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Aqueous biphasic separation of thallium from aqueous solution using alcohols and salts

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ABSTRACT

The behavior of aqueous biphasic extraction of thallium (Tl) using different alcohols and salts was investigated. The extraction of Tl(III) was driven by the Tl-chlorocomplex ($TlCl_4^-$) that formed with Tl(III) and chloride. The addition of appropriate amount of salt and alcohols helped form the organic-water stratification, in which Tl and alcohols were enriched in the upper phase while the most water and salt were separated in the bottom phase. Both the two-phase systems of alcohols (propanol and butanol)-NaCl and alcohols-$(NH_4)_2SO_4$ were effective in Tl(III) extraction but poor for Tl(I) separation. The ethanol-$(NH_4)_2SO_4$ system allowed good separability of Tl(III) from Tl(I) while ethanol-NaCl one gave no stratification. In *n*-propanal-NaCl extraction system, the Tl(III) extraction was stable at the contact time ranging from 0.5 to 10 min. Reaction temperature and acidity had little effect on the extraction performance. Tl(I) oxidized by ozone, bromine water, hydrogen peroxide, and hypochlorite yielded high fractional extraction of Tl(III). The alcohols-salts two-phase system can not only be a potential means to the analysis of Tl speciation but also an alternative technique to the extraction of Tl in water and wastewater.

Keywords: Thallium; Aqueous biphasic separation; Extraction; Oxidation; Heavy metals; Aqueous two-phase system

1. Introduction

Thallium (Tl) is a highly toxic heavy metal that is listed as a priority pollutant by many countries [1–6]. It exists in the aquatic environment with two oxidation states, Tl(I) and Tl(III) [7]. The chemical property of Tl(I) resembles K^+, which is highly mobile and stable; while the Tl(III) is sensitive and reactive, being capable of forming complexes with halide and organics, and being easily hydrolyzed in alkaline conditions or reduced by reducing agents [5,8,9]. The dominant Tl species in the environment is usually in the form of Tl(I) [7,10], since Tl oxidation needs strong oxidants which are often absent unless intentionally dosed by humans.

For the Tl species separation analysis, ion exchange resins include Dowex A-1 [11] and Chelex-100 [5,7,12] have been used for removal of Tl(III) under acidic condition. Diethylenetriaminepentaacetic acid (DTPA) [9] or ethylenediaminetetraacetic acid (EDTA) [13] coupled with cation resins

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has been proposed to separate Tl(I) and Tl(III). However, the cation (Na^+ and K^+) and the anion (Cl^- and NO_3^-) also have high affinity to the cationic/anionic resins, which hinder their extensive use. Moreover, the resins technique is not accurate for quantitative separation of Tl from complex industrial wastewater. Formation of ion-pair complexes between Tl(I) and a variety dyes has also been proven feasible to distinguish Tl(I) [14]. Some organic solvents such as benzene [15], TBP [16], and tribenzylamine [15] have been tested for Tl extraction. However, the dyes and organic solvents are usually toxic chemicals that may pose severe safety issues for operators and technicians. Therefore, the pursuit of green techniques for Tl separation is necessary.

The aqueous biphasic system has a great potential to separate metal ions from aqueous solutions due to its nontoxicity and cost-effectiveness [17–20]. However, very limited studies on the separation of thallium (Tl) using aqueous two-phase systems have been reported. Chung et al. reported the early use of aqueous biphasic separation with *iso*-propanol and NaCl for selective extraction of Tl(III) from aqueous solutions [14], pointing out the feasibility of using green extractants for quantitative Tl separation. This salting-out technique allows the extraction of $TlCl_4^-$ into the highly polar organic solvents, forming the ion-pairs of Na^+ and $TlCl_4^-$. For the aqueous biphasic system, alcohols and salts were often used to create the organic-water stratification [21], in which the organic phase usually has high polarity that may favor the binding of negatively charged $TlCl_4^-$. Therefore, it is hypothesized that most the alcohols and salts, not restricted to the *iso*-propanol and NaCl system, be able to extract the Tl(III) species.

The overarching goal of this study is to test the various salting-out systems of alcohols and salts for Tl(III) extraction. The influencing factors of the selected extraction method were also systematically examined. The possible application on Tl species analysis of wastewater treatment was also tested.

