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ARTICLE

Extraction of zinc in presence of cobalt through hollow fibre supported liquid membrane from simulated industrial wastewater

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Many industrial wastewaters contain toxic metals such as zinc, chromium, cobalt in the form of fluorides and nitrates as anions. Transport of Zn^{2+} from simulated industrial wastewater was studied using di-2-ethylhexyl phosphoric acid (D2EHPA) diluted in kerosene as the organic phase. The hollow fibre supported liquid membrane was operated in continuous recycle mode. Effect of feed phase pH, carrier concentration, sulphuric acid concentration in the strip phase, and flow rate on Zn^{2+} transport was examined. The feed phase pH was varied in the range of 1.5–2.5. The organic phase concentration was varied in the range of 10–30%. At the feed phase pH of 2, the extraction rates were found to be high. About 12% rise in mass transfer flux of Zn^{2+} ions was observed with an increase in D2EHPA concentration from 10% to 20%. The mass transfer flux of Zn^{2+} ions was found to be increased by 28% with an increase in sulphuric acid concentration from 0.5 M to 1 M. The flow rate variation study suggests that mass transfer resistance is mainly contributed by diffusion mechanism through the membrane.

Keywords: D2EHPA; facilitated transport; HFSLM; industrial wastewater; recycling; zinc;

1. Introduction

The discharge of industrial wastewater into the environment is a serious matter and hence calls for its proper treatment. This study deals with the separation and recuperation of valuable and/or toxic species from industrial wastewater. Many industrial wastewaters contain toxic metals such as zinc, chromium, cobalt in the form of fluorides and nitrates as anions. The wastewater used in the present study consists of a very high concentration of zinc to the tune of about 10 g/L. Zinc is biologically important, but too much of it can lead to lethargy and depression[1]. The threshold limit of Zn^{2+}in surface water is 5 ppm as per Indian regulations[2]. These metals in aqueous solutions must be removed before water recycling or discharging directly into surface water. In the electroplating industry, zinc electroplating followed by chromium passivation is a surface finishing technique. These techniques are commonly employed to enhance corrosion protection and decorative features of metallic pieces[3]. However, these chromium-based passivation baths become contaminated by zinc and iron impurities. The contents of the passivation bath are usually discarded and managed as hazardous. The zinc ion is one of the most useful of all the metals in this bath and should be removed and recycled[4].

One of the strategies for waste minimisation in the electroplating industry is the regeneration of baths or bath life extension. The available technologies for the removal of metal ions are ion-exchange[5], electrolysis[6], reverse osmosis[7], and membrane electrodialysis[8]. The limitations of these processes are inadequate selectivity, high residual metal concentration, and periodical batch processes.

The conventional solvent extraction process is associated with the mixing of the aqueous feed phase and the organic extractant phase. This results in the contamination of the organic phase and extractant loss. To overcome these problems, a supported liquid membrane (SLM) system can be adopted that combines extraction and stripping into a single step. This membrane-based process provides the maximum driving force for the separation of the desired species. The process is proven to be a very effective tool for zinc removal[9]. The composition of this zinc sulphate solution is similar to the purified acidic zinc solutions coming from hydrometallurgical processes. The previous work was done on the recovery of zinc from zinc-containing wastes or secondary resources where sulphuric acid was used as a leaching agent[10].

Parhi and Sarangi[11] investigated the separation of copper, zinc, cobalt, and nickel ions from simulated leach liquor using a supported liquid membrane. The deployed concentration of zinc was 40.83 mol/m^3 (~ 2670 ppm). The membrane was impregnated with D2EHPA. In these studies, zinc extraction was found to be maximum at pH 2.25–2.5. It was found that the flux of Zn^{2+} increased from 0.176×10^{-5} to 5×10^{-5} mol/(s.m^2) with an increase in pH from 1.2 to 3.65. The diffusivity of the metal-D2EHPA complex was found to be 1.714×10^{-10} m^2/s.

Pereira et al.[12] studied the recovery of zinc sulphate from industrial effluents by liquid-liquid extraction using D2EHPA. The zinc concentration in industrial effluent was 13.462 g/L (13462 ppm). At pH 2.5, practically 100% of zinc was extracted at D2EHPA concentration level of 25% (w/w). The continuous mixer-settler tests have shown that zinc can be removed using 3 extraction stages and 3 stripping stages.

