Solvent Extraction of Gold using Ionic Liquid Based Process

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Abstract. In decades, many research and mineral processing industries are using solvent extraction technology for metal ions separation. Solvent extraction technique has been used for the purification of precious metals such as Au and Pd, and base metals such as Cu, Zn and Cd. This process uses organic compounds as solvent. Organic solvents have some undesired properties i.e. toxic, volatile, excessive used, flammable, difficult to recycle, low reusability, low Au recovery, together with the problems related to the disposal of spent extractants and diluents, even the costs associated with these processes are relatively expensive. Therefore, a lot of research have boosted into the development of safe and environmentally friendly process for Au separation. Ionic liquids (ILs) are the potential alternative for gold extraction because they possess several desirable properties, such as a the ability to expanse temperature process up to 300°C, good solvent properties for a wide range of metal ions, high selectivity, low vapor pressures, stability up to 200°C, easy preparation, environmentally friendly (commonly called as "green solvent"), and relatively low cost. This review paper is focused in investigate of some ILs that have the potentials as solvent in extraction of Au from mineral/metal alloy at various conditions (pH, temperature, and pressure). Performances of ILs extraction of Au are studied in depth, i.e. structural relationship of ILs with capability to separate Au from metal ions aggregate. Optimal extraction conditon in order to gain high percent of Au in mineral processing is also investigated.

Keywords: solvent extraction, gold separation, metal ions, ionic liquids, mineral processing

INTRODUCTION

Gold is an indispensable and nonsubstitutable strategic resource due to its broad applications in industry, electronics, jewelry, medicine, as well as national economy [1, 2]. High value of gold along with increasing demand makes people try to recover gold from secondary sources (e.g. waste catalysts, mobile phones, and computer circuit boards) [3, 4]. Among selection of recovery methods, solvent extraction is the most efficient techniques to separate and preconcentrate gold. There are many selection of solvent for gold extraction such as amide derivatives [5, 6], calixarene derivatives [7, 8], and sulfur-containing reagents [9]. Nevertheless, those solvents have limitations in terms of selectivity and toxicity [10]. Ionic liquid (IL) is an attractive alternative to cope said problems due to its inherent "green" nature and high performance potential [11, 12].

Gold (III) is the major source of gold separated using solvent extraction technique. The gold (III) extraction usually conducted in aqueous chloride media continued by using high molecular weight amines or tertiary amines diluted in nonpolar organic solvents. This way, gold (III) in the form of anionic tetrachloroaurate ($[AuCl_4]^-$) is extracted by cationic protonated amines [5, 13-15]. ILs have been said applicable to replace those solvents for gold (III) extraction [16-20].

ILs are low melting temperature salt composed of organic cations and organic or inorganic anions [21-23]. ILs have some beneficial properties such as environmentally friendly [24], low vapor pressure [25], non-flammable [26], good thermal stability [27], and wide electrochemical window [28]. In addition, many works have been performed to replace conventional organic solvents for metallic ions liquid-liquid extraction [29]. In extraction metal from aqueous, the range or metal recovery can achieve >98 %. Generally, ILs work in room temperature and has weak anion and cation bond so it does not need to be heated [30].

IL for the solvent extraction of gold is one promising alternative to cope the limitation of existing solvent. However, the selection of IL solvent is still the main challenge in its commercialization. The potential of IL for gold solvent extraction has been demonstrated well by various authors [31-33]. This review paper is focused to investigate of ILs that have the potentials as solvent in extraction of Au from mineral/metal alloy at various conditions (pH, temperature, and pressure). Performances of ILs extraction of Au are discussed in detail. Structural relationship of ILs with capability to separate Au from metal ions aggregate and optimal conditions extraction in order to gain high percent of Au in mineral processing is also investigated.

GENERAL METHODS TO SEPARATE METAL IONS

Separation of ionic species from mixtures has become an interesting topic which leads to researches since a long time ago. Depends on the main component of interest, the separation can be either the removal or the extraction of those ionic compounds. In the case of metal ions, especially the rare earth metal, the main separation process is extraction prior to stripping process to acquire purified stream of metal-bearing aqueous solution.