2. Materials and methods

2.1. Chemicals, reagents, and wastewater

All the chemicals (NaCl, $(NH_4)_2SO_4$, $TlNO_3$, and $Tl(NO_3)_3$) and reagents (HCl, ethanol, *n*-propanol, *iso*-propanol, *n*-butanol, and *iso*-butanol) were of analytical grade and used as received from the suppliers (Aldrich, USA). The Tl(I) and Tl(III) solutions were prepared with $TlNO_3$ and $Tl(NO_3)_3$ as needed, respectively. The deionized water was used to prepare the chemical solutions. The wastewater used was collected from the zinc oxide production plant in Shaoguan, Guangdong Province, China.

2.2. Extraction procedures

Briefly, a designated amount of salts (NaCl or $(NH_4)_2SO_4$), wastewater (synthetic or industrial wastewater), alcohols (ethanol, propanol, or butanol), and HCl (1 mol/L) was added into the funnels, shaken, and mixed for a desired time. After that, the mixture was allowed to settle for 10 min then both the water and organic phases were separated then digested for Tl detection.

In a typical NaCl-alcohols extraction test, 1.6 g NaCl, 6 mL wastewater and 3 mL alcohols, 1 mL HCl (1 mol/L), and 3 min contact time were used; while in a typical $(NH_4)_2SO_4$-alcohols extraction test, 3.0 g $(NH_4)_2SO_4$, 6 mL wastewater and 3 mL alcohols, 1 mL HCl (1 mol/L), and 3 min contact time were applied. Unless specific instruction, the reaction temperature was 298 K, the initial Tl concentration was 50 μM. During the factorial experiments, only the studied factor varied while the other factors remained fixed at the typical level specified earlier. For example, during the experiments on factor of contact time, the NaCl dosage, wastewater volume, alcohols volume, and HCl concentration were fixed at the typical values of 1.6 g, 6 mL, 3 mL, and 1 mol/L, respectively, while the reaction time varied in eight levels: 0.25, 0.5, 1, 2, 3, 5, 7, and 10 min. Similarly, during the experiments on factor of salt dosage, only the salt dosage varied in six levels: 100, 120, 140, 160, 180, and 200 g/L; the other factors fixed at the typical conditions. For the experiments on factor of reaction temperature, the reaction temperature varied in six levels: 298, 303, 308, 313, 318, and 323 K. For the experiments on factor of HCl concentration, the HCl concentration varied in six levels: 0, 0.05, 0.1, 0.25, 0.5, and 1 mol/L. For the experiments on factor of propanol dosage, the propanol dosage varied in seven levels: 0.5, 1, 2, 3, 4, 5, and 6 mL. For the experiments on factor of initial Tl concentration, the initial Tl concentration varied in eight levels: 0.005, 0.05, 0.5, 1, 2, 4, 8, and 16 mmoL/L.

For the extraction of Tl from different oxidation systems, different oxidants including O_3, H_2O_2, bromine water, and hypochlorite were used to oxidize both synthetic Tl(I) solution and industrial wastewater. The *n*-propanol-NaCl extraction scheme consisting of 1.6 g NaCl, 6 mL oxidized/nonoxidized wastewater and 3 mL alcohols, 1 mL HCl (1 mol/L), and 3 min contact time were used for Tl(III) extraction.

2.3. Analytical methods

An atomic adsorption spectrometer (Thermo Scientific, USA) was used to measure the Tl concentration. When the Tl concentration was lower than 0.5 mg/L, an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (NexION 300, PerkinElmer Inc., USA) was applied for Tl measurement. For industrial wastewater, all metal concentrations were measured by ICP-MS. The distribution coefficient (D) of Tl was defined as the ratio of Tl concentration in organic phase to that in the water phase. Fourier-transform infrared (FT-IR) spectra were obtained using a Tensor27 (Bruker, Germany) FT-IR spectrometer. Zeta potential was measured by a zeta potential analyzer (DelsaMax PRO, Beckman Coulter, USA).