Owusu[13] investigated the selective extraction of Zn^{2+} from the mixture of Zn-Cd-Co-Ni in a sulphate solution using D2EHPA. A plant solution containing 83.2 g/L of Zn^{2+} (83200 ppm), 2 g/L of Co^{2+} (Zn:Co ratio = 41.6:1) was extracted using D2EHPA at pH 2.0 in one stage. The sulphuric acid solution was used for stripping in the second stage. It was found that at a pH value less than 3, zinc could be extracted from the mixed electrolyte solution with little or no contamination from the other metals. Almost complete Zn extraction was achieved in three counter-current stages. Zinc loaded organics were almost completely stripped in one stage using sulphuric acid.

Thus, it can be seen that there is hardly any literature reported for selective separation of zinc from electroplating bath spent solutions containing Co, Cr, Cu, Fe, Zn. Also, there is no literature reported for the selective separation of zinc from electroplating bath spent solutions containing Co, Cr, Cu, Fe, Zn, using hollow fibre supported liquid membrane (HFSLM). Therefore, it was decided to conduct the present work of HFSLM in a recycling mode. In this mode, the feed and strip phases are circulated continuously. Extractant D2EHPA diluted with kerosene has been used as the membrane phase. The Zn^{2+} ion concentration in the aqueous feed phase was taken at 10 g/L (10000 ppm), which is typical of the actual electroplating bath spent solution. The novelty of the present work lies in the fact that this is the first-ever report on the removal of zinc from simulated industrial wastewater containing a very high concentration of zinc from simulated electroplating bath spent solution using HFSLM.

2. Materials and Method

2.1. Materials

D2EHPA was obtained from Spectrochem India Pvt. Ltd., Mumbai, and was used as the carrier. Kerosene, sodium hydroxide, and 4-(2-pyridylazo) resorcinol (PAR) were procured from S. D. Fine Chemicals India Pvt. Ltd., Mumbai.

2.2. Experimental set-up

Experiments were conducted in an HFSLM module, fitted with two reservoirs, peristaltic pumps for feed and strip phases, flow meters, pressure gauges, and NaOH tank. The HFSLM module used is a LIQUI-CEL® X50 membrane contactor procured from Alting, France (surface area = 1.4 m^2, effective pore size = 30 nm, Porosity = 40%, effective fibre length = 15 cm). During the experimental runs, feed solution was passed through the fibre side whereas strip solution was passed through the shell side in a counter-current flow. The exit solutions from the module were recycled back to the respective reservoirs. Feed phase pH was controlled by continuous addition of NaOH with the help of a syringe until the desired pH is reached. The volumes of the feed/strip reservoirs were 1000 mL each. The detailed specifications of the module are as shown in our previous work[14]. The set-up diagram of the module is given in our previous work[15].

2.3. Method

2.3.1. Impregnation of the carrier liquid

The HFSLM was prepared by pumping carrier solution (D2EHPA + kerosene) through the lumen side of the module at a pressure of 20 kPa in recirculation mode. Complete soaking of the membrane pores was ensured when the carrier solution started percolating from the lumen side to the shell side and was continued until the steady flow was achieved from the shell side. This took about half an hour. The excess of carrier solution was washed out completely with distilled water (approximately 3 L), before the introduction of feed and strip solution.

2.3.2. *Transport study*

The reaction of Zn^{2+} ions with organic extractant D2EHPA is represented by the following equilibrium reaction, where D2EHPA is $(HR)_2$.

$$Zn^{2+}_{(aq)} + 2(HR)_{2(org)} \rightleftharpoons ZnR_2 \cdot 2HR_{(org)} + 2H^{+}_{(aq)} \quad \ldots (1)$$

$ZnR_2 \cdot 2HR$ is the carrier-–metal complex (extracted species) in the supported liquid. This system is called *counter-coupled* transport because the metal ions (Zn^{2+}) and the H^+ ions are transported in opposite directions.

