

Removal of Pb(II) ions from aqueous solution using complexation-ultrafiltration

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Ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) is a membrane technique based on a separation process which can be used for removal of target metals from an aqueous solution. This method involves adding both a metal complexing ligand and surfactant molecule to the aqueous solution under conditions where most of the molecules are present as micelles. This ligand can be attached to the surface of micelles by solubilization and forms the ligand complexes with the metal ion. The aqueous solution is then treated through a membrane which has to be smaller pore sizes than those of the complexes. Hence, permeate water is then purified from the heavy metals. In this study, divalent lead is the target ion in a solution. Filtration experiments were performed with ultrafiltration membrane system, equipped with a regenerated cellulose membrane with a 5000 Daltons cut-off. The pressure was fixed at 4.0 bar with a permeate flow rate of 500 mL min⁻¹. Complexes of Pb²⁺ ions with three ligands were investigated in micellar medium of different surfactants at different pH values to determine the ligands which could provide separation. Different parameters affecting the percentage rejection of the Pb²⁺, such as pH and surfactant concentration were also discussed. Results have shown that the maximum percentage of the Pb²⁺ ions rejection were obtained using sodium dodecyl sulfate (SDS) as a surfactant and dithizone (DZ) as the lead-specific ligand. A waste stream sample from a battery plant was subjected to LM-MEUF process in the optimum conditions determined in this study and it was shown that Pb²⁺ ions in a waste stream could be removed by LM-MEUF effectively.

Keywords: Ligand-modified MEUF, Pb²⁺ ions, DZ, and SDS.

INTRODUCTION

Wastewaters containing heavy metals have always attracted widespread attention because of the significant threat they pose to the environment and human health¹. The heavy metal lead is among the most common pollutant found in industrial effluents. Lead is widely used in mining, refining, battery manufacturing, electrical wiring, construction, painting, ceramic glazing, and the making of stained glass². The increasing presence of lead is very problematic to surface and underground water due to their mobility and great toxicity³.

Even at low concentration, this metal can damage central nervous system, the kidney, liver and reproductive system, basic cellular processes, and brain functions⁴. The U.S. Environmental Protection Agency (EPA) requires lead not to exceed 0.015 mg L⁻¹ in drinking water⁵. Therefore, from the viewpoint of pollution, environmental chemistry, and geochemistry, it is necessary to establish a rapid and simple procedure to remove lead. There are lots of methods for the removal of metal toxicants. For instance: solvent extraction, distillation, adsorption, and also membrane techniques: electrodialysis, dialysis, micro-filtration, nanofiltration or reverse osmosis⁶⁻⁸. However, these techniques present shortcomings, such as secondary pollution by deposition, inconvenient operation, high cost, and the difficulties of recycling heavy metals. During the last decade, membrane separation processes such as Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO) have been constantly increasing used for a wide form of waste water containing heavy metals. Most of researchers present the utilization of micellar enhanced ultrafiltration (MEUF)⁹⁻¹³.

In order to enhance selectivity and efficiency of MEUF, the ligand-modified micellar enhanced ultrafiltration

should be used. This method involves the addition of an amphiphilic ligand and a surfactant to the feed solution under conditions where most of the surfactant is present as micelles. The ligand reveals a high degree of solubilization in the micelles and a tendency to selectively complex the target metal ion. Then, the solution is passed through an ultrafiltration membrane with pore sizes small enough to block the passage of micelles¹⁴⁻²¹. As micelles are rejected, the solubilized ligand and its complexed ions will also be rejected. The unsolubilized ligand, uncomplexed ions, and surfactant monomers pass through the ultrafiltration membrane to the permeate side. Fig. 1 shows a schematic of the LM-MEUF processes.

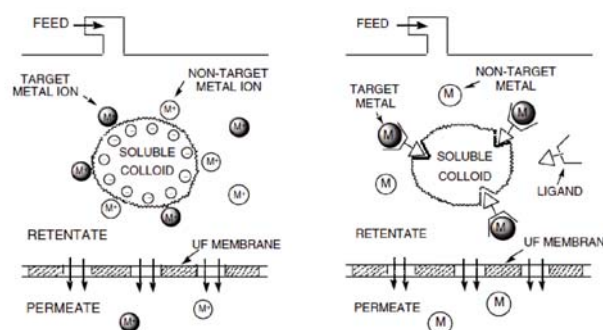


Figure 1. Schematic representation of the MEUF (A) and LM-MEUF (B) processes

Klepac et al. investigated divalent copper removal ion in a solution also containing divalent calcium by LM-MEUF²². A cationic surfactant is used with N-n-dodecyl-iminodiacetic acid as the copper-specific ligand. Rejections of copper up to 99.2% are observed, with no rejection of calcium, showing that LM-MEUF has almost