3. Results and discussion

3.1. Influencing factors

3.1.1. Effect of contact time on Tl(III) extraction

The fractional Tl content in the organic phase reached up to over 95%, and the Log D kept at over 1.2, implying that the Tl(III) extraction was steadily effective at the contact time ranging from 0.5 to 10 min, and that the contact time studied had little effect on Tl(III) extraction (Fig. 1). The advantages of aqueous biphasic separation are simple mixing, low shear and short contact time [22,23]. Previous research reported that 2.0 min was sufficient to reach extraction equilibrium in polyethylene glycol-based aqueous biphasic systems for metal ions separation [24]. In addition, the fast stratification time was within 1 min, suggesting the effectiveness and simplicity of the alcohols-NaCl two-phase system.

3.1.2. Effect of salt dosage on Tl(III) extraction

The salt dosage at 1 g resulted in 86% Tl(III) extraction (Fig. 2). The increase in the salt dosage to over 1.4 g reached a peak extraction of Tl(III), and the Log *D* kept at 1.2–1.3 when the salt dosage was from 1.4 to 2.0 g, which is consistent with the previous study using NaCl-*iso*-propanol for Tl(III) extraction [14]. The dosage of salt plays an important role in the phase stratification and the target compounds extraction [14,25]. The NaCl is not only critical to cause phase separation but also is important to provide the counter ions (Na^+) for the capture of the chloro-Tl(III) complex anion ($TlCl_4^-$) into the organic phase. The NaCl dosage at 1.4–2.0 g is suitable for Tl(III) extraction.

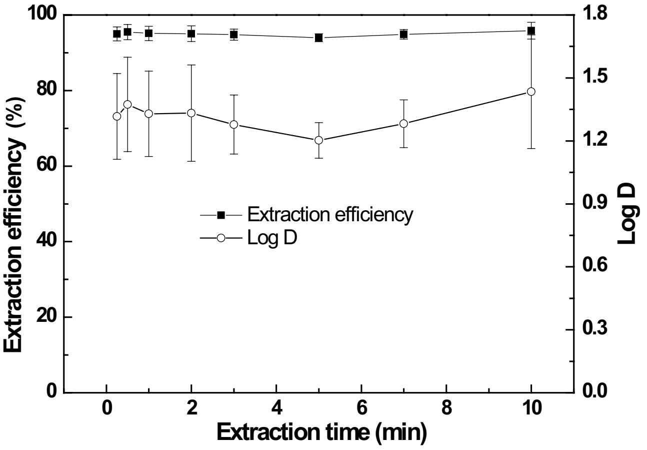

Fig. 1. Effect of contact time on Tl(III) extraction (Tl_0 50 μmol/L, 1.6 g NaCl, 6 mL wastewater, 3 mL alcohols, 1 mL HCl (1 mol/L), and 298 K).

3.1.3. Effect of reaction temperature on Tl(III) extraction

The Tl(III) extraction at the reaction temperature ranged from 298 to 323 K was constantly stable and effective (over 95%), appearing to have almost no obvious effect on the Tl(III) extraction (Fig. 3). The reaction temperature could affect the solubility of salting-out agents and the ion-pair products [26], and thus influencing the extraction efficiency [27]. The solubility of NaCl in water at the temperature range of 298–323 K is very close (360.1–368.0 g/L) [26]. Low variation in solubility of NaCl in ethanol is also observed at 298–323 K (58.2–69.5 g/L) [26]. The reaction temperature posed an inconspicuous impact on Tl(III) extraction, indicating that the temperature studied herein might have little effect on the solubility of the ion-pair products of Na^+ and $TlCl_4^-$ in both water and ethanol.

3.1.4. Effect of HCl concentration on Tl(III) extraction

In terms of the Tl extraction efficiency, the role of HCl was not important, because the Tl(III) extraction reached over 95% without addition of HCl (Fig. 4). This indicates that the NaCl plays an important role in the formation of $TlCl_4^-$. The increase in HCl dosage from 0.1 to 0.5 mol/L led to a subtle enhancement on Tl(III) extraction in terms of Log *D*. Further increase in HCl did not improve the Tl(III) extraction. Depending on the targeting compounds and the used salts, the solution pH is a crucial parameter during aqueous biphasic separation [21]. In the alcohol-NaCl system for Tl(III) extraction, it appears that the content of the chloride instead of the H^+ determines the extraction process, because the NaCl itself provides the chloride for formation of the Tl(III)-chlorocomplexes [14]. For the alcohol-$(NH_4)_2SO_4$ system, the dosage of HCl is crucial for Tl(III) extraction (Fig. S1). As expected, the Tl extraction was very low in the absence of the HCl addition, and it increased with the increase in HCl concentration (Fig. S1). This is because the chloride from HCl

