Green recovery of mercury from domestic and industrial waste

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HIGHLIGHTS

- An aqueous two-phase system was used for the extraction of Hg(II).
- Hg(II) was selectively extracted from complex samples.
- The methodology yielded a high percentage of Hg(II) extraction.

GRAPHICAL ABSTRACT
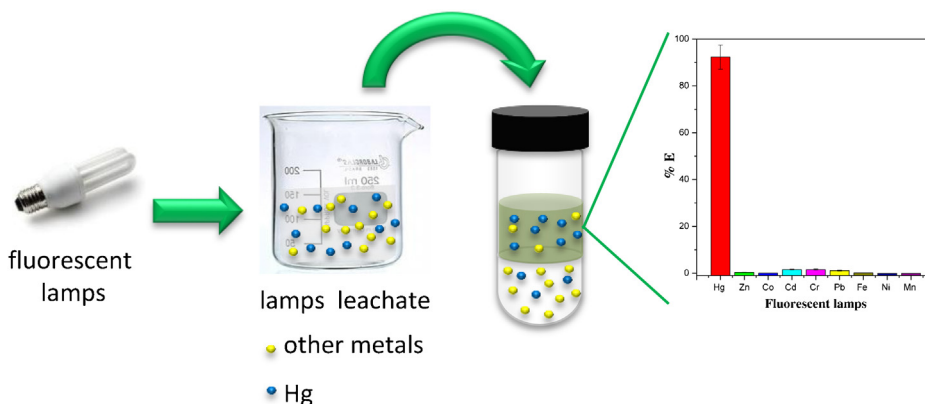
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ABSTRACT

Recovery of mercury from effluents is fundamental for environmental preservation. A new, green method was developed for separation of mercury from effluent containing different metals. The extraction/separation of Hg(II) was studied using aqueous two-phase system (ATPS) comprising by polyethylene oxide (PEO1500) or triblock copolymers (L64 or L35), electrolyte (sodium citrate or sodium sulfate) and water in the presence or absence of chloride ions. The extraction behavior of the Hg(II) for the macromolecule-rich phase is affected by the following parameters: amount of added extractant, pH, and the nature of the electrolyte and macromolecule of the ATPS. The APTS of PEO1500 + sodium citrate + H_2O (pH 1.00 and 0.225 mol kg^{-1} KCl) produced the highest Hg(II) %E = (92.3 ± 5.2)%. Under the same conditions, excellent separation factors ($1.54 \times 10^2 - 3.21 \times 10^{10}$) for recovery of mercury in the presence of co-existing metals were obtained. Efficient and selective extraction of Hg(II) from domestic and industrial synthetic effluents was achieved using this ATPS.

1. Introduction

Mercury is considered one of the most dangerous elements [1] due to its high toxicity and bioaccumulative effect [2,3], and is listed as a priority pollutant by the US Environmental Protection Agency (EPA). Mercury occurs in different physical and chemical forms, where the mercuric ion (Hg^{2+}) is predominant and exerts high cell toxicity. Mercury in the environment may be derived from natural

or anthropogenic sources [4–6], including the industrial production of chlor-alkali, pulp and paper, batteries, and fluorescent lamps [7].

Ion exchange [8], precipitation [9], electrolysis [10], adsorption [11,12], membrane separation [13], and solvent extraction [14] have been developed as strategies to minimize environmental mercury discharge. Solvent extraction (SE) is quite attractive because the number of analytes to be separated can be increased by changing the solvent and extractant. However, SE is not environmentally safe as it requires organic solvents that are often toxic and/or flammable [15–17]. A system employing a liquid phase at thermodynamic equilibrium without the presence of organic solvents is a strategic substitute for the classic SE. Thus, the aqueous two-phase system (ATPS) is an interesting alternative because it consists mainly of water with small amounts of polymers, salts, or ionic liquids, which conform well to the requirements of Green Chemistry [18]. ATPS has been used quite effectively in the recovery and purification of metals [19–26]; however, studies of mercury recovery using ATPS are still incipient.

Rogers and Griffin [27] studied the partitioning behavior of mercury using PEG5000 + (NH$_4$)$_2$SO$_4$ + H$_2$O ATPS. Metal partitioning into the polymer-rich phase occurred after the formation of complexes with halides in the following order Cl$^-$ < Br$^-$ < I$^-$. Larger distribution coefficients were obtained with the use of NaI, where the distribution coefficients were greater than 907 for the PEO5000, 40% (m/m), + (NH$_4$)$_2$SO$_4$, 3.5 mol L^{-1}, ATPS.

Roy and Lahiri [28] separated Hg(I), Hg(II), and methylmercury using an ATPS formed by PEG4000 and electrolytes (Na$_2$SO$_4$, K$_2$CO$_3$, Na$_3$PO$_4$, or NaOH). Extraction of the electrolyte-rich phase(ERP) consisting of sodium sulfate yielded 100% recovery of Hg(I) and Hg(II) and 80% methylmercury. Lahiri and Roy [29] showed too, in other paper, high Hg radionuclides extraction was obtained when a PEO4000 + Na$_2$SO$_4$ + H$_2$O ATPS was used to extraction.

These studies demonstrate the potential of ATPS for extraction of mercury into the polymer-rich phase. However, no studies of mercury separation in relation to other metals have been presented.