Some alternative methods can be chosen to separate ionic compounds including the most common solvent extraction [34], ion exchange [35], electrophoresis [36], chromatography [37], magnetic field [38], adsorption [39], membrane separation [40], and also IL separation [41]. Each separation method has been studied separately to improve the performance. Varying the pH and complexing the species have become the most common methods used in improving the separation performance. The combination of both is also possible to achieve a better separation [42]. The idea of complexation is to modify the properties such as the interaction between the ions/complexes with the adsorptive materials in adsorption process [39]. Furthermore, the complex formation and pH variation were also reported to enhance the separation in other mentioned methods [34-41]. Various separation methods for ionic species are summarized in Table 1.

TABLE 1. Various separation and their corresponding enhancement method for some metals

Separation Method	Compound Separated	Enhancement Method	Enhancement Agent	Ref
Adsorption	Ga^{3+}, In^{3+}, Fe^{3+}, Cu^{2+}, Mo^{6+}, Ni^{2+}, V^{4+}, Zn^{2+}, Co^{2+}, Al^{3+}, Mn^{2+}	Complex Formation	EDTA (ethylenediaminetetraacetic acid)	39
Electrophoresis	Na, K	Electric Voltage	electricity	36
Electrophoresis	Eu, Gd, Dy, Y	Ligand Formation	acetic Acid	42
Ion Exchange	Zu, Zn, Fe, Zr, Sc, Y	Complex formation	EDTA (ethylenediaminetetraacetic acid)	35
Magnetic Field Separation	Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, and Cd^{2+}	Magnetic Field	ND	38
Ultrafiltration	Ni^{2+}	Micelle formation	anionic and nonionic surfactant	40
Ultrafiltration	Co^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}	Ligand Formation	ND	43
Ultrafiltration	Cr^{6+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}	Complex formation	ND	44
Ultrafiltration	Cs^+, Sr^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, and Cr^{3+}	Micelle formation	SDS	45

Besides utilizing the interaction of ionic species, membrane separation also separates ionic compounds based on their size. However, the ions are very small in size and considering the membrane separation range, the process should be in the nanofiltration or reverse osmosis range. However, some modifications have been performed to increase the size of the compound by complex or micellar formation [40, 46]. A micelle can be formed by addition of surfactants hence surround the ions and form a bigger species. Thus, the separation can be performed in ultrafiltration regime with bigger pore size and lower pressure. The illustration of micelle formation is shown in
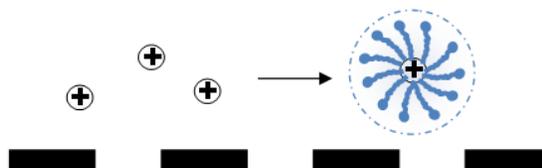

FIGURE 1. Schematic illustration of micelle formation in ultrafiltration

GENERAL SOLVENT EXTRACTION OF GOLD SEPARATION

Solvent extraction is an old method that has been studied in the 1970s case of metal separation, especially for gold. The extraction mechanism utilizes the properties that the metal is more soluble in the extraction solvent. The solubilization process appears due to a complex or chelate formation between the metal and the extractant.

Specifically for gold separation, the most common extractant used is tri-n-butyl phosphate $(CH_3CH_2CH_2CH_2O)_3PO)$ and other alcohol derivatives [47-49] which extracting gold from cyanide media. Moreover, several extractants are used for gold extraction in commercial operation such as dibutyl carbitol (DBC), MIBK (methyl isobutyl ketone) and DIBK (diisobutyl ketone). Some companies developed commercial amine-derivatives as the extracting agents which was claimed to have better separation performance, such as Lix (LIX 84-I was used for nickel extraction, LIX 63 was used for copper extraction) [49, 50], Hostarex [51] and Cyanex [52]. Those were reported to give significant improvements in term of kinetic to reach equilibrium, organic phase diluent and the concentrations of metal and the extractant [52].

Researchers have studied deeper in the solvent extraction technique in order to improve its performance. Richter [53] proposed an accelerated extraction technique by utilizing elevated temperature and pressure. On the other hand, Mooiman [54] reported that addition of organic phosphorous compounds can enhance the extraction process. Nowadays, some external driving forces have been integrated to the extraction process giving the assisted separation processes which are more efficient. Kislik [34] summarized the improved extraction process may include pressurized liquid extraction, microwave-assisted extraction, supercritical fluid extraction, subcritical water extraction, liquid membrane extraction and IL extraction.