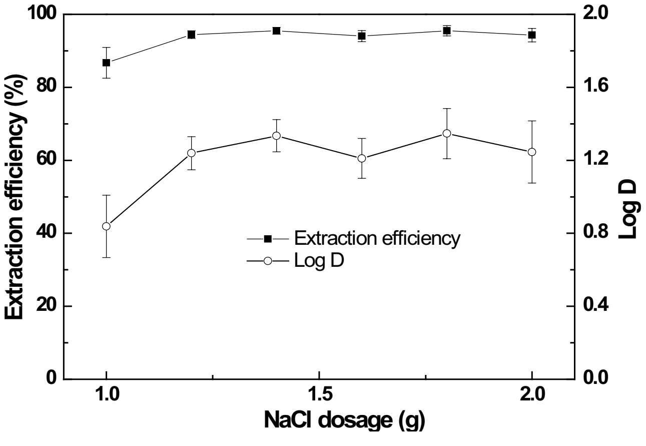

Fig. 2. Effect of NaCl dosage on Tl(III) extraction (Tl_0 50 μmol/L, 6 mL wastewater, 3 mL alcohols, 1 mL HCl (1 mol/L), reaction time 3 min, and 298 K).

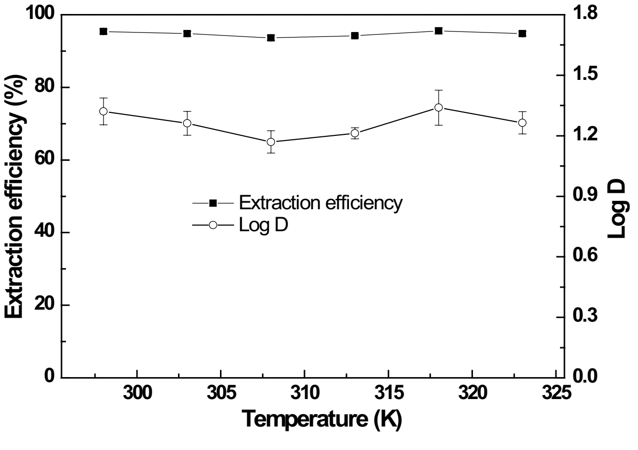

Fig. 3. Effect of reaction temperature on Tl(III) extraction (Tl_0 50 μmol/L, 1.6 g NaCl, 6 mL wastewater, 3 mL alcohols, 1 mL HCl (1 mol/L), and contact time 3 min).

is necessary for formation of $TlCl_4^-$, which is in line with the above-mentioned explanation.

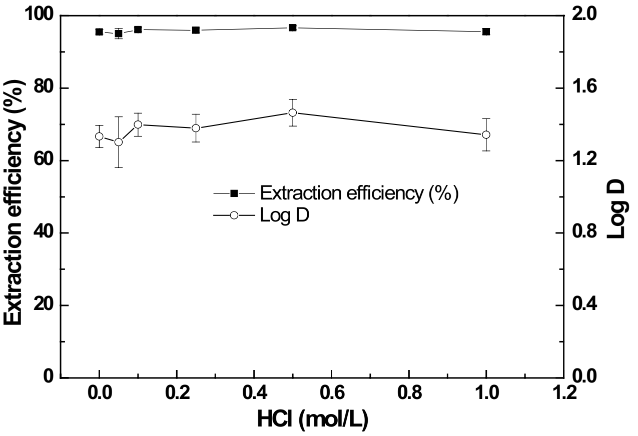

Fig. 4. Effect of HCl concentration on Tl(III) extraction (Tl_0 50 µmol/L, 1.6 g NaCl, 6 mL wastewater, 3 mL alcohols, 1 mL HCl, reaction time 3 min, and 298 K).

