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# Separation of cadmium and lead from wastewater using supported liquid membrane integrated with *in-situ* electrodeposition

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ABSTRACT

A novel process for separation of heavy metals from liquid wastes and/or industrial effluents has been developed as described in this paper wherein the technique of supported liquid membrane based extraction and stripping of heavy metals has been augmented with electroplating inside the stripping chamber of SLM. Wastewater, infested with cadmium and lead, has been subject of research in this work. The said process is employed in transporting the heavy metals from the polluted source phase (wastewater) to the sink (or strip) phase while simultaneously depositing the heavy metals *in-situ* on the electrode placed inside the strip phase, and thereby the strip phase is remained ever-unsaturated. This arrangement yields high gradient of chemical potential across the liquid membrane and thereby facilitates enhanced and faster recovery of said heavy metals and also yields value added component, *viz.* electroplated items, for suitable end use.

## 1. Introduction

Process industries that generate huge amount of effluent containing heavy metals (such as lead, cadmium, mercury etc.) are real concern of this hour. Heavy metals, even if they are found in trace quantity in the wastewater, cause enormous contamination of aquatic environment when discharged into the water body and in turn leads to massive ill-effect to human health due to their highly toxic, carcinogenic and non-biodegradable nature [1,2]. In this paper, we address the possible ways of mitigating two such heavy metals, *viz.* lead and cadmium, whose permissible limits in wastewater are 10 ppb and 3 ppb respectively, as set by the World Health Organization (WHO) [3]. The heavy metals Pb and Cd are usually found as their chloride salts in industrial effluent. Bhatluri et al. [1,2] gave a detailed account on the sources of these heavy metals, problems with their traditional mitigation procedures and usefulness of supported liquid membrane (hereafter abbreviated as SLM) technique for separation of these heavy metals and purification of wastewater. SLM is a well-known technique for selective separation and pre-concentration of solute (such as metals). Detailed description of SLM based technologies are available elsewhere [4]. However, SLM produces concentrated pollutant at its downstream side, i.e. strip phase and it does not address its effective mitigation.

Electrodeposition is another well-known technique that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on electrodes. Electrode coatings are now extensively employed for the improvement of performance of modern electrochemical instruments [5]. Moreover, substantial modification to the physical properties and catalytic activities of the said coating may be possible through doping and fabrication of nanostructured deposits [6]. The standard potential for lead in aqueous solution is −0.12 V. High hydrogen over potential of lead yields easy deposition from strong acidic solutions with cathodic efficiency approaching 100% [7]. The electrochemical equivalent for the reaction, $Pb^{++} + 2e \longrightarrow Pb$, is 3.865 $gAh^{-1}$. Electroplated lead finds a huge field of application in the process industries. All the parts that come into contact with sulphuric acid are usually plated with 200 $\mu$m lead. The base material is usually copper, however, there is also reference of using the aluminum that has the advantage of lesser weight. Moreover, the use of electrodeposited lead for the applications in the field of superconductivity is referred elsewhere [8–16]. Electrodeposition of lead-cadmium alloy also has good potential for application as a surface coating on bearings. Lead-indium alloy is otherwise a good bearing alloy due to its high fatigue strength and corrosion resistance against oxidation. However, indium is very costly metal. Lead-cadmium alloy, on the other hand, with cadmium content of up to 30% is a better

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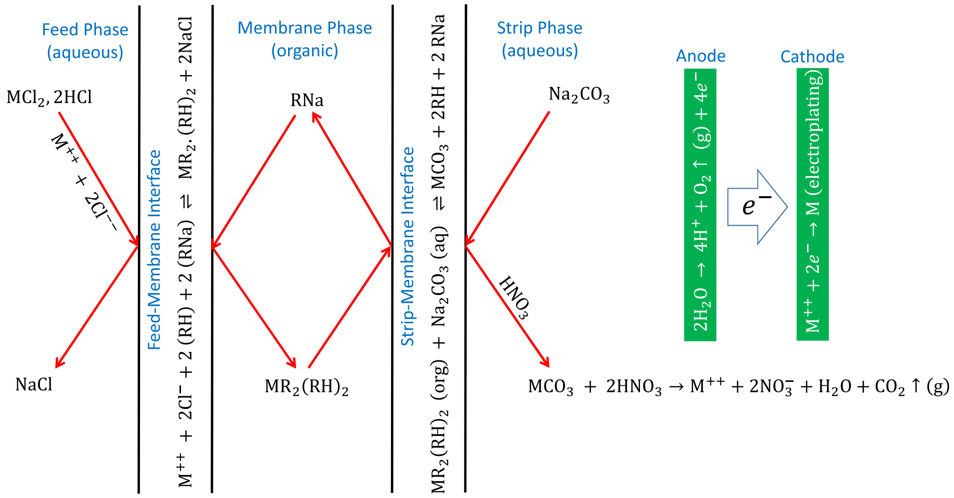

**Fig. 1.** Schematic diagram of transport and reaction mechanism of liquid membrane based separation followed by electrodeposition.

alternative. Owing to the closeness of the standard potential of the lead and cadmium, the co-deposition from their solutions is adequately possible [17–20].

