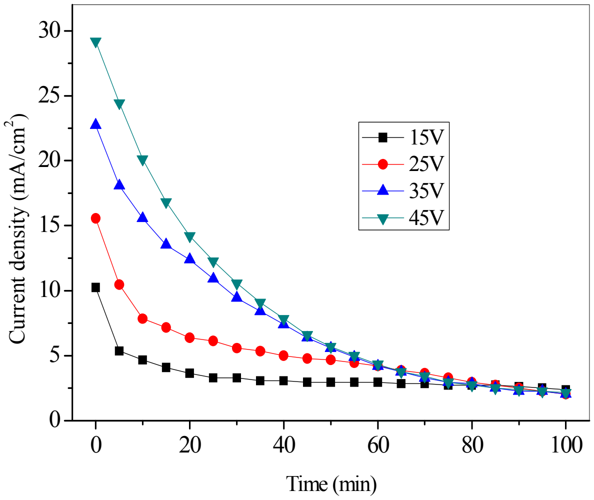

Fig. 2 The current density across the stack with various voltages (Initial concentration of C2, flux rate of 4.17 mL/s)

Fig. 2 showed the influence of applied voltage on current density over time. For certain solution, the current density across the membrane stack was proportional to voltage. It is because that the ratio of the irreversible (the voltage drop or energy used to overcome the electrical resistance) to reversible contribution to the electric potential became larger with increasing current density [28]. During the initial 70 min operation of ED, current density decreased rapidly over time, which was closely related to the conductivity of the stack with the constant voltage (including the conductivity of the membranes and the DS, CS and ES). The decrease of DS concentration resulted in lower conductivity and higher electrical resistance of the stack, thus the stack current density was decreased rapidly according to Ohm's law [38]. Then, the current density kept relatively unchanged in the remaining period of ED operation (70-100 min) because the equilibrium of ion migration determined the constant of total conductivity of DS and CS.

3.2 The effects of the ED operation conditions in the circulation experiment

3.2.1 Effect of applied voltage

Applied voltage is one of the most important parameters for the removal efficiency in potentiostatic mode [36]. Fig. 3 depicts the removal rates of cyanide and copper as a function of operation time under different applied voltage. As expected, the removal rate was improved with the increase of voltage due to higher driving force (direct current, DC) accompanied with higher voltage. Under a higher voltage, ions were faster transferred from the diluted compartment to the concentrated compartment through the ion-exchange membrane. When the applied voltage was 45 V, the removal of cyanide and copper were 99.83% and 99.41%, respectively. After 100 min, both of the concentrations of copper (0.28 mg/L) and cyanide (0.41 mg/L) in DS were below 0.5 mg/L, which can meet the grade one of “the national integrated wastewater discharge standards” GB8978-1996 [5].

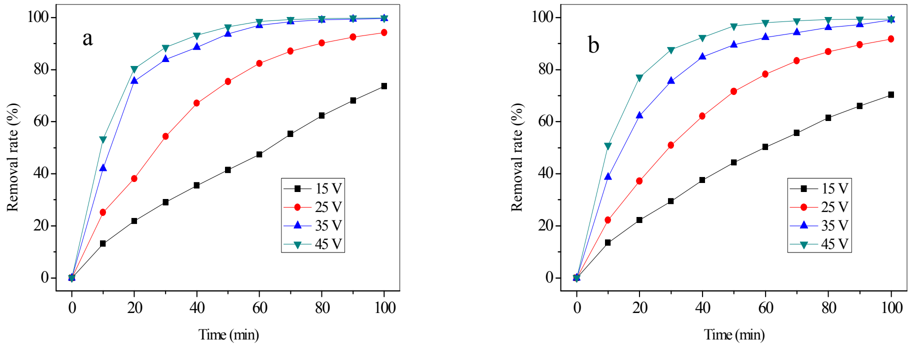

Fig. 3 The removal rates of cyanide (a) and copper (b) with various applied voltages (Initial concentration of C2, flux rate of 4.17 mL/s)

Fig. 4 shows that the current efficiency of CN^- increased sharply from 14.31 % at 15 V to 21.37 % at 25 V, and then relatively plateaued after 35 V at a level of around 22 %. According to the Eq. (2), this phenomenon could be attributed to the variation of removal rate and current with time. In terms of the energy consumption, it increased linearly from 3.72 $kwhm^{-3}$ to 28.47 $kwhm^{-3}$ with the voltage increasing from 15 V to 45 V. This trend was mainly attributed to that a greater part of the total electrical energy was consumed to overcome the electrical resistance as the voltage increased [23]. As a result, in the view of removal rate, energy consumption and current efficiency, 25 V was adopted as the optimal applied voltage for ED process in simulated gold mine effluent treatment.

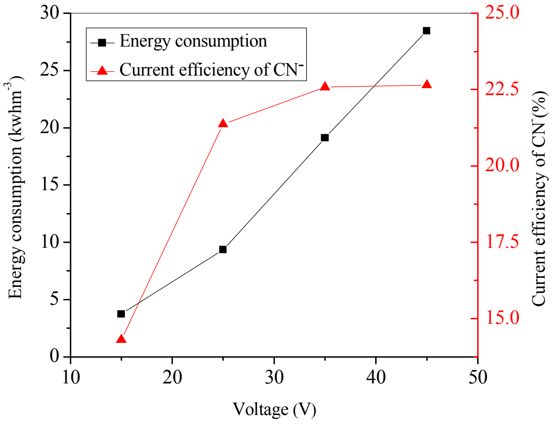

Fig. 4 Variation of the energy consumption and current efficiency of CN^- with various applied voltages (Initial concentration of C2, flux rate of 4.17 mL/s)