The extraction equilibrium constant (K_{ex}) is given by,

$$K_{ex} = \frac{[ZnR_2 \cdot 2HR]_{org}[H^{+}]^{2}_{aq}}{[Zn^{2+}]_{aq} \cdot [(HR)_2]^{2}_{free,org}} \quad \ldots (2)$$

At steady-state conditions, the transport mechanism for metal ion comprises of the following steps occurring in series:

(i) Transport of Zn^{2+} from the bulk feed phase to the feed-membrane interface.

(ii) Complexation of Zn^{2+} with D2EHPA at the feed-membrane interface to give a carrier-metal complex in the organic phase, followed by the release of H^+ ions in the aqueous phase.

(iii) Diffusion of H^+ ions from the feed-membrane interface to the bulk feed phase.

(iv) Diffusion of the carrier-metal complex through membrane pores from feed-membrane interface to strip-membrane interface.

(v) Diffusion of H^+ ions from the bulk strip phase to the strip-membrane interface.

(vi) Decomplexation of the carrier-metal complex with H^+ ions at the strip-membrane interface to give Zn^{2+} in the aqueous phase, and D2EHPA in the organic phase. The free D2EHPA diffuses backwards to the feed-membrane interface.

(vii) Transport of Zn^{2+} from the strip-membrane interface to the bulk strip phase.

(viii) Steps (i), (iii), (iv), (v) and (vii) represent mass transfer and steps (ii) and (vi) represent chemical reaction equilibrium. In the case of steps (i), (iii), (v), and (vii), diffusion of metal ions through the aqueous film can be assumed to be based on film theory, and hence linear concentration gradients are assumed.

(ix) The feed solution used was simulated industrial wastewater containing various metal ions and anions as listed in Table 1. The feed phase pH was 1.5 and varied in the range of 1.5 to 2.5 by continuous addition of 4 M NaOH. Also, D2EHPA concentration was varied in the range of 10–30% (v/v). Aqueous sulphuric acid of 0.5–3 M concentration range was employed as the stripping medium. The mass transfer fluxes for all the operating parameters for the present study are shown in Table 2. These fluxes were necessary to quantify and compare the effects of various parameters. Mass transfer fluxes were calculated for the linear behaviour during the initial period of operation for Zn^{2+} removal experiments as follows:

$$J = \frac{V}{A}\left(\frac{dC}{dt}\right) \quad \ldots (3)$$

Table 1. Composition of simulated industrial wastewater

Sr. No.	Ion	Concentration
1	Cr	3 to 5 g/L
2	Co	0.3 to 0.6 g/L
3	Cu and Fe	in traces
4	Zn	10 g/L (10000 ppm)
5	Fluorides	0.5 to 1.5 g/L
6	Nitrates	5 to 15 g/L

2.3.3. *Sample analysis*

The quantification of zinc ions in the aqueous sample was done by Chemito UV-Visible double beam recording spectrophotometer (Model 160-A, Japan) using the 4-pyridylazo 2-resorcinol (PAR) reagent method at 520nm wavelength. A digital pH meter (procured from Hanna instruments) was used to measure the pH of samples at the ambient laboratory temperature of 25±0.1 ^{O}C.

3. Results and Discussion

3.1. Effect of pH of the feed phase

Experiments were conducted for the different values of feed phase pH (Fig. 1). The pH of the feed phase was varied in the range of 1.5–2.5 using 4 M aqueous NaOH. It was observed that the removal of zinc was affected during 60 minutes of the experiment in the pH range employed. Afterwards, the removal of zinc was found to be steady-state until 120 minutes of the experiment. The mass transfer flux of $Zn^{2+}$is shown in Table 2. It can be seen that with an increase in feed phase pH, the mass transfer flux increased slightly. This indicates that with an increase in feed phase pH, the reaction equilibrium shifts towards the higher formation of metal-complex as per equation (1). However, at a pH of 2.5, cobalt transport was also observed, which is not desirable as shown in Fig. 2. The mass transfer flux of Co^{2+}ion was found to be 0.00002 mol $m^{-2}min^{-1}$ as shown in Table 2. This undesirable cobalt transport may be taking place due to the lower concentration of H^+ ions in the feed, which results in a less stable complex of $CoNO_3$as compared to Co-D2EHPA. Therefore, all further experiments were conducted at pH 2. The H^+ ion concentration in the bulk feed phase is always kept low by buffering of the feed phase. The H^+ ions formed at the interface diffuse through the feed-side into the bulk of the feed phase.