IONIC LIQUID POTENTIAL IN SOLVENT EXTRACTION

ILs have been proposed for extraction of various materials and referred as "green" solvents [55]. They show unusual solubility behavior in water and organic solvents. Moreover, the selection of anions and cations can make huge different making them tunable for specific purposes. ILs appear to be a suitable replacement of organic solvent in liquid-liquid extractions [31].

Many ILs employed for metal ions extraction have hydrophobic character allowing them to extract hydrophobic compounds in biphasic separations. Unfortunately, metal cations tend to favor to stay in the aqueous solution. Therefore, metal ions hydrophobicity needs to be increased to remove them from aqueous solution. Extractants (or chelators, ligands) are usually needed to form metal complexes to overcome said problem [18-20]. The solvation of crown-ether complexes in IL is favored compared with conventional organic solvents in terms of thermodynamics [19]. This is the key advantage of ILs for metal ion extractions. There are several key factors to control the extraction efficiency of ILs [33]:

1. Variation of IL structure (especially its cation side chain) may change its hydrophobicity that can boost the partition coefficients of metal ions [18, 21]
2. Modification of extractants (e.g. crown ethers) to optimize selectivity for a specific application [22]
3. Modification of system pH to control the efficiency of metal complexes [23]

There have been a lot of works to investigate the performance of IL for solvent extraction of various metal ions. For example, 1-alkyl-3-methylimidazolium hexafluorophosphate or [CnMIM][PF$_6$] has been used to extract alkali metals (Li^+, Na^+, K^+, Rb^+, Cs^+) [21, 56, 57], alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) [21, 56], and even heavy and radioactive metals (Pb^{2+}, Cu^{2+}, Ag^+, Hg^{2+}, U^{2+}, Th^{4+}) [21, 30, 32, 58-60]. Furthermore, Zang et al. [61] used silica gel modified N-3-(-3-triethoxysilylepropyl)-3-methylimidazolium chloride (SG-[(TESP)MIM]Cl) to separate Fe (III) in aqueous solution (natural water sample), which recovery is ranged from 94.0% to 99.8%. Yang et al. [62] were also separated Eu (III) from rare earth metal ions using three types of ILs i.e. [C$_4$MIM], [C$_8$MIM], and [C$_{12}$MIM] [Tf$_2$N] showed at [C$_{12}$MIM] it took 5 minutes to reach equilibrium, and was attained within 5 minutes in [C$_4$MIM]. The other researchers [63] separated lanthanide ions from rare earth with 1-decyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide/bis (perfluoroethanesulfonyl) imide ([C$_{10}$MIM][NTf$_2$]/[BETI]) based process, the method that they used was IL-based TALSPEAK (Trivalent actinide-lanthanide separation). While, Regel-roso with coworkers [64] have been removed the mixture of Zn (II), Fe (II), and Fe (III) from chloride solution used phosphonium ILs such as trihexyl (tetradecyl) phosphonium chloride (Cyphos IL 101) and trihexyl (tetradecyl) phosphonium bis (2,4,4-trimethylpentyl) phosphinate (Cyphos IL 104) with the efficiency extraction result of Zn (II)

was 100%. The difference of each separation is the extractant/metal chelator used as stated before. Moreover, task-specific ILs (TSIL) have been proposed to not only serve as the hydrophobic solvent but also the extractant at the same time [33].

PERFORMANCE AND MODIFIED OF IONIC LIQUIDS EXTRACTION IN GOLD SEPARATION

There are some extraction methods for gold separation e.g. aqueous two phase systems (ATPs), leached using aqueous alkaline cyanide (AAC), cloud point extraction (CPE), liquid-liquid microextraction, microemulsion extraction, and ion exchange extraction [65-69]. IL extraction is a potential alternative method to separate gold from mixture of metal ions. As an example, (1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$)) is known has potential to increase solubility of metal include Au nanoparticles [65, 70].