3.2.2 Effect of initial concentration

The effect of the initial concentration of effluents is of great importance in order to assess the optimum domain of applicability of the ED process investigated [39]. In order to study the influence of initial concentrations (cyanide and copper), four effluents with different concentrations were used in this experiment and their detailed compositions are presented in Table 2. Fig. 5 shows that the removal rates of cyanide and copper increased with more operational time, and a higher ion removal rate could be achieved with a lower initial concentration. Fig.6 shows that higher concentrated solution led to higher energy consumption of ED process, which could be attributed to that the higher concentrated solution led to higher electrical conductivity of solution and lower electrical resistance. According to Ohm's Law [38], operating current would be higher at a constant voltage, which would result in higher energy consumption in accordance with Eq. (3). In terms of the current efficiency, increasing initial concentration increases current efficiency of CN^- up to a maximum value of 21.37 % at initial concentration of C2 (concentration of copper and cyanide were 47 mg/L and

242 mg/L) and then decreases it to about 19.86 % for the more concentrated effluent. This variation of current efficiency with initial concentration could be also explained by the decrease in the electrical resistance of the solutions when increasing concentration [39]. Hence, data in Fig.6 suggested that the enhancement in the migration rate was greater than the increase in current intensity on the concentration range C1 to C2, and therefore current efficiency increased in accordance with Eq. (2), while the situation was reversed for the concentrations higher than C2 investigated here and thus resulted in lowering of current efficiency values.

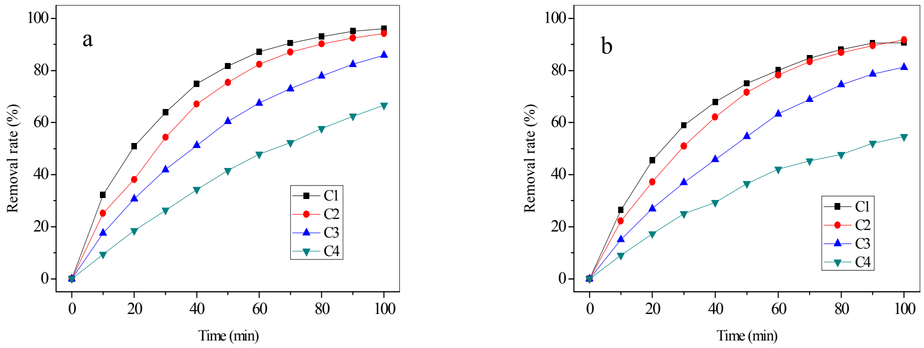

Fig. 5 The removal rate of cyanide (a) and copper (b) with various initial concentrations (Applied voltage of 25 V, flux rate of 4.17 mL/s)

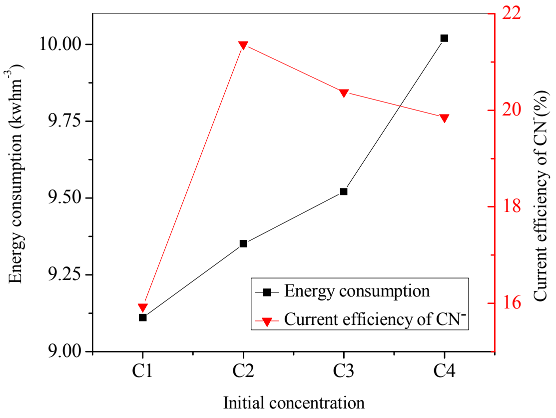

Fig. 6 Variation of the energy consumption and current efficiency of CN^- with various initial concentrations (Applied voltage of 25 V, flux rate of 4.17 mL/s)

3.2.3 Effect of flux rate

Fig. 7 shows that the removal rate of cyanide increased from 66.12 % to 94.21 % after 100 minutes' operation. With the initial increase of the operational flux, the removal rate of copper increased as well, with the highest removal rate obtained at 4.17 mL/s. This could be ascribed to that the increase of flow rate could shorten the cycle time and increase the cycle number. The turbulence in compartments would be strengthened so that the migration rate of $[Cu(CN)_4]^{3-}$, $[Cu(CN)_3]^{2-}$and CN^- would also be increased. As a result the removal rate of cyanide and copper was increased with the initial rise of the flux rate. Further increase the flux rate of higher than 4.17 mL/s did not significantly improve the removal rate of cyanide and even led to reduced removal rate of copper. This phenomenon could be attributed to that over-high flow rate would limit the retention time of solution in DC, and some ions in solution were taken out of ED stack without penetrating through the membrane. Therefore, the removal rate of copper or cyanide wasn't increasing sustainably as flow rate increased. Moreover, the increase of flow rate would raise the hydraulic pressure between membranes. It might damage membranes and shorten the membrane life [39]. At the same time, the energy consumption of ED process would also be increased due to the energy requirement of higher flux. As a result, in the view of ions removal rate, the best flux rate was 4.17 mL/s (Average flow velocity at the membrane water interphase 1.32 cm/s) for the ED system.

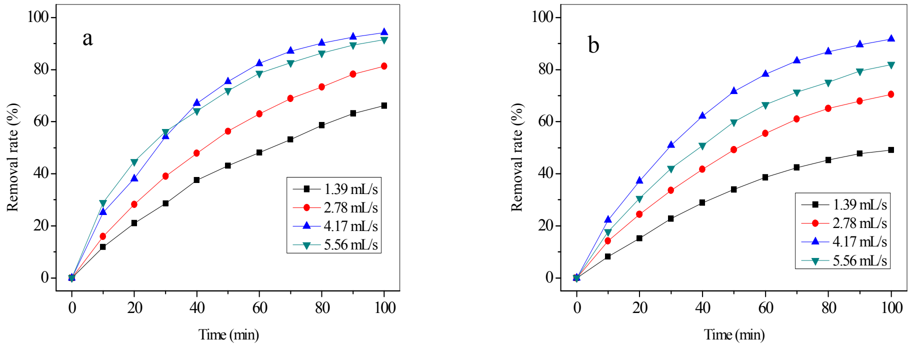

Fig. 7 The removal rate of cyanide (a) and copper (b) with various flux rates (Applied voltage of 25 V, initial concentration of C2)