perfect selectivity, as well as high capacity in this case. Later work was done with a commercial alkyl- β -diketone extractant as a ligand which again showed greater than 99% rejection of copper with no rejection of calcium²³. Some efforts have been made to target metals other than copper. Pramauro et al. used derivatized salicylic acid ligands in nonionic and nonionic/cationic surfactants to preconcentrate iron with more than 98% rejection²⁴ and Roach used ligands derived from nitrilotriacetic acid with CPNO₃ cationic surfactant or polyelectrolyte to separate lead with 99.9% rejection²⁵. Advantages of that technology over the other conventional technologies are: the low energy requirements involved in ultrafiltration, very fast reaction kinetics, and the high selectivity of separation.

In this study, we will be focusing on investigating the applicability of the complexation-ultrafiltration process for removal of Pb²⁺ ions from synthetic wastewater solutions. To highlight the removal of metal performance, the main operating conditions which are pH, surfactants and ligand concentration will be investigated.

PROCESS DESCRIPTION

Material

Anionic Sodium dodecyl sulfate (SDS) (Merck), cationic Cetyltrimethyl ammonium bromide (CTAB) (Aldrich), and non-ionic surfactant; Polyoxyethylene(10) isooctylphenyl ether (TX100) (Riedel) were used as received without further purification. Pb(NO₃)₂ (Merck) was used as sources of Pb²⁺ ions. (After being dried in an oven at 60°C, then stored inside a desiccator over calcium chloride). The pH of the aqueous solutions was adjusted using Nitric acid (HNO₃) (Merck) and caustic soda (NaOH, (Merck) were used for pH adjustments. Three different ligands, ditiyocarbamat (DTC), Thio-urea and Diphenylthiocarbazon (DZ) were used as complexing agents.

Deionized water was used throughout the study.

Apparatus and procedure

All the experiments were carried out in a batch-stirred cell (Amicon 8050, Millipore, USA; Fig. 2). Organic regenerated cellulose membranes (Millipore, USA) having a molecular weight cut-off (MWCO) values of 5000 Da were used for all the MEUF experiments. The cell was operated at a constant transmembrane pressure (TMP) of 4.0 bar, regulated with pressurized air, and stirred at 500 rpm. This stirring speed was selected because it could lead to an effective agitation in the cell. The stirrer speed was measured using a digital tachometer (Optic DT-838). The influence of different experimental parameters, *i.e.*, transmembrane pressure, stirring speed and membrane porosity, on the flux and surfactant concentration were investigated in the preliminary experiments.

A 30 mL of feed solution was charged into the cell. The run was continued until approximately 5 mL of retentate sample remained in the cell. The first 5 mL of the permeate was discharged to avoid contamination in sampling lines. Metal rejection was determined by analyzing subsequent 20 mL of the permeate.

The Pb²⁺ concentrations of the permeate and feed were determined by inverse differential pulse polaro-

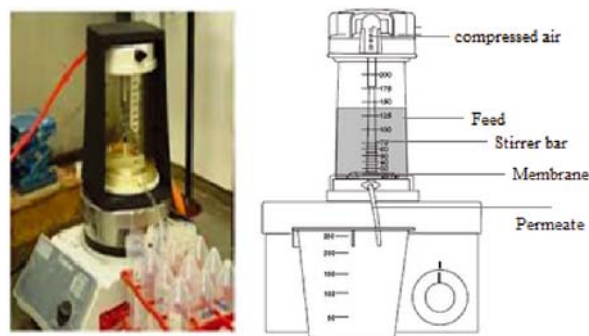


Figure 2. UF cell used in the experiments

graphic method (DPASV). For the polarographic measurements a PAR Model 14 A polarographic analyzer system equipped with a PAR mercury drop timer was used. A Kalousek electrolytic cell with a reference saturated calomel electrode (SCE), separated by a liquid junction, was used in a 3-electrode configuration. The counter electrode was platinum wire. The natural drop time of the mercury electrode was 2–3 s (2.2 mg s⁻¹). It was outfitted with a Model ABB SE-790 X-Y recorder. Measurements were taken by the triple standard addition method. 10 mL supporting electrolyte of HNO₃ solution (pH 1) were placed in an electrolytic cell, then 1.0 mL of permeate was added. Polarographic curve was recorded, then the standard solution of Pb²⁺ of concentration 1.0 × 10⁻³ M/ 0.1 mL was added and the curve was recorded once again. DP polarograms were recorded under the conditions of 1s, a scan rate of 5 mV/ s⁻¹ and a pulse amplitude of 25 mV.