In this work, a novel design has been invented wherein SLM based separation module has been integrated with electroplating module in order to capitalize the merits of both the techniques. The electrodes are housed inside the stripping chamber of the SLM setup where simultaneous stripping and electroplating take place. This phenomenon facilitates separation and recovery of trace amounts of costly heavy metals in their purest (atomic) form for further utilization as value added product. The parameters of the said integrated process have been optimized through experimental means in order to ensure best recovery of the product.

## 2. Reaction mechanism and transport methodology

The target metals for recovery from wastewater and subsequent electrodeposition, *i.e.* lead and cadmium, are referred to in this paper with a common symbol "M" for easy understanding. The transport methodology of M from feed phase to the strip phase has been illustrated in this section (vide Fig. 1). The reaction mechanism indicates that $MCl_2$ at a moderately acidic condition of feed phase (pH 5) dissociates in the form of $M^{++}$ at the feed phase. HCl is used for maintaining the desired level of acidity (pH 5) in the aqueous feed phase. Dimeric acidic carrier, *viz.* Di-(2-ethylhexyl)phosphoric acid (often abbreviated as D2EHPA), exchanges $H^+$ at the feed side interface and forms metal-carrier complex which diffuses to the strip-membrane interface due to concentration gradient. The stripping agent, *viz.* sodium carbonate, strips the metal from the said metal-carrier complex at the strip-membrane interface in exchange of sodium. The sodium-carrier complex diffuses back to the feed-membrane interface due to concentration gradient that eventually exchanges $Na^+$ with $M^{++}$ at the feed side interface to form another metal-carrier complex. The transport of metal from feed phase to strip phase thus continues in a cyclic manner until the strip phase would ideally get saturated. Significantly, the presence of nitric acid in the strip phase enhances the acidity of the solution and at the same time inhibits the formation of metal carbonate precipitate. With application of electric potential metal is deposited on the cathode plate. D2EHPA, i.e. $(C_8H_{17}O)_2POOH$, is referred to as RH in the remaining part of this paper where $R \equiv (C_8H_{17}O)_2POO$. The sodium salt of D2EHPA is denoted by RNa. The reaction mechanism for transportation of M (metal) is thus summarized as follows:

$$MCl_2 \rightleftharpoons M^{++} + 2Cl^- \qquad (1)$$

$$M^{++} + 2Cl^- + 2(RH) + 2(RNa) \rightleftharpoons MR_2(RH)_2 + 2NaCl \qquad (2)$$

$$MR_2(RH)_2\,(org) + Na_2CO_3\,(aq) \rightleftharpoons MCO_3 + 2RH + 2RNa \qquad (3)$$

$$MCO_3 + 2HNO_3 \longrightarrow M^{++} + 2NO_3^- + H_2O + CO_2 \uparrow (g) \qquad (4)$$

$$2H_2O \longrightarrow 4H^+ + O_2 \uparrow (g) + 4e^-\ (\text{anode}) \qquad (5)$$

$$M^{++} + 2e^- \longrightarrow M\ (\text{electrodeposition on cathode}) \qquad (6)$$

Lead and cadimum are interchangeably referred with Pb(II) and Cd(II) respectively in this paper.

## 3. Materials and methods

### 3.1. Chemicals and reagents

All the chemicals and reagents used in this work were of guaranteed reagent (GR) grade. The extractant D2EHPA was procured from Spectrochem Pvt. Ltd. (India). All other chemicals such as $Na_2CO_3$, HCl (35%), ammonia solution (25%) and $HNO_3$ (69%) were obtained from Merck (India). Parachute® coconut oil (Marico India limited, India) was purchased from local market. Polyvinylidene Fluoride (PVDF) membrane (Hydrophobic, pore size 0.2 $\mu$m and thickness 127 $\mu$m) was procured from Pall Corporation Pvt. Ltd. (India). Accutrace® reference standard lead and cadmium solutions (1000 ppm) were procured from AccuStandard (USA) for AAS analysis. Synthesized pollutant comprising of chloride salts of target heavy metals, *viz.* lead and cadmium, were fed into the feed phase chamber of SLM at different initial concentrations of the metals for experimentations. The membrane phase was prepared by dissolving an appropriate amount of carrier agent in coconut oil. Concentration of carrier (in % v/v) is defined as the ratio of the volume of carrier to volume of membrane phase without carrier. The stripping phase was prepared by dissolving the required amount of $Na_2CO_3$ in 500 mL of Milli-Q® deionized water.

### 3.2. Analytical instruments

The concentrations of lead and cadmium in the feed and stripping solutions were determined by using Atomic Absorption Spectrometer (AAS) (Make: Varian Australia, Model: AA240FS) using flame mode. A digital pH meter (Eutech Instruments, EUTECH 510) was used for the measurement of pH. The electron-dispersive X-ray analysis was carried out in Scanning Electron Microscope (SEM) (LEO1430vp) instrument facilitated with EDX analysis. DC power supply (Crown, Dual output DC regulated