3.1.5. Effect of propanol dosage on Tl(III) extraction

The gradual increase in the propanol dosage resulted in a progressive improvement on the Tl(III) extraction (Fig. 5), indicating the importance of the propanol dosage to the alcohol-NaCl two-phase system on Tl ions separation. The propanol dosage over 3 mL was close to the peak extraction efficacy, the Log *D* kept increasing to around 1.8 with the further increase in alcohol dosage to 6 mL, suggesting the "the more the better role." It has been frequently reported that the increase in the organic content leads to the enhancement on the extraction of the targeting metal ions into the organic phase [28]. The main chemical species of Tl(III) in aqueous solution containing chloride concentration over 1 mol/L is $TlCl_4^-$ [13], which is tetrahedral and the coordination sites of Tl(III) are fully occupied by chloride [14,29], thus resulting in its extraction into the organic phase instead of the water phase. The higher alcohol dosage leads to more contact of $TlCl_4^-$ with alcohols and hence the near complete extraction of Tl(III) into the organic phase.

3.1.6. Effect of initial Tl(III) concentration on Tl extraction

The Tl(III) extraction was steadily effective (efficiency over 95% and Log *D* of 1.15–1.36) when the initial Tl(III) concentration ranged from 0.005 to 16 mmol/L (Fig. 6). The constantly high distribution coefficient over a wide range of tested Tl ions may suggest that the extracted chemical species is monomeric, with ionic pair of Na^+ and $TlCl_4^-$ as the extracted product in the organic phase [14]. This also points out that this extraction technique could be used for the extraction and recovery of Tl in the high Tl-containing industrial wastewater, or for the determination of Tl species since Tl(I) could barely be extracted.

3.2. Extraction of Tl under different oxidation systems

Different strong oxidants (O_3, H_2O_2, bromine water, and hypochlorite) were also tested for the oxidation of Tl(I) from both synthetic solutions and industrial wastewaters (Tables 1 and S1). Strong oxidants including H_2O_2, bromine water, and hypochlorite were highly effective in oxidation of Tl(I) to Tl(III), while the O_3 exhibited slightly less extraction efficiency than the others likely due to the low solubility of O_3 in water. The H_2O_2 is a green and effective reagent for oxidation of Tl while the hypochlorite is competitive with low cost. For synthetic Tl(I) solution without oxidation, very low Tl was extracted, indicating that only Tl(III) can be extracted by the alcohol-salt biphasic system. Similar phenomenon was also observed for the real industrial wastewater, revealing that most Tl in this wastewater was Tl(I) and that the Tl can be effectively extracted by combination of oxidation and salts-alcohols extraction (Table S1). For synthetic Tl(III) solution of $Tl(NO_3)_3$ without oxidation, the fresh one exhibited over 96.1% of Tl(III) extractability, while 4 months later it slightly decreased to 95.8% of extraction. Under normal conditions, the commercial reagent ($Tl(NO_3)_3$ from Aldrich) is trustworthy with high quality, and the preservation of Tl(III) with acid (1 mol/L HNO_3) is simple and reliable.

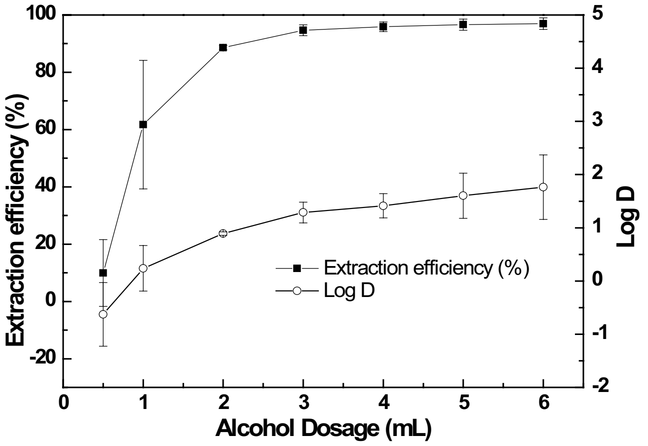

Fig. 5. Effect of alcohol dosage on Tl(III) extraction (Tl_0 50 µmol/L, 1.6 g NaCl, 6 mL wastewater, 1 mL HCl (1 mol/L), reaction time 3 min, and 298 K).