In preliminary studies, membranes were used repeatedly in successive experiments. After each experiment the UF cell was rinsed with 50 mL of deionized water (DI) for 30 min to prevent the formation of a surfactant layer over the membrane surface and disperse the surfactant molecules. Then, membranes were washed with 20 mL of DI water at a pressure of 4 bar. The membrane permeability was checked to ensure that the permeability remains almost constant between successive runs.

To evaluate the separation efficiency of Pb²⁺ ions from the feed solution, the classical rejection coefficient equation was used:

$$R(\%) = \left(1 - \frac{C_p}{C_i}\right) \times 100$$

where C_i is the initial concentration of the Pb²⁺ ion in the feed solution and C_p is the Pb²⁺ ion concentration in the permeate.

RESULTS AND DISCUSSION

Determination of ligands for removal of Pb²⁺ ions

In this study, complexation-ultrafiltration technique was used to remove the Pb²⁺ ions. Two ligand characteristics are important for a successful separation. First, the ligand must have a high affinity for the target metal. For instance, in order to achieve 99% rejection of the metal, the conditional binding or formation constant (K_{ML}) must be at least 1.0 × 10⁷ M⁻¹ for a solution initially containing 1 mM ligand and 1 mM metal. Second, the ligand should have a high solubility in the chosen surfactant but very low solubility in water²⁶. This minimizes

the amount of ligand, as well as complexed metal, which will pass through the membrane during the ultrafiltration. Other characteristics of the ligand and its target metal complex are considered in order to get the best separation efficiency with the minimum material costs, high concentration factor, chemical stability and reusability.

Optical absorption spectra of surfactant, Pb^{2+} and ligand solutions; binary solutions of surfactant with ligands and Pb^{2+} ion; and ternary solutions composed of surfactant, ligand and Pb^{2+} ion were recorded at different pHs to determine the ligands that could be used to LM-MUF process for separation of Pb^{2+} ions. Thus, 36 spectra were obtained using three compounds as ligands (UNICAM UV2-100 spectrophotometer). In these experiments, the concentrations of Pb^{2+} and ligand solutions were kept as 2.0×10^{-4} M and 2.5×10^{-4} kgL⁻¹, respectively. The surfactants; SDS, CTAB, TX100 were also used to be 2.5×10^{-3} , 5.0×10^{-3} , 5.0×10^{-3} M and, respectively.

Pb²⁺-DTC complex/Pb²⁺-DTC-surfactant solution: The complex was quickly formed but it was decomposed gradually with time as a result of oxidation or pH effect.

Pb²⁺-DZ complex/Pb²⁺-DZ-surfactant solution: Pb^{2+} complexed with dithizone was not decomposed in acidic and basic medium.

Pb²⁺-Thiourea complex/Pb²⁺-Thiourea-surfactant solution: The crystalline products were generally heterogeneous and after the addition of NaOH to a solution of Pb^{2+} -Thiourea-surfactant (except CTAB), the complex was decomposed.

As a result, dithizone was formed stable complexes with Pb^{2+} ions (Figure 3), and dithizone was chosen as the working ligand for LM-MEUF process.

Dithizone compound is subject to keto-enol tautomerism²⁷. The keto form provides primary dithizonates of the ML_n composition (low pH), the enol form provides secondary dithizonates of ML_{n/2} composition (higher pH value).

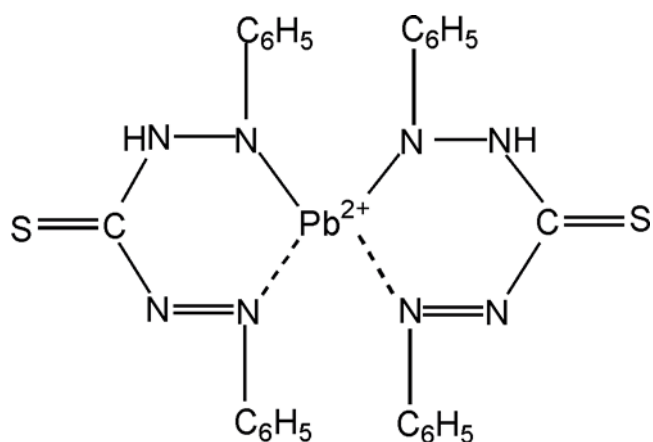


Figure 3. Pb^{2+} - DZ complex

Determination of surfactant for removal of Pb^{2+} ions

The Pb^{2+} -DZ complex is insoluble in water and thus spectrophotometric determination is performed after extraction into organic solvent. $Pb(II)$, $Ag(I)$, $Cu(II)$, $Cd(II)$ and $Ni(II)$ can be determined with dithizone by extraction spectrophotometry²⁸. Since methods involve