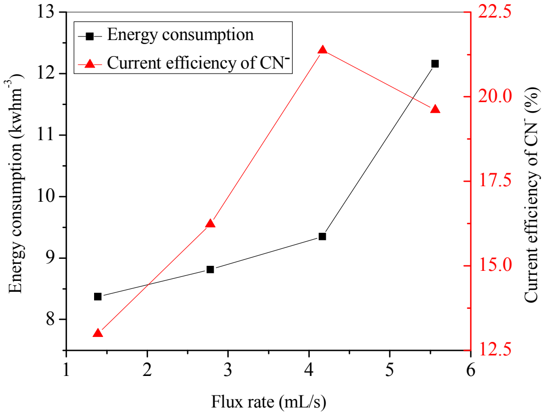

Fig. 8 Variation of the energy consumption and current efficiency of CN^- with various flux rates (Applied voltage of 25 V, initial concentration of C2)

As shows in Fig. 8, the energy consumption increased slowly with the flux rate increasing from 1.39 mL/s to 4.17 mL/s, while it increased sharply with the flux rate increasing from 4.17 mL/s to 5.56 mL/s. This variation of energy consumption was closely related to the conductivity of the solutions in compartments with a constant voltage. It could be explained by the increase of current intensity as the flux rate increased according to Eq. (3). After all, the increased electrical energy was consumed as the current intensity increased. The current efficiency of CN^- with various flux rates was also calculated, which is also presented in Fig. 8. It increased nearly linearly from 12.99 % at 1.39 mL/s to 21.37 % at 4.17 mL/s but decreased from 21.37 % at 4.17 mL/s to 19.61 % at 5.56 mL/s. As mentioned above, the ion migration rate was closely related to the flux rate. The variation of current efficiency can be ascribed to that the migration rate of CN^- increased with the initial rise of the flux rate but decreased with the continuing increase of flow rate. On the other hand, according to Eq. (1) and Eq. (2), the increase of removal rate (η) of CN^- could lead to an increase of current efficiency of CN^- with the constant value of C_0, Z, N, V, F and t. Therefore, the variation trend of current efficiency of CN^- with various flux rates was similar to that of removal rate. For our simulated solution, the optimized operational parameters were voltage of 25 V, initial concentration of C2 (concentration of copper and cyanide were 47 mg/L and 242 mg/L), and flux rate of 4.17 mL/s with the removal rate of

94.21 % (cyanide) and 91.72 % (copper).

3.3 The removal of cyanide and copper from gold mine effluent

After the optimization of the ED parameters with simulated solution, the real gold mine effluent was also treated by applying the optimized parameters (voltage of 25 V and flux rate of 4.17 mL/s). In addition to copper, zinc is also a toxic heavy metal and presented in the gold mine effluent, thus the content of zinc in the samples was determined and the removal rate was calculated. The results were represented in Table 4. On the other hand, in order to lower the concentrations of copper and cyanide, the voltage of 45 V was applied in the ED process, and the results were represented in Table 5. Due to the higher current flowing through the ED stack, the energy consumption values obtained from the experiments performed with the gold mine effluent were higher than that of simulated solution. This could be explained by the presence of salts, and especially sodium cyanide, which was used excessively in the process of gold extraction [18].

It could also be seen from the table 4 and 5 that the removal rate of copper was close to that of zinc, whereas the removal rate of cyanide was higher than that of copper or zinc. The reason was that the $[Cu(CN)_4]^{3-}$, $[Cu(CN)_3]^{2-}$ or $[Zn(CN)_4]^{3-}$ was more voluminous than CN^-, which indicated that it was more difficult to transport larger ions through the anion exchange membrane [24]. When the real gold mine effluent was tested, current efficiency of CN^- decreased, and longer time was required for the same removal rates of ion. In terms of cyanide, with simulated solution, the removal rate of 93.0 % was achieved after 80 min with energy consumption of 9.35 $kwhm^{-3}$, whereas with the gold mine effluent, the removal rate of 93.0 % was achieved after 140 min with energy consumption of 17.88 $kwhm^{-3}$. The reason should be associated to the competition between the much more anions which presented in real gold mine effluent ($[Cu(CN)_4]^{3-}$, $[Cu(CN)_3]^{2-}$, $[Zn(CN)_4]^{3-}$, CN^-, Cl^-, etc.) [25] Still, the concentrations of copper (0.44 mg/L), cyanide (0.48 mg/L) and zinc (0.34 mg/L) in treated effluent were all below the regulatory limits (copper, cyanide ＜0.5 mg/L, zinc <2.0 mg/L) [5]. The highest removal rates were 99.80 %, 99.07 % and 98.90 %, respectively. Another point should be noted that the removal rates of cyanide and copper in this work were higher than that in similar research (cyanide 93.3 %, copper 93.9 %) [8, 27]. Thus, the results could verify the feasibility of the removal copper and cyanide in gold mine effluent by using the ED technique. The removal rate of cyanide and metals has been improved after conditions optimization.