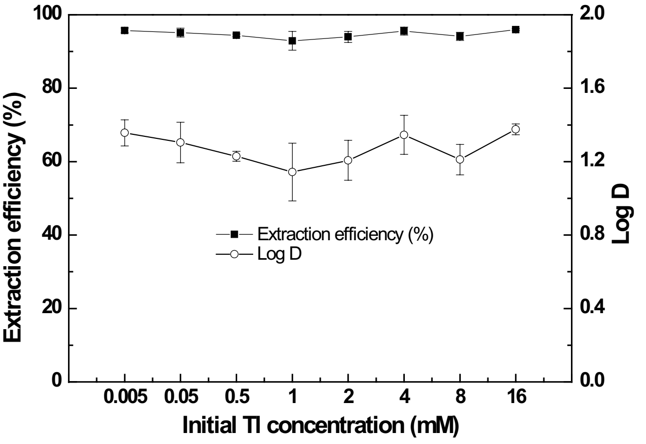

Fig. 6. Effect of initial Tl concentration on Tl(III) extraction (1.6 g NaCl, 6 mL wastewater, 3 mL alcohols, 1 mL HCl (1 mol/L), reaction time 2 min, and 298 K).

Table 1
Extraction of Tl using *n*-propanol-NaCl under different oxidation conditions (Tl_0 50 μmol/L, 1.6 g NaCl, 6 mL wastewater, 3 mL alcohols, 1 mL HCl (1 mol/L), 3 min contact time, and 298 K)

Oxidants	Dosage	Reaction time (min)	Mean ± SD (%)
O_3	10 g/h	30	93.28 ± 0.21
H_2O_2	1 mL/L	30	97.82 ± 0.21
Hypochlorite	1 mL/L	30	97.57 ± 0.10
Bromine water	1 mL/L	30	97.32 ± 0.12
No oxidant (Tl^+)	No	No	2.81 ± 1.41
No oxidant (Fresh Tl^{3+})	No	No	96.14 ± 0.33
No oxidant (4-month Tl^{3+})	No	No	95.77 ± 0.24

3.3. Extraction of Tl with different alcohols-salts systems

Two salts including NaCl and $(NH_4)_2SO_4$ were compared for Tl(III) extraction in combination of alcohols in aqueous two-phase systems (Table 2). Both extraction systems were fast to reach organic-water stratification, in which most Tl and alcohols were enriched in the upper phase while most water and salt were separated in the bottom phase (Fig. S2). Both the biphasic systems of alcohols (propanol and butanol)-NaCl or alcohols-$(NH_4)_2SO_4$ were effective in extraction of Tl(III) instead of Tl(I). The ethanol-$(NH_4)_2SO_4$ system allowed good separability of Tl(III) as well, while the ethanol-NaCl one gave no stratification (Fig. S2). Our previous study on using the ethanol-$(NH_4)_2SO_4$ biphasic system for Tl species analysis of a zinc oxide wastewater showed that over 99% of Tl in that saline wastewater was Tl(I) and that H_2O_2 is effective in oxidation of Tl(I) to Tl(III) [30].

3.4. Extraction mechanism

The FT-IR (Fig. 7) and Zeta potential (Fig. 8) spectra were used to give more insight into the extraction mechanism. The broad peaks at 3447 cm^{-1} and 1638 cm^{-1} for NaCl were assigned to the stretching vibration of the OH-groups from the trace amount of adsorption water [31,32], and were enlarged after biphasic extraction in propanol-NaCl and propanol-$(NH_4)_2SO_4$ systems due to the presence of more water in the organic phase (Fig. 7) spectra. In propanol-NaCl system, the sharp peaks at 2963, 2937, and 2874 cm^{-1} attributed to the CH_3-and CH_2-groups from pure propanol slightly shifted to 2969, 2942, and 2883 cm^{-1} due to more water was present with propanol after propanol-NaCl biphasic extraction, which is in line with the previous findings [32]. The weak bands at 1457 cm^{-1} owing to bending vibration of CH_2-group from propanol became weaker after propanol-NaCl biphasic extraction. The strong bands at 968 cm^{-1} belonged to the CH_2-OH group and the peaks at 1050 cm^{-1} belonged to the CH_2-CH_2 group [32] did not shift and their intensity decreased slightly due to mixing with the Tl complexes and trace amount of water and NaCl.