solvent extractions are lengthy, time-consuming and lack selectivity due to much interference²⁹. This problem has been overcome in recent years by introducing a hydrophobic micellar system generated by a surfactant similar to that employed in phase-transfer reactions. The presence of a micellar system avoids the previous steps of solvent extraction and also increases the solubility of Pb^{2+} -DZ complex. In the first step, the presence of Pb^{2+} ions and dithizone, the apparent critical micelle concentration (C_m) of surfactants was calculated by surface tension (ST) method. The C_m values of SDS, CTAB, TX100 in saturated solution of dithizone and 2.5×10^{-4} M of Pb^{2+} solution were determined to be 4.0×10^{-3} M, 7.2×10^{-4} M and 2.1×10^{-4} M, respectively.

In order to find a suitable surfactant to remove Pb^{2+} ions from aqueous solutions a series of experiments were conducted at pH 5.0 (Table 1). pH 5 was chosen as the working pH since most industrial wastewaters are expected to have pH levels near 5.0. In this study, surfactants were used at least three times higher than C_m . SDS was found to be the best surfactant for the LM-MUF process.

Table 1. Determination of suitable surfactant for removing Pb^{2+} ions

Surfactant	Concentration 10 ⁴ M	C _p [mg/L]	R [%]
SDS	12.0	13.99	73.00
CTAB	21.60	32.04	38.00
TX100	6.30	18.51	65.00

Determination of amount of dithizone

The excess of ligand should be added to the sample solution to form good complexes with metal ions. It is excessive, some problems occur in the process of filtration due to too much materials were created in the solution together with the ligand. Therefore, a proper amount of the ligand is needed. For this reason, the solubility of DZ in 1.0×10^{-2} M SDS was determined (see Figure 4). To 8.5 mL of SDS solution in a 10 mL volumetric flask was mixed with 0.0–1.2 mL of ethyl alcohol and 1.5–0.3 mL an ethanolic solution of DZ. The absorbance was measured at 500 nm against a corresponding reagent blank. From the calibration graph, its solubility was found to be 3.06×10^{-5} M.

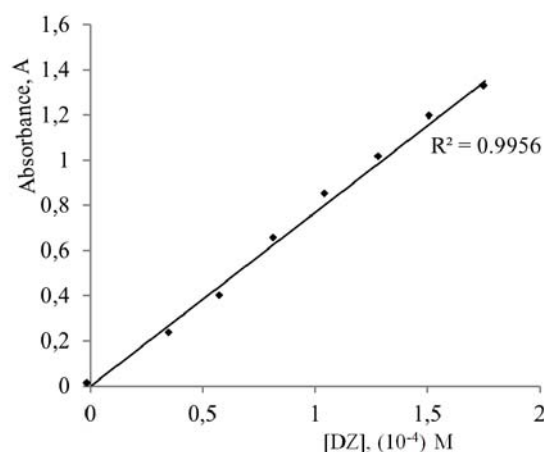


Figure 4. Calibration graph of DZ in 1×10^{-2} M SDS

Effect of the pH on the removal of Pb²⁺

The formation of metallic complexes with a ligand is pH dependent. The effects of the solution pH in the range 3.0–9.0, at a fixed concentration of SDS saturated with dithizone (1.2×10^{-3} M) and pressure of 4 bar were evaluated. Figure 5 shows the result of the experiments carried out for Pb²⁺ separation from solutions of different acidity.

The results indicate that more than 80% Pb²⁺ could be removed from the solutions studied at relatively low pH. The near quantitative removal of Pb²⁺ indicated that Pb²⁺ in both the conditions i.e. acidic and alkaline is attached or solubilised in the tail of the SDS surfactant and SDS makes sufficiently bigger micelles which could easily be retained.