Table 4 Performance of ED in real gold mine effluent (25V)

Time (min)	Current (A)	Removal rate of cyanide (%)	Removal rate of copper (%)	Removal rate of zinc (%)	Current efficiency of CN^- (%)	Energy consumption ($kwhm^{-3}$)
0	1.73	0	0	0	0	0
20	1.04	32.14	22.00	19.45	6.50	5.77
40	0.74	53.94	38.54	36.37	7.67	9.48
60	0.52	71.49	55.82	57.28	9.64	12.10
80	0.41	82.35	68.18	67.33	10.56	14.04
100	0.34	88.44	80.34	78.51	10.94	15.60
120	0.27	91.02	85.67	86.18	11.82	16.88
140	0.21	93.22	91.00	91.50	13.34	17.88

Table 5

Performance of ED in real gold mine effluent (45V)

Time (min)	Current (A)	Removal rate of cyanide (%)	Removal rate of copper (%)	Removal rate of zinc (%)	Current efficiency of CN^- (%)	Energy consumption ($kwhm^{-3}$)
0	2.76	0	0	0	0	0
20	1.37	55.12	42.55	43.80	8.46	15.49
40	0.83	73.96	65.91	68.26	9.37	23.74
60	0.55	87.05	79.53	79.50	11.10	28.91
80	0.36	94.16	89.63	92.11	13.75	32.33
100	0.24	96.73	95.04	94.07	16.95	34.58
120	0.21	98.94	97.51	96.95	16.52	36.26
140	0.20	99.80	99.07	98.90	14.99	37.80

3.4 Ion-exchange membranes fouling analysis

It is well known in ED that the precipitation on ion-exchange membranes can be a consequence of operating above the limiting current density [24]. In this case water could be dissociated in H^+ and OH^- ions, which might cause changes in the pH of the boundary layer formed in the membrane/solution interface, leading to a local change in the characteristics of the ionic species presented in the solution. Insoluble compounds can be formed and then precipitated on the ion-exchange membrane [25]. In order to understand the membrane fouling behavior during the gold mine effluent ED treatment process, experiments were carried out with following parameters: for test 1, with the voltage of 25 V and the flux rate of 4.17 mL/s, the sodium hydroxide was added to adjust the pH of DS to alkaline range 9-10 during ED process. For test 2, with the voltage of 25 V and the flux rate of 4.17 mL/s, and without pH adjustment, pH of DS in the late process changed from 9.89 to 7.02, and even 3.57.

3.4.1 Analysis by FTIR

The FTIR spectrum of the original and used membranes is presented in Fig. 9. Compared with the FTIR spectrum of original membrane (spectrum a-1), the absorption band at 2174 cm^{-1} (spectrum a-2) and 2175 cm^{-1} (spectrum a-3) could be attributed to the presence of CuCN, the absorption band at 2099 cm^{-1} (spectrum a-2) and 2098 cm^{-1} (spectrum a-3) could be attributed to the presence of $[Cu(CN)_3]^{2-}$ [2, 40-41]. The two peaks in spectrum a-3 are much stronger. Besides, the absorption bands at 3571 cm^{-1} and 686 cm^{-1} arise from stretching and bending vibrations of bulk OH groups of $Cu(OH)_2$, strongly suggesting the presence of $Cu(OH)_2$ on the surface of AEM a-3 [42-43]. Metal–oxygen characteristic bands are typically observed in an interval from 600 cm^{-1} to 400 cm^{-1}. A band at 445 cm^{-1} and a shoulder at around 500 cm^{-1} can be due to Zn-O and Zn-OH lattice vibrations[44-47]. In addition, the absorption band at 1617 cm^{-1} (HOH bending) and the broad bands around 3400 cm^{-1} (O-H stretching) are assigned to both OH group of the precipitations and water molecules absorbed from air [41, 43, 48].

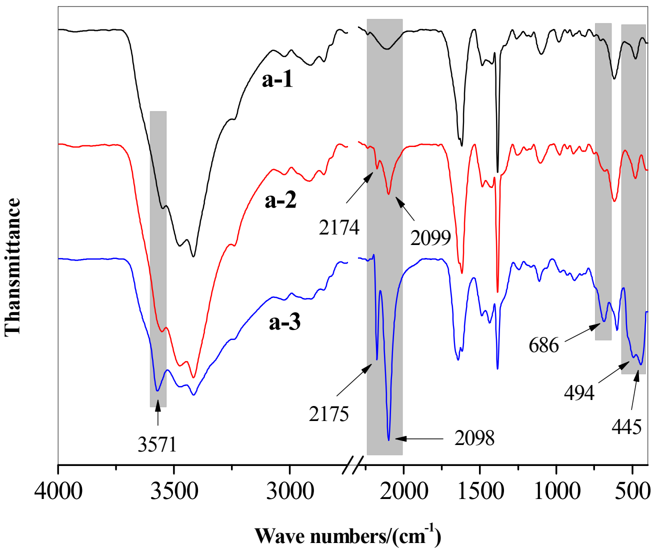

Fig. 9 the FTIR spectra of the original AEM (a-1), the used AEM (a-2) in test 1, the used AEM (a-3) in test 2

3.4.2 Analysis by SEM-EDX

In order to further understand fouling compositions and surface morphologies of membranes, samples including original membranes, and used membranes in two tests were analyzed by SEM-EDX. The SEM images are shown in Fig.9. It could be clearly seen that the surface morphologies of AEMs and CEMs were distinctly different. Compared to AEMs, the surfaces of CEMs were smooth and no obvious fouling was found (Fig. 9 (b)). However, the surfaces of AEMs were rough with crevices, and membrane fouling was more likely to happen as shown in Fig.9 (a). In terms of AEMs, the precipitation was observed clearly on the surface of a-3 (test 2), which was much more than that on the surface of a-2 (test 2).