ILATPs have made interest pay attention for some recent researchers to separate gold in industrial scale since currently to recover gold from secondary source acid leaching or organic solvent extraction is still used. The utilization of acid or organic solvent is not environmentally friendly and high cost [66, 69, 71, 72]. Zheng et al.[66] applied imidazolium IL-based ATPs for gold (III) extraction, the IL used was 1-hexyl-3-methyl imidazole dodecyl sulfonate ($[C_6MIM][C_{12}SO_3]$), which is was used in and ATPs with PEG6000. Their research showed that the IL has good performance to recover gold is about 98%. Moreover, Yang and coworkers [65] have been separated gold used $[C_8MIM][PF_6]$ from gold leached using aqueous alkaline cyanide with recovery of 98 %. Based on several researches, it is shown that IL has good properties to increase the performance of gold separation. The performance of various IL in gold separation is summarized in Table 2.

Table 2 show that IL has better performance than organic solvent such as poly(oxyethylene)-9-nonyl phenyl ether that can only recover 63% of Au [67]. Frequent types of IL used is $[C_nMIM]^+$ cation and some organic and inorganic anions as successor of organic solvent to separate gold particles. $[C_nMIM]^+$ is structurally similar to the quaternary ammonium in general and it follows the similar extraction mechanism for gold, which is through ion exchange and neutral complex formation. $[C_nMIM]^+$ cation is also very similar with quaternary ammoniums follows extract metals mechanism through ion exchanges and neutral complexes formation such as $[C_nMIM]^+$ $AuCl_4^-$ [73-75]. Length effect of carbon chain in $[C_nMIM]^+$ cation has significant impact in gold separation. the gold ions has good solubility in water, so a solvent with high hydrophobicity properties is needed, such as those that have been exposed by several researchers [29, 65, 66, 76]. Futhermore, another IL like Cyphos IL-101 (tetraalkylphosphonium chloride) is also has the potential to separate gold, because it has a stronger affinity for Au(III) than another metal ions *viz.* Pd(II), Zn (II), and Pt(IV) based on the competition effect (in large excess of the competitor metal) [77-79]. Consequently, liquid-liquid extraction that use Cyphos IL-101 has made the separation occurred consistent, gold is adsorbed on the Cyphos IL-101 through the stoichiometric interaction of $R_3R'P^+$ with $AuCl_4^-$, therefore recovery % the extraction efficiency of Au is high, in quantitative extraction (>99%) can be achieved, because 90% or even 95% is not considered sufficient for gold extraction.[77-79].

Accordingly, modified approach of IL structure is needed to improve the performance in gold separation. Some modifications that can be done are modification of cation carbon chain to increase hydrophobicity and increasing the acidic value of cation to trap gold anion in the cation. Thus, that process can decrease the solubility of gold in water or polar solvent including metal ions mixture.

OPTIMIZATION OF GOLD SEPARATION CONDITION BY IONIC LIQUIDS EXTRACTION

As explained above, IL has potential as an extractant to separate gold. The condition of separation is still in the development stage to obtain maximum recovery. Therefore, a lot of researchers are worked further deeply to get best structure of IL for gold separation [1, 2, 29, 65, 78, 80]. Basically, IL working in specific conditions sample, to obtain the optimum extraction of gold can be achieved by the setting of the character (chemical structure) of IL [58, 69, 75, 81]. The character of IL can be changed by adjusting cation and anion framer, nevertheless adjusting cation and anion does not always give a significant effect [82, 83]. Yang et al. [62, 65] showed that the separation of Au is not dependent to anion. However, increasing carbon number of cation in alkyl group may cause an increase in the extraction of Au. This indicated that shortening the cation alkyl group does not increase its Au extraction capability. The same result was reported by Regel-Rosocka et al. [64] who showed that shorter cation alkyl groups and anions phosphonium do not give any effect on liquid extraction efficiency of Au (II).