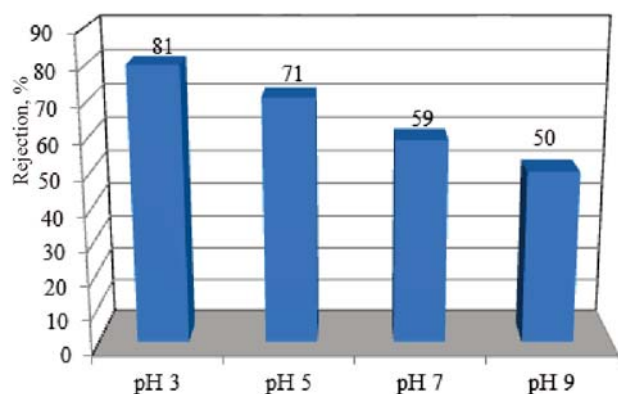


Figure 5. Effect of the pH on the removal of Pb²⁺. The Pb²⁺ concentration and operating pressure were 2.5×10^{-4} M and 4 bar, respectively at room temperature

Effect of the concentration of SDS on the removal of Pb²⁺

Following the determination of the optimum pH, another sets of experiments were performed at pH 3.0 to determine the optimum SDS concentration for Pb²⁺ removal from solutions.

The rejection coefficient of Pb²⁺ reaches its maximum when the concentration of SDS amounts to 1.0×10^{-2} M. This is understandable since at higher SDS initial concentrations more surfactant monomers are in micellar form (see Figure 6).

Figure 6 shows retention rate of Pb²⁺ as a function of SDS initial concentration. When dithizone is used, the retention of Pb²⁺ increases from 62% to 82%. This clearly indicates that the Pb²⁺-DZ complex is solubilized on the

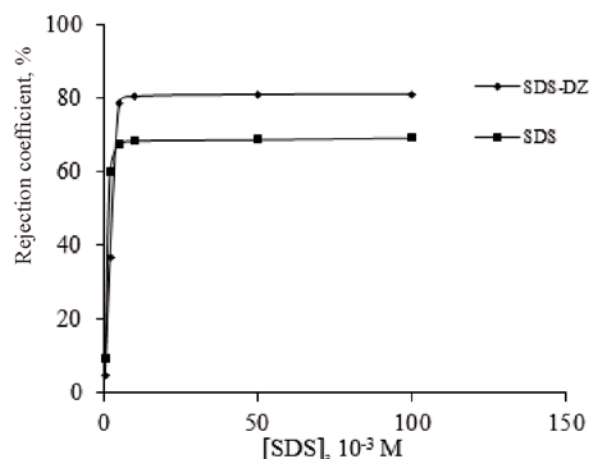


Figure 6. Effect of the concentration of SDS on the removal of Pb²⁺ at pH 3.0; • SDS, ♦ SDS-DZ

surfactant micelles, which are subsequently retained by the ultrafiltration membrane.

The selected analytical parameters obtained with the optimization experiments are summarized in Table 2.

Application

Afterwards, a waste stream sample from a battery plant was analysed in the analytical conditions determined in optimization experiments (Table 3). It has been demonstrated that Pb²⁺ ions can be almost completely removed from the waste stream in the presence of SDS by MEUF. It can be concluded that this method is effective for the determination of Pb²⁺ in environmental samples.

CONCLUSIONS

It has been shown that complexation-ultrafiltration can be applied for removal of Pb²⁺ using diphenylthiocarbazone as a good complexing agent. LM-MEUF technique which has advantages (compared with other separation methods) of being simple, inexpensive, less time consuming and expected to be soon incorporated as a clean technology to treat water and wastewater has been applied in this investigation. The removal of Pb²⁺ at pH 3, attained ~82% in the presence of DZ and SDS as a surfactant. Moreover, the recommended procedure was successfully applied to waste stream sample from a battery plant.

Table 2. Selected analytical parameters obtained with optimization experiments

Complexing Agents	DTC, Thiourea, DZ	DZ
Surfactants	SDS, CTAB, TX100	SDS
pH	3.0–9.0	3.0
Surfactant / 1% SDS	5.0×10^{-4} – 1.0×10^{-1}	1.0×10^{-2}
Temperature / °C	25±5	25±5
Reagent / DZ	3.5×10^{-5} – 1.8×10^{-4}	3.06×10^{-5}

Table 3. Pollution Item of The Wastewater of a Battery Plant

Item of the wastewater	Lead concentration [mg/L]	pH	SS [mg L ⁻¹]	Turbidity [NTU]	Conductivity ms cm ⁻¹
Value	10.3	5.84	2.4	2.0	0.26

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