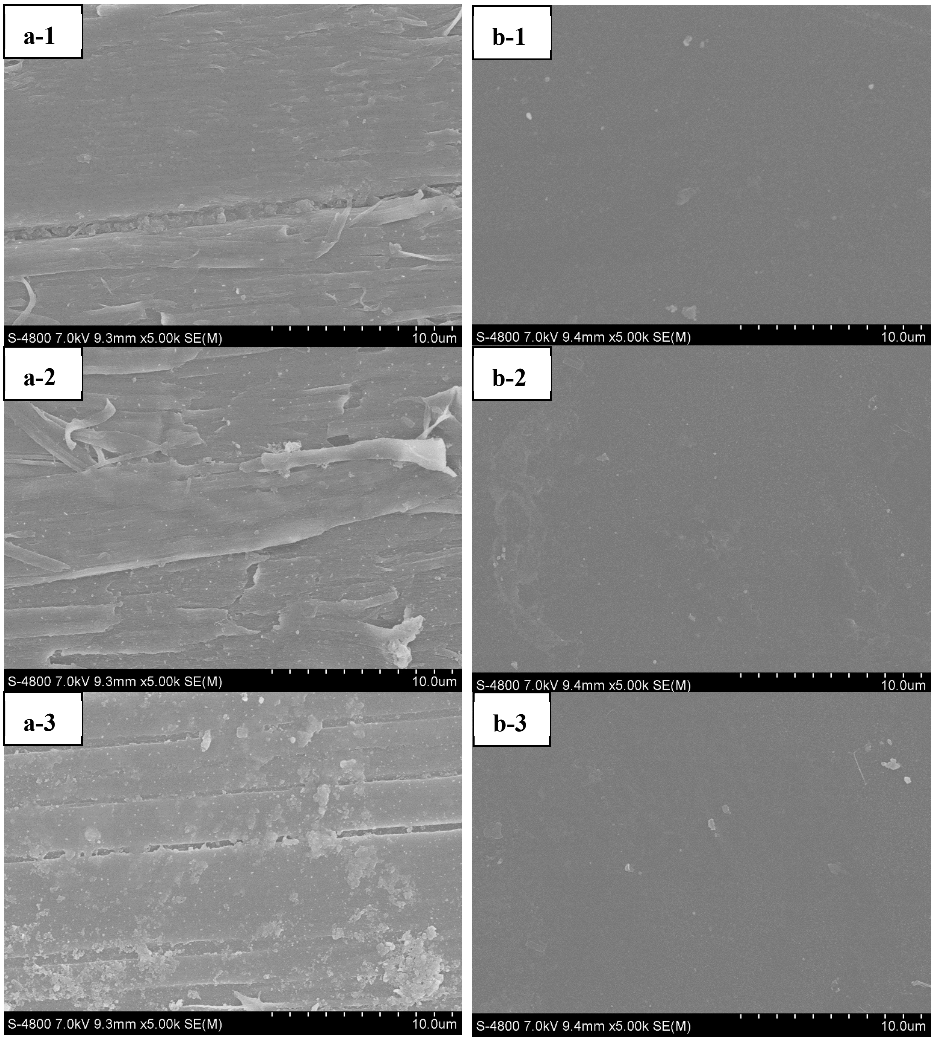

Fig. 10 SEM images (original magnification, 5000*) of the original AEM (a-1), the used AEM (a-2) in test 1, the used AEM (a-3) in test 2; the original CEM (b-1), and the used CEM (b-2) in test 1, the used CEM (b-3) in test 2.

The results of elemental analysis are presented in table 6. It was observed that the surface of the original AEM a-1 is consisted of two elements: carbon (C) and oxygen (O). Compared with a-1, the used AEM a-2 has a decrease in C contents but there are 2.3 % of Cu and 3.01 % of N in its surface indicating precipitation occurred. This phenomenon is in agreement with the present of CuCN and $[Cu(CN)_3]^{2-}$, which has been proven via FTIR spectrum. On the other hand, the used AEM a-2 has even more decrease in C content and a large amount of Cu, the contents of O and N also increase on the surface of a-3. This can be ascribed to the increase of CuCN and $[Cu(CN)_3]^{2-}$ and the present of $Cu(OH)_2$, which has been mentioned in the results of molecular analysis (FTIR). In addition to the increase of O, N and Cu, the increase of Zn and the present of Fe, Na, and Cl also resulted in the decrease of C percent.

According to literature 13, 31, and 49, the copper cyanide complex might be destructed and subsequent formed on the electrode and membranes surface of CuOOH (Eq. 4-1), which could change into $Cu(OH)_2$ and/or CuO species (Eq. 4-2).

$$[Cu(CN)_n]^{1-n} + 2H_2O \Leftrightarrow CuOOH + 3H^+ + nCN^- + 2e^- \qquad (4\text{-}1)$$

$$CuOOH + e^- \leftrightarrows Cu(OH)_2 + CuO \qquad (4\text{-}2)$$

Combined with the results of molecular analysis (FTIR), the specie presented on membrane (a-3) surface was $Cu(OH)_2$. In addition to copper and cyanide, zinc and cyanide were mainly present in the forms of $[Zn(CN)_4]^{3-}$ in the gold mine effluent as mentioned above. There is equilibrium between compounds with cyanide and hydroxyl as it can be seen in the reaction below (Eq. 5) [50]:

$$[Zn(CN)_4]^{2-} + 4OH^- \Leftrightarrow [Zn(OH)_4]^{2-} + 4CN^- \qquad (5)$$

This demonstrated that Zn could present in the forms of zinc cyanide or zinc hydroxide on the surface of membrane. Combined with the existence of Zn-O and Zn-OH characteristic bands in FTIR spectrum, It was obvious that $Zn(OH)_2$ exist in the precipitation (a-3).

Table 6

The elemental analysis (expressed as atomic percentage %) of AEMs

Membrane	Atomic percentage (%)							
	C	O	N	Cu	Zn	Fe	Na	Cl
a-1	90.32	9.68						
a-2	83.88	9.98	3.01	2.34	0.79			
a-3	49.63	15.59	13.82	15.47	3.46	1.38	0.36	0.29

3.4.3 Analysis by membrane resistance and static contact angle

The membrane resistance and static contact angle were also measured before and after the experiments, and the results are shown in Table 7. Compared to Original membranes (a-1 and b-1), no significant increase of membrane resistance was observed from the used CEMs (b-2 and b-3) and AEM a-2, whereas the membrane resistance of a-3 increased obviously. This phenomenon suggested that there was more fouling on the surface of a-3 [28-29]. On the other hand, in comparison to a-1, the significant decrease of static contact angle only observed from a-3, the static contact angle of a-2 decreased slightly. The result was in agreement with that of membrane resistance and demonstrated that the ion-exchange membranes fouling of AEM can be decreased significantly via pH adjustment, which has been proven in the results of FTIR and SEM-EDX.