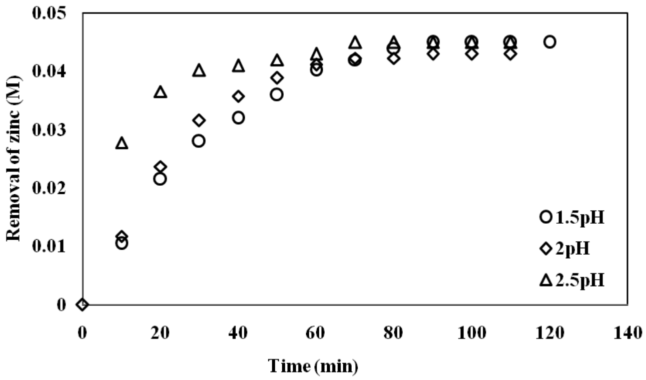

Fig. 1 Effect of feed phase pH on Zinc transport. Feed phase (1000 mL): Carrier, 20% (v/v) D2EHPA in kerosene; Strip phase: 2M H_2SO_4 (1000 mL); Feed and Strip phase flow rates, 200 mL/min

3.2. Effect of D2EHPA concentration

Fig. 3 shows the effect of D2EHPA concentration on Zn2+ extraction in the range 10–30 % (v/v). It was seen that almost complete extraction was achieved within about 50 minutes with the D2EHPA concentration of 20–30 % (v/v). However, it took about 60 minutes to get complete extraction when 10 % (v/v) D2EHPA concentration was employed. Since the ratio of D2EHPA to Zn2+ is less at low D2EHPA concentration, the extraction of Zn2+ ions was slower, and increased with an increase in D2EHPA concentration. H+ ion concentration is maintained constant in the bulk feed phase by pH control. This, in turn, helps maintain the H^+ ion concentration in the bulk feed phase, which is essential for regenerating D2EHPA. This leads to an increase in the H^+ ion concentration at the feed-membrane interface with a corresponding rise in the D2EHPA concentration. This happens because a higher concentration of D2EHPA concentration leads to more complexation to maintain the equilibrium. This ensures that sufficient free D2EHPA molecules are available at the feed-membrane interface, thus facilitating Zn^{2+} ion extraction. At higher D2EHPA concentration, the complexation rate is higher. A similar effect was observed in the case of mass transfer flux (Table 2). The increase in mass transfer flux of Zn^{2+} ion was 16.25 % and 25 % for 20% and 30% D2EHPA concentration respectively, as compared to the base case of 10% D2EHPA concentration.

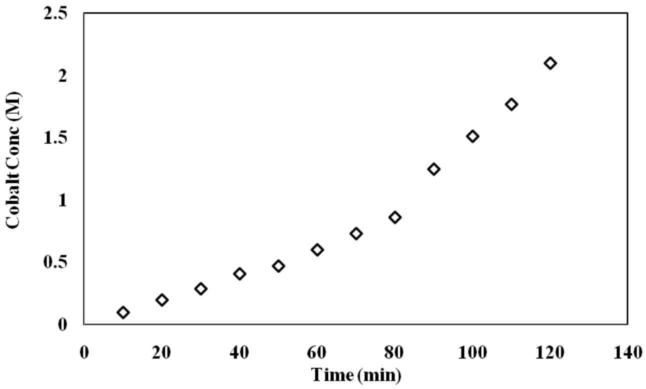

Fig. 2 Effect of feed phase pH on cobalt transport. Feed phase (1000 mL): Carrier, 20% (v/v) D2EHPA in kerosene; Strip phase: 2M H_2SO_4 (1000 mL); Feed / Strip phase flow rates, 200 mL/min