Table 2
Extraction of Tl(III) with different alcohols-salts systems (Tl_0 50 μmol/L, 1.6 g NaCl (or 3.0 g $(NH_4)_2SO_4$), 6 mL wastewater, 3 mL alcohols, 1 mL HCl (1 mol/L), 3 min contact time, and 298 K)

Combination	Run 1 (%)	Run 2 (%)	Run 3 (%)	Mean ± SD (%)
NaCl+*n*-Propanol	94.38	93.22	96.73	94.78 ± 1.46
NaCl+*iso*-Propanol	88.29	89.79	88.40	88.83 ± 0.68
NaCl+ *n*-Butanol	96.83	97.34	96.87	97.01 ± 0.23
NaCl+ *iso*-Butanol	94.41	96.22	95.42	95.35 ± 0.74
$(NH_4)_2SO_4$+Ethanol	96.18	97.82	96.84	96.95 ± 0.67
$(NH_4)_2SO_4$+*n*-Propanol	96.48	98.08	97.06	97.21 ± 0.66
$(NH_4)_2SO_4$+*n*-Butanol	95.27	96.58	96.04	95.96 ± 0.54

In propanol-$(NH_4)_2SO_4$ system, the N–H stretching vibration at 3144 cm^{-1} for pure $(NH_4)_2SO_4$ [33] became weaker, and the peaks of CH_3-and CH_2-groups from propanol nearly disappeared. The H–N–H bending deformation vibration band at 1400 cm^{-1}, the stretching vibration band at 1113 cm^{-1} and the bending vibration at 620 cm^{-1} due to SO_4^{2-} became weaker after biphasic extraction. There was unnoticeable band shift due to the bonding of Tl complexes with propanol.

For propanol-NaCl system, the mean Zeta potential of the organic (*n*-propanol) phase increased from 84.71 to 90.49 mV after salts were added, and decreased to 67.45 mV after Tl was extraction (Fig. 8). Similar pattern of Zeta potential profile was found for the propanol-$(NH_4)_2SO_4$ system. The extraction of Tl(III)-Chrocomplex anion ($TlCl_4^-$) into the organic phase led to a decrease in the Zeta potential [27]. The positive charge of the organic phase is adverse to the bonding of the metal cations [27], but is favorable to the extraction of the anion ($TlCl_4^-$) due to the electrostatic attraction.

Therefore, the $TlCl_4^-$ does not chemically interact with the propanol in both the propanol-NaCl and propanol-$(NH_4)_2SO_4$ systems. The highly hydrophobic $TlCl_4^-$ is transferred to the organic phase due to the salting-out effect.

3.5. Environmental implications

Both NaCl and $(NH_4)_2SO_4$ can be used as the salting-out agents (Table 2), and many alcohols with more than two

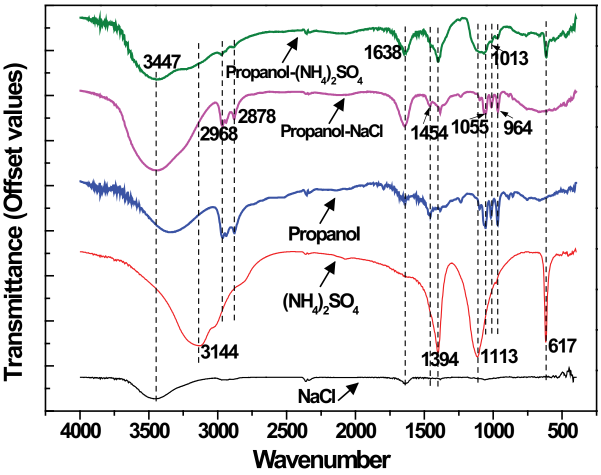

Fig. 7. The FT-IR spectra of the organic phase in the related alcohols-salts systems for Tl extraction.

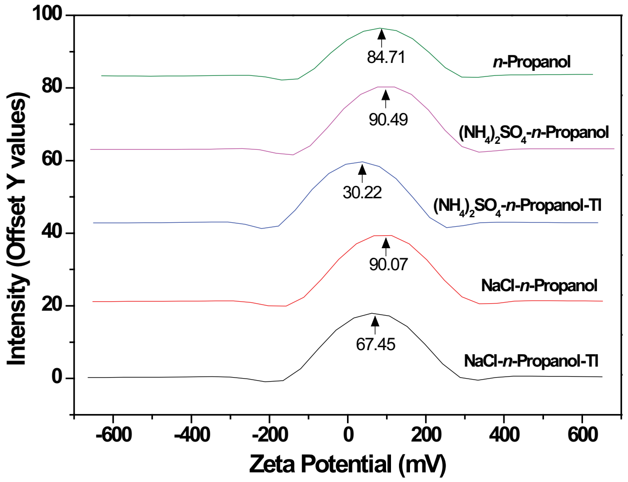

Fig. 8. The Zeta potential spectra of the related alcohols-salts systems for Tl extraction.