Table 7

Membrane resistance and contact angle of membranes in experiment

Project	Original		Test 1		Test 2	
	AEM (a-1)	CEM (b-1)	AEM (a-2)	CEM (b-2)	AEM (a-3)	CEM (b-3)
Membrane resistance (Ωcm^{-2})	5.78	3.67	5.82	3.73	6.12	3.77
Static Contact angle (◦)	64.05-66.56	60.90-62.28	61.21-63.17	58.12-60.87	33.04-41.35	56.91-64.13

4. Feasibility analysis

ED has proven to be an efficient technology for many industrial applications. In this research, the removal rates of cyanide (99.80 %) and copper (99.07 %) has been improved and were higher than that in similar research [8, 27]. The concentration of copper (0.28 mg/L) and cyanide (0.41 mg/L) in the treated effluent were below the regulatory discharge limits (＜0.5 mg/L). In addition, the ion-exchange membrane fouling can be controlled to a minimum with pH adjustment. Generally, the capital and operating costs of an ED plant depend strongly on the quality of feed and product water, the total membrane area, the plant capacity, the site characteristics, the prices for membranes, and other plant components and their useful life under operating conditions so it is difficult to analyse and to compare the costs of electrodialysis and other methods [51-52]. However, many industrial applications and studies have proven the economic feasibility of ED in many cases [19-21]. The ion-exchange membranes, electrodes and spacers are easy to get and the cost of them is becoming more inexpensive along with the development of related technologies[19, 22-23]. Therefore, ED is worth to be studied and used for the treatment of gold mine effluent. At least it can be used as a complementary method in some cases.

This method has advantages such as little chemicals consumptions or no sludge problems. However, the experiment was carried out without considering the further treatment of CS. In addition to the application mentioned above for the treatment of gold mine effluent, the operation cost of this method could be further reduced by reusing the useful ingredients in CS. Thus, it was indispensable for further study to recover the cyanide and metals in concentrated gold mine effluent.

5 Conclusions

In the present work, ED was proposed for the treatment of simulated and real gold mine effluents. The effects of applied voltage, initial concentration, and flux rate on ED performance were investigated. The results showed that increasing flow rate and initial concentration increased current efficiency to a maximum value and further increasing decreased it. The increases of removal rate and current efficiency were fast firstly and then slow with applied voltage increasing from 15 to 45 V. It was found out that the removal rates of cyanide and copper has been improved after optimization of the conditions. Then, the lowest concentration of copper and cyanide in the treated effluent were below the regulatory discharge limits. Therefore, the results could verify the feasibility of the removal copper and cyanide in gold mine effluent by using the ED technique. In addition, ion-exchange membrane fouling was studied and the results showed The results showed the presences of CuCN, $[Cu(CN)_3]^{2-}$, $Cu(OH)_2$, and $Zn(OH)_2$ in precipitations, and the ion-exchange membrane fouling of AEM can be decreased significantly via pH adjustment. This research provides a new insight into the removal of copper and cyanide from gold mine effluent.

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References

1 X. Dai, A. Simons, P. Breuer. A review of copper cyanide recovery technologies for the

cyanidation of copper containing gold ores, Miner. Eng. 25 (2012) 1-13.

2 G.C. Lukey, J.S.J. van Deventer, S.T. Huntington, R.L. Chowdhury, D.C. Shallcross. Raman study on the speciation of copper cyanide complexes in highly saline solutions, Hydrometallurgy. 53 (1999) 233-244.

3 D. Donato, O. Nichols, H. Possingham, M. Moore, P. Ricci, B. Noller, A critical review of the effects of gold cyanide-bearing tailings solutions on wildlife, Environ. Int. 33 (2007) 974-984.

4 R. R. Dash, A. Gaur, C. Balomajumder, Cyanide in industrial wastewaters and its removal: A review on biotreatment, J. Hazard. Mater. 163 (2009) 1-11.

5 National integrated wastewater discharge standards GB 8978-1996, Beijing: China Environmental Science Press, 1996 (In Chinese).

6 O. Alonso-González, F. Nava-Alonso, A. Uribe-Salas Copper removal from cyanide solutions by acidification, Miner. Eng. 22 (2009) 324-329.

7 Y.B. Patil, K.M. Paknikar, Development of a process for biodetoxification of metal cyanides from wastewater, Process Biochem. 35 (2000) 1139–1151.

8 F. Xie, D. Dreisinger, Recovery of copper cyanide from waste cyanide solution by LIX 7950, Miner. Eng. 22 (2009) 190-195.

9 D. Pak, W. Chang, Oxidation of aqueous cyanide solution using hydrogen peroxide in the presence of heterogeneous catalyst, Environ. Technol. 18 (1997) 557-561.

10 F. Barriga-Ordonez, F. Nava-Alonso, A. Uribe-Salas, Cyanide oxidation by ozone in a steady-state flow bubble column, Miner. Eng. 19 (2006) 117-122.

11 W. Zhang, W. Liu, Y. Lv, B. Li, W. Ying, Enhanced carbon adsorption treatment for removing cyanide from coking plant effluent, J. Hazard. Mater. 184 (2010) 135-140.

12 F. Gurbuz, F. Ciftci, A. Akcil, Biodegradation of cyanide containing effluents by Scenedesmus obliquus, J. Hazard. Mater. 162 (2009) 74-79.

13 S.C. Cheng, M. Gattrell, T. Guena, B. MacDougall, The electrochemical oxidation of alkaline copper cyanide solutions, Electrochim. Acta. 47 (2002) 3245-3256.

14 D. Bachiller, M. Torre, M. Rendueles, M. Diaz, Cyanide recovery by ion exchange from gold ore waste effluents containing copper, Miner. Eng. 17 (2004) 767-774.