This study assesses the extraction of Hg(II) in ATPSs in the presence of various metals (Cr(III), Fe(III), Co(II), Cd(II), Cu(II), Ni(II), Pb(II), Mn(II), and Zn(II)). The effects of the presence of chloride ions, presence different macromolecules and electrolyte in the system, pH, and the tie-line length (TLL) on mercury extraction are investigated. The PEO1500 + sodium citrate + H$_2$O ATPS system is applied to separation of mercury from three different synthetic wastes: fluorescent lamps, button-type battery (Zn–air), and the chlor-alkali industrial effluent.

2. Material and methods

2.1. Chemicals

All reagents were of analytical grade. Poly(ethylene oxide), PEO1500, with an average molar mass of 1500 g mol^{-1}, and H$_2$O$_2$ were purchased from Synth (Brazil); the triblock copolymers: (HO-(EO)$_{11}$(PO)$_{16}$(EO)$_{11}$-H), denoted L35, with an average molar mass of 1900 g mol^{-1} and (HO-(EO)$_{13}$(PO)$_{30}$(EO)$_{13}$-H), denoted L64, with an average molar mass of 2900 g mol^{-1}, HNO$_3$, KCl, and (CrCl$_3$·6H$_2$O were purchased from Aldrich (USA). FeCl$_3$·6H$_2$O, HgCl$_2$, CuSO$_4$·5H$_2$O, MnSO$_4$·H$_2$O, Pb(NO$_3$)$_2$, Ni(NO$_3$)$_2$·4H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, sodium citrate dihydrate (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O), Na$_2$SO$_4$, and NaOH were purchased from Vetec (Brazil); CdCl$_2$·H$_2$O, CoCl$_2$·6H$_2$O, HCl, and H$_2$SO$_4$ were obtained from Merck (Germany).

2.2. Composition and preparation of ATPS

An aqueous solution of HCl, H$_2$SO$_4$, or NaOH (pH 1.00, 3.00, 6.00, 9.00, or 12.0) was used as the solvent to prepare the macromolecule and electrolyte stock solutions.

Table 1
Masses of macromolecule (m_m), electrolyte (m_e) stock solutions, and water (m_w) used for preparation of the ATPS.

ATPS	TLL /%(m/m)	m_m/g	m_e/g	m_w/g
PEO1500 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	35.87	12.1	29.9	13.0
PEO1500 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	43.35	13.5	32.9	8.60
PEO1500 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	50.33	15.2	36.1	3.70
PEO1500 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	56.04	16.3	38.7	0.00
PEO1500 + Na$_2$SO$_4$ + H$_2$O	35.96	12.7	33.3	9.00
L35 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	34.78	12.4	21.6	21.0
L35 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	48.18	16.2	26.6	12.1
L35 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	54.84	17.9	30.1	7.00
L35 + Na$_2$SO$_4$ + H$_2$O	57.50	18.2	36.7	0.10
L64 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	36.58	14.4	16.1	24.5
L64 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	42.56	16.6	17.0	21.4
L64 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	45.58	16.5	19.7	18.8
L64 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O	52.96	18.8	21.6	14.6

The PEO1500 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O [30], PEO1500 + Na$_2$SO$_4$ + H$_2$O [31], L35 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O [32], L35 + Na$_2$SO$_4$ + H$_2$O [33], and L64 + Na$_3$C$_6$H$_5$O$_7$ + H$_2$O [34] ATPSs were prepared in centrifuge tubes by mixing adequate amounts stock solutions of PEO1500 60.0% (m/m), L64 54.8% (m/m), or L35 63.0% (m/m) with Na$_3$C$_6$H$_5$O$_7$ 27.5% (m/m) or sodium sulfate 20.0% (m/m) as described in Table 1. The centrifuge tubes were then manually stirred for 3 min and centrifuged at 2900 × g for 30 min. The tubes were kept in a thermostatic bath at (25.0 ± 0.1) °C for 24 h until two clear phases were obtained.

The TLL is determined from the differences in the concentrations of the components in each phase according to Eq. (1):

$$\text{TLL} = \sqrt{\left(C_P^{TP} - C_P^{BP}\right)^2 + \left(C_E^{TP} - C_E^{BP}\right)^2} \tag{1}$$

where C_P^{TP} and C_P^{BP} are the macromolecule concentrations, and C_E^{TP} and C_E^{BP} are the electrolyte concentrations (in % (m/m)) in the top phase (TP) and bottom phase (BP), respectively.

2.3. Mercury extraction

The ATPS phases obtained in Section 2.2, were separated and stocked. 2.00 g of the to TP containing an appropriate amount of the KCl extractant (0–0.449 mol kg^{-1}) and 2.00 g of the BP containing Hg(II) at a concentration of 1.50 mmol kg^{-1} were mixed in a centrifuge tube. After combining the two phases, the tube was manually stirred for 3 min, centrifuged at 9503 × g for 10 min at 25 °C and placed in the thermostatic bath (25.0 ± 0.1) °C for 20 min. Aliquots from the TP were collected and diluted for the determination of mercury by FAAS (Varian AA-240 spectrometer, Australia) under the operating conditions summarized in Table S1. To calculate the extraction percentage (%E) was used in Eq. (2). All experiments were performed in triplicate.

$$\%E = \frac{(n_M x+)_{TP}}{(n_M x+)_T} \times 100 \tag{2}$$

where $(n_M x+)_{TP}$ is the amount metallic ions in the TP, and $(n_M x+)_T$ is the total amount of metallic ions in the system.

2.4. Effect of the amount of extractant

To study the effect of the amount of extractant on the %E of the mercury, samples were prepared by mixing 2.00 g of the electrolyte solution containing 1.50 mmol kg^{-1} Hg(II) and 2.00 g of the macromolecule solution containing the extractant with concentrations ranging from 0 to 0.449 mol kg^{-1}.