carbon atoms can be combined with the above salts as biphasic separation systems (except NaCl-ethanol, Fig. S2). This implies that both the alcohols-NaCl and alcohols-$(NH_4)_2SO_4$ aqueous biphasic systems can be applied in the analysis of the valence of Tl in the wastewater. Based on the comparison of extraction with and without oxidation (Table 1), this technique can be also used to assess the oxidizability of the oxidants to Tl. Efficient extraction of Tl can be achieved by combining oxidation with strong oxidants for both synthetic (Figs. 1–6) and industrial wastewater (Table S1) in which Tl(I) dominates against Tl(III). This suggests that Tl can be extracted using a combination of oxidation and this alcohols-salts biphasic system, by which the alcohols in the organic phase and the salts in the water phase can both be recovered by evaporation.

4. Conclusions

Both the alcohols-NaCl and alcohols-$(NH_4)_2SO_4$ aqueous biphasic system show highly effective extraction of Tl(III) from wastewater. The systematical study on *n*-propanol-NaCl extraction system suggests that the contact time, reaction temperature, acidity, and initial Tl concentration have little impact on the Tl(III) extraction, while the dosage of NaCl and *n*-propanol play important roles in the salting-out and Tl(III) extraction. Strong oxidants including O_3, H_2O_2, bromine water, and hypochlorite are effective in oxidation of Tl(I) to Tl(III). The chloride from NaCl in alcohols-NaCl system or from HCl in alcohols-$(NH_4)_2SO_4$ system is vital for the complexation of Tl(III) to $TlCl_4^-$. The alcohols-salts two-phase system is not only a potential means to the analysis of Tl speciation but also an alternative technique to extraction of Tl in water and wastewater.

Acknowledgments

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Supplementary information

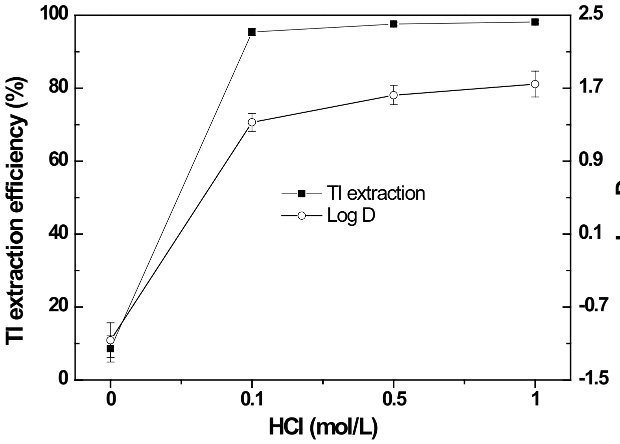

Fig. S1. Effect of HCl concentration on Tl(III) extraction by alcohols-$(NH_4)_2SO_4$ system (Tl_0 50 μmol/L, 3.0 g $(NH_4)_2SO_4$, 6 mL wastewater, 3 mL alcohols, 1 mL HCl 3 min contact time, and 298 K).

Table S1
Extraction of Tl from zinc oxide production wastewater using *n*-propanol-NaCl system (1.6 g NaCl, 6 mL wastewater, 3 mL alcohols, 1 mL HCl (1 mol/L), 3 min contact time, and 298 K)

Oxidants	Dosage	Reaction time (min)	Mean ± SD (%)
No oxidant	No	No	4.67 ± 0.82
O_3	10 g/h	30	97.29 ± 1.63
H_2O_2	1 mL/L	30	98.97 ± 1.07
Hypochlorite	1 mL/L	30	98.48 ± 0.64
Bromine water	1 mL/L	30	98.95 ± 0.75

Fig. S2. The photo of the stratification of the *n*-propanol-NaCl and the ethanol-NaCl systems (Tl_0 50 μmol/L, 1.6 g NaCl, 6 mL wastewater, 3 mL alcohols, 1 mL HCl (1 mol/L), 3 min contact time, and 298 K).