15 N. Kuyucak, A. Akcil, Cyanide and removal options from effluents in gold mining and

metallurgical processes, Miner. Eng. 50-51 (2013) 13-29.

16 J. Hou, G. Dong, B. Luu, R.G. Sengpiel, Y. Ye, M. Wessling, V. Chen, Hybrid membrane with TiO_2 based bio-catalytic nanoparticle suspension system for the degradation of bisphenol-A, Bioresour. Technol. 169 (2014) 475-483.

17 J. Hou, G. Dong, Y. Ye, V. Chen, Enzymatic degradation of bisphenol-A with immobilized laccase on TiO2 sol–gel coated PVDF membrane, J. Membr. Sci. 469 (2014) 19-30.

18 A. Güvenc, B. Karabacakoglu. Use of electrodialysis to remove silver ions from model solutions and wastewater, Desalination 172 (2005) 7-17.

19 H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications. Desalination 264 (2010) 268-288.

20 D. C. Buzzi, L. S. Viegas, M. A. S. Rodrigues, A. M. Bernardes, J. A. S. Tenório, Water recovery from acid mine drainage by electrodialysis, Miner. Eng. 40 (2013) 82-89.

21 R. K. McGovern, A. M. Weiner, L. Sun, C. G. Chambers, S. M. Zubair, J. H. Lienhard V, On the cost of electrodialysis for the desalination of high salinity feeds, Appl. Energ. 136 (2014) 649-661.

22 A.H. Galama, M. Saakes, H. Bruning, H. H. M. Rijnaarts, J. W. Post, Seawater predesalination with electrodialysis, Desalination 342 (2014) 61-69.

23 Y. Wei, Y. Wang, X. Zhang, T. Xu, Comparative study on the treatment of simulated brominated butyl rubber effluent by using bipolar membrane electrodialysis (BMED) and conventional electrodialysis (ED), Sep. Purif. Technol. 110 (2013) 164-169.

24 L. Marder, G. O. Sulzbach, A. M. Bernardes, J. Z. Ferreira, Removal of Cadmium and Cyanide from Aqueous Solutions through Electrodialysis, J. Braz. Chem. Soc. 14 (2003) 610-615.

25 L. Marder, A. M. Bernardes, J. Z. Ferreira, Cadmium electroplating wastewater treatment using a laboratory-scale electrodialysis system, Sep. Purif. Technol. 37 (2004) 247-255.

26 C.A. Young, T.S. Jordan, Cyanide remediation: current and past technologies, in: Proceedings of the 10th Annual Conference on Hazardous Waste Res, 1995, pp. 104–129.

27 X. J. Luo, K. Luo, Application of liquit membrane technology in treating cyanide leach solution of gold ore, Miner. Eng. 2 (2004) 58-62. (In Chinese)

28 Y. Yang, X. Gao, A. Fan, L. Fu, C. Gao, An innovative beneficial reuse of seawater

concentrate using bipolar membrane electrodialysis, J. Membr. Sci. 449 (2014) 119-126.

29 V. Lindstrand, G. Sundström, A. S. Jönsson, Fouling of electrodialysis membranes by organic substances, Desalination 128 (2000) 91-102.

30 X. Zuo, L. Wang, J. He, Z. Li, S. Yu. SEM-EDX studies of SiO_2/PVDF membranes fouling in electrodialysis of polymer-flooding produced wastewater: Diatomite, APAM and crude oil, Desalination 347 (2014) 43-51.

31 J. Lu, D.B. Dreisinger, W.C. Cooper, Thermodynamics of the aqueous copper–cyanide system, Hydrometallurgy. 66 (2002) 23-36.

32 G.C. Lukey, J.S.J. van Deventer, R.L. Chowdhury, D.C. Shallcross, The effect of salinity on the capacity and selectivity of ion exchange resins for gold cyanide, Miner. Eng. 12 (1999) 769-785.

33 O. Alonso-González, F. Nava-Alonso, A. Uribe-Salas, D. Dreisinger, Use of quaternary ammonium salts to remove copper–cyanide complexes, Miner. Eng. 23 (2010) 765-770.

34 A.J.B. Dutra, G.P. Rocha, F.R. Pombo, Copper recovery and cyanide oxidation by electrowinning from a spent copper-cyanide electroplating electrolyte, J. Hazard. Mater. 152 (2008) 648-655.

35 J.M. Chiaplello, J.Y. Gal, Recovery by electrodialysis of cyanide electroplating rinse waters, J. Membr. Sci. 68 (1992) 283.

36 F. Karas, J. Hnat, M. Paidar, J. Schauer, K. Bouzek, Determination of the ion-exchange capacity of anion-selective membranes, Int. J. Hydrogen Energ. 39 (2014) 5054-5062.

37 P. Długołęcki, K. Nymeijer, S. Metz, M. Wessling, Current status of ion exchange membranes for power generation from salinity gradients, J. Membr. Sci. 319 (2008) 214-222.

38 M. Sadrzadeh, T. Mohammadi, Treatment of sea water using electrodialysis: Current efficiency evaluation, Desalination 249 (2009) 279-285.

39 C. V. Gherasim, J. Krˇivcˇík, P. Mikulášek, Investigation of batch electrodialysis process for removal of lead ions from aqueous solutions, Chem. Eng. J. 256 (2014) 324-334.

40 R.A. Penneman, L.H. Jones, Infrared absorption studies of aqueous complex ions: II Cyanide complexes of Cu(I) in aqueous solution, J. Chem. Phys. 24 (1956) 293-296.

41 W. Zheng, Y. Wang, L. Yang, X. Li, L. Zhou, Y. Li, Novel adsorbent of polymeric complex derived from chaleting resin with Cu(II) and its removal properties for cyanide in aqueous

solution, Colloid. Surface. A 455 (2014) 136-146.