Table 2. Effect of various parameters on mass transfer flux

pH of Feed	H_2SO_4 Concentration in strip phase	Flow rate (mL/min)	Carrier liquid Concentration (%v/v)	Mass transfer flux	
				Zn^{2+} (mol/m^2.min)	Co^{2+} (mol/m^2.min)
1.5	2	200	20	0.0072	—
2	2	200	20	0.0093	—
2.5	2	200	20	0.009	0.00002
2	1	200	20	0.007	—
2	3	200	20	0.01	—
2	0.5	200	20	0.0052	—
2	2	300	20	0.009	—
2	2	400	20	0.009	—
2	2	200	10	0.008	—
2	2	200	30	0.01	—
2	2	200	20		—

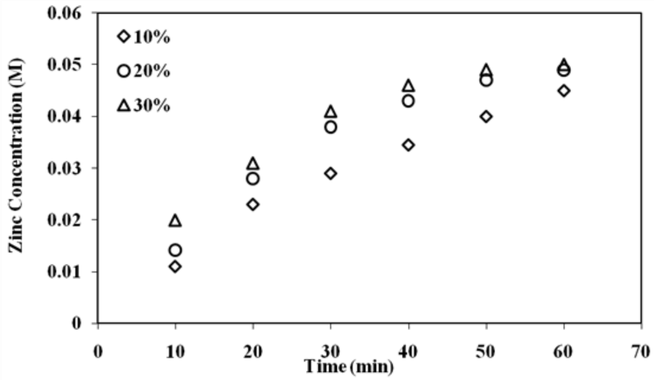

Fig. 3 Effect of D2EHPA concentration on zinc transport. Feed phase: at 2 pH (1000 mL); Strip phase: 2M H_2SO_4 (1000 mL); Feed / Strip phase flow rates, 200 mL/min

3.3. Effect of H_2SO_4 in strip phase

The effect of strip phase H_2SO_4 concentration (range of 0.5–3 M) on the extraction of Zn^{2+} ions is depicted in Fig. 4. It can be seen that the strip phase acid concentration has a profound effect on the extraction of Zn^{2+} ions. This observation is seen by the mass transfer flux shown in Table 2. However, for all values of strip phase H_2SO_4 concentration, almost 70–90% extraction was achieved in about 60 minutes. This proves the abundant availability of H+ ions in the strip phase at 1 M H_2SO_4 concentration of 1 M H_2SO_4. Equation (1) indicates that the H^+ ions in the strip phase are in a far excess supply of the stoichiometric requirement. Therefore, there will be no appreciable drop in the acid concentration of the strip phase at complete Zn2+ extraction. The Zn^{2+} ion concentration in the bulk feed phase is decreased because of extraction. The increase in the mass transfer flux of Zn^{2+} ion was found to be about 34.61%, 78.84%, and 92.30% for 1 M, 2 M, and 3 M H_2SO_4 concentrations, respectively, as compared to the base case of 0.5 M H_2SO_4 concentration. This results in less number of Zn^{2+} ions diffusing through the aqueous film to the feed-membrane interface.

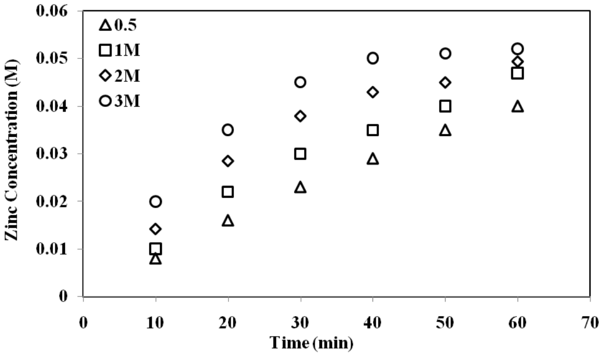

Fig. 4 Effect of H_2SO_4 strength on zinc transport. Feed phase: at 2 pH (1000 mL); Carrier: 20% (v/v) D2EHPA in kerosene; Feed / Strip phase flow rates, 200 mL/min

3.4. Effect of feed and strip phase flow rates

Experiments were conducted at different flow rates of the feed phase and strip phase in the range of 200–400 mL/min. It helps to predict the contribution of feed and strip phase resistances to the transport of Zn^{2+} ions. Fig. 5 and Table 2 demonstrate that an increase in the feed phase flow rate did not have any pronounced effect on the Zn^{2+} ion transport. This suggests that mass transfer resistance is almost entirely present in the diffusion through the membrane is much slower in comparison with the rate of mass transfer through aqueous boundary layers and the rate of reactions at membrane interfaces. Therefore, diffusion through the membrane was considered to be the rate-controlling step. The mass transfer flux of the Zn^{2+} ion was found to be constant within the range of the studied flow-rate. Experiments are repeatable with an accuracy of ±10%, which suggests that the system is stable under the conditions studied. Repeatability of experiments was checked for 5 consecutive runs shown in Fig. 6.