TABLE 2. Performances of ILs and organic solvent extraction in gold separation

Ionic Liquids	Components in Sample	Recovery % of Au	Reference
1-hexyl-3-methylimidazolium hexafluorophosphate [HMIM][PF$_6$] Combined with chelating agent: N-(4-{4 (anilinocarbothioyl)amino]benzyl}phenyl)-N-phenylthiourea	Au (III) and Ag (I)	>95	[84]
Hidrophobic imidazolium: 1-butyl-3-methylimidazolium hexafluorophosphate([C$_4$MIM][PF$_6$]),1-hexyl-3-methylimidazolium hexafluorophosphate ([C$_6$MIM][PF$_6$]), 1-octyl-3-methylimidazolium hexafluorophosphate ([C$_8$MIM][PF$_6$]), and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide([C$_8$MIM][N Tf$_2$])	Au (I) from alkaline cynide	With [C$_8$MIM][PF$_6$]) is >98, another ILs are >90	[65]
TX-100, TX 114 (IL based surfactants)	Gold nanoparticles in water	89.6-100	[68]
1-hexyl-3-methyl imidazole dodecyl sulfonate [C$_6$MIM][C$_{12}$SO$_3$]	Gold chloride, HAuCl$_4$.4H$_2$O, HAuCl$_4$·4H$_2$O in dilute hydrochloric acid	97.56	[66]
Poly(oxyethylene)-9-nonyl phenyl ether		63	[67]
[C$_{14}$-4-C$_{14}$IM]Br$_2$ as an ionic-liquid type imidazolium gemini surfactant	HAuCl$_4$·4H$_2$O	99.55	[29]
Guanylthiourea, 1-methylimidazole, 2-mercapto-1-methylimidazole ligands	Gold (I) from ammonium buffer and ammoniac thiosulphate solutions	99	[85]
Tetraalkyl phosphonium chloride (Cyphos IL-101)	Gold from HCl solutions	95	[79]
(Cyphos IL-101) was immobilized on Amberlite XAD-7	Au(III) recovery from HCl	>99	[78]
[BMIM][PF$_6$]	Gold nanoparticles	99	[76]
Cyphos IL-101 embedded in the PVC polymer inclusion membrane	Au (III)	>94	[77]

The important parameter to optimize the performance IL extraction is its operating condition, such as temperature stirring time, and the most important is setting of cation and anions framer to produce IL. The setting of anions and cations is not a simple matter. The experimental results showed that the addition of soft anions will decrease the capability of Au extraction [30, 76, 86]. Therefore, to improve the IL performance in Au separation, an extractant can also be modified by adding chelator [62, 63, 79, 87]. Au has similar properties such as has ion charge is 2+ in aqueous condition as like as other ion metals such as Cu, Ag, Zn, and Pd, so that one of the most important task is to separate the ions from one another. Researchers should pay attention of the solubility of each ion metals in water [69, 77, 81, 85].

Since Au ions has good solubility in water or polar solvent, a solvent with high hydrophobicity is needed to seperate Au from ions metal mixture [65, 70, 87]. The most widely studied IL cation include 1-alkyl-3-methylimidazolium [C$_n$MIM]$^+$ and N-alkylpyridinium [C$_n$py]$^+$ where the alkyl group is typically an alkane and its length (n) or branching allows for moderate adjustment of the resulting properties such as hydrophobicity, melting point, or viscosity [82, 88, 89]. Anions such as PF$_6^-$, BF$_4^-$, and a series of fluorinated anions have been used to produce hydrophobic IL [83, 90, 91]. Accordingly, further research on the modification of IL is continuously developed to obtain appropriate characteristics needed in the separation of Au.

SUMMARY

Based on numerous paper reviewed, many ILs employed for metal ions extraction have hydrophobic character allowing them to extract hydrophobic compounds in biphasic separations. ILs have the potential as a solvent in gold separation from ions metal mixture and alloy. Common cations used are 1-alkyl-3-methylimidazolium [C_nMIM]$^+$ and N-alkyl pyridinium [$C_n$py]$^+$, while common anions used are PF6-, BF4-, and a series of fluorinated anions. Functional ILs that have been studied and give the best result in gold separation are (Cyphos IL-101) immobilized on Amberlite XAD-7, [BMIM][PF$_6$], and [C_{14}-4-C_{14}IM]Br$_2$ as an ionic-liquid type imidazolium Gemini surfactant. The important things in preparing IL as solvent are structure relationship with the capability to trap gold ion (decreasing the solubility of Au in water) and separation condition e.g. temperature, pH solutions, and hydrophobicity of IL. Therefore, modification approach of IL structure is needed to improve the performance in gold separation, which is long carbon chain of cation to increase the hydrophobicity of IL, even increasing the acidic value of cation, so that it can easily trap the gold (usually as AuCl$_4^-$ anion) within cation, so that recovery % of Au will be maximum.

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