42 B. J. W. Eerd, A. G. Young, N. I. A. Salim, T. Kemmitt, N. M. Strickland, Ligand-functionalised copper(II) hydroxide for quantum dot photoluminescence quenching, J. Colloid Interf. Sci. 346 (2010) 288-295.

43 H. Niu, Q. Yang, K. Tang, A new route to copper nitrate hydroxide microcrystals, Mat. Sci. Eng. B 135 (2006) 172-175.

44 D. Japic, M. Bitenc, M. Marinšek, Z. C. Orel, The impact of nano-milling on porous ZnO prepared from layered zinc hydroxide nitrate and zinc hydroxide carbonate, Mater. Res. Bull. 60 (2014) 738-745.

45 M. Y. Ghotbi, N. Bagheri, S.K. Sadrnezhaad, Nanocrystalline copper doped zinc oxide produced from copper doped zinc hydroxide nitrate as a layered precursor, Adv. Powder Technol. 23 (2012) 279-283.

46 M.Z.B. Hussein, M.Y. Ghotbi, A.H. Yahaya, M.Z. Abd Rahman, The effect of polymers onto the size of zinc layered hydroxide salt and its calcined product, Solid State Sci. 11(2009) 368–374.

47 M.Z.B. Hussein, M.Y. Ghotbi, A.H. Yahaya, M.Z. Abd Rahman, The effect of polymers onto the size of zinc layered hydroxide salt and its calcined product, Mater. Chem. Phys. 113 (2009) 491-496.

48 H. S. Jung, J. K. Lee, J. Y. Kim, K. S. Hong. Crystallization behaviors of nanosized MgO particles from magnesium alkoxides, J. Colloid Interf. Sci. 259 (2003) 127-132.

49 I.G. Casella, M. Gatta, Anodic electrodeposition of copper oxide/hydroxide films by alkaline solutions containing cuprous cyanide ions, J. Electroanal. Chem. 494 (2000) 12-20.

50 M.A.S. Rodrigues, C. Korzenovski, E. Gondran, A.M. Bernardes, J.Z. Ferreira, Evaluation of changes on ion-selective membranes in contact with zinc-cyanide complexes, J. Membr. Sci. 279 (2006) 140-147.

51 S. Lahnid, M. Tahaikt, K. Elaroui, I. Idrissi, M. Hafsi, I. Laaziz, Z. Amor, F. Tiyal, A. Elmidaoui, Economic evaluation of fluoride removal by electrodialysis, Desalination 230 (2008) 213-219

52 M. Turek, Cost effective electrodialytic seawater desalination, Desalination 153 (2002) 371-376.

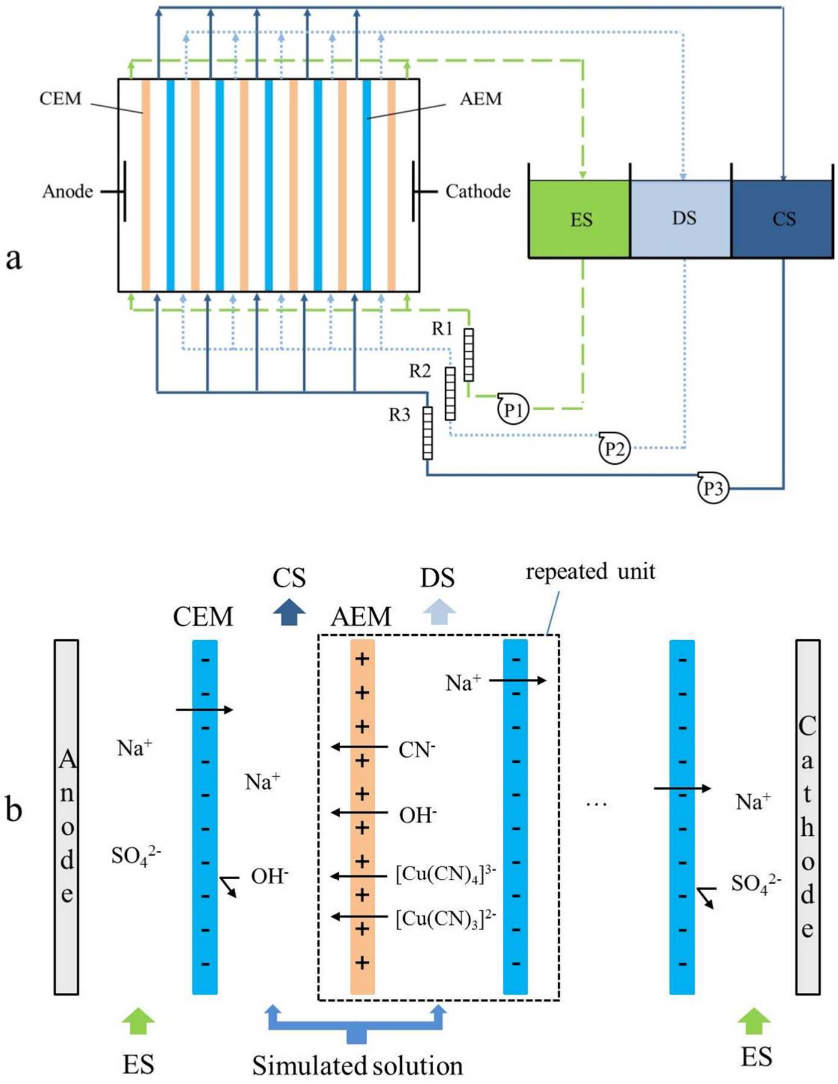

Fig. 1 Flow diagram of the experimental setup (a) and ionic species transport in the ED stack with the simulated solution (b) (AEM, anion exchange membrane; CEM, cation exchange membrane; DS, diluted solution; CS, concentrated solution; ES, electrode solution; P1—pump for ES, P2—pump for DS, P3—pump for CS; R1—rotameter for ES, R2—rotameter for DS, R3—rotameter for CS.)