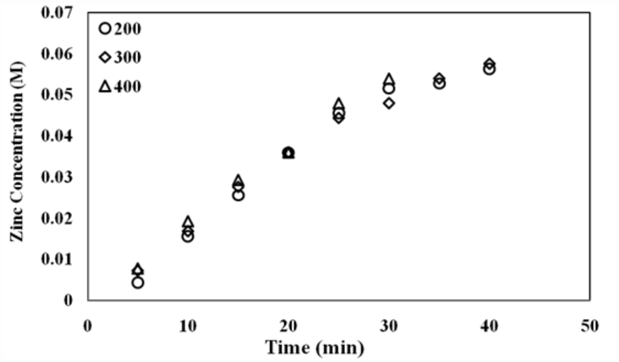

Fig. 5 Effect of flow rate on zinc transport. Feed phase: at 2 pH (1000 mL); Carrier: 20% (v/v) D2EHPA in kerosene; Strip phase, 2M H_2SO_4 (1000 mL)

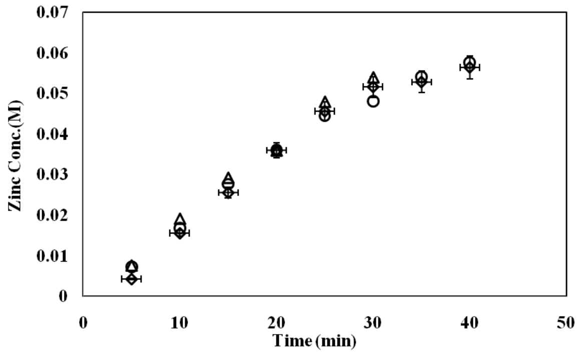

Fig. 6 Repeatability of experiment for zinc transport. Feed phase: at pH 2 in water (2000 mL); Carrier: 20% (v/v) D2EHPA in kerosene; Strip phase: 2M H_2SO_4 (2000 mL); Feed / Strip phase flow rates, 100 mL/min

4. Conclusions

The extraction and simultaneous stripping of Zn^{2+} ions were studied with D2EHPA as an extractant using hollow fibre supported liquid membrane operated in a recycling mode. An exceedingly small fraction of cobalt was also found at operating conditions of pH 2.5, 2 M H_2SO_4 concentration, 200 mL/min flow rate, 20% carrier liquid concentration. Decent extraction flow rate, 20% carrier liquid concentration. Decent extraction rates were obtained when the feed phase pH value is maintained at 2. The Zn^{2+} ion extraction rates were found to increase with an increase in D2EHPA concentration. Moreover, the experiments with the variation in the strip acidity showed that 1 M H_2SO_4 furnished sufficient H^+ strip phase to affect the de-complexation of the metal-organic complex at the strip-membrane interface. This showed that the mass transfer resistance was negligible on the strip side. Also, the independence of extraction rates on flow rates proved that mass transfer resistance is almost entirely present in the membrane. Therefore, it was concluded that the rate of mass transfer through the membrane was much slower in comparison with the rate of mass transfer through aqueous boundary layers and the rate of reactions at membrane interfaces. Therefore, diffusion through the membrane was proved to be the rate-controlling step. There is about a 12% rise in mass transfer flux with an increase in D2EHPA concentration from 10% to 20%. Mass transfer flux was also found to increase by 28% with an increase in H_2SO_4 concentration from 0.5M to 1M.

Nomenclature

K_{ex}	Extraction equilibrium constant of the metal complexation reaction
t	time, min
dC	change in concentration of Zn^{2+} with respect to time
J	molar flux, mol per min per square metre
A	membrane area, square metre
V	volume of feed reservoir, L

5. References

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