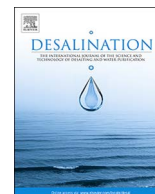




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## A critical review on membrane extraction with improved stability: Potential application for recycling metals from city mine

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## ABSTRACT

Mining from the city is one of the future directions for sustainable resource management. The separation of highly dispersed, low concentration valuable metals requires highly efficient extraction technology, where membrane extraction has shown significant advantages owing to its potentially high selectivity and low footprint. This review summarizes the recent progress in membrane extraction with respect to the development of membrane materials and the process configurations with special focus on preventing the loss of the organic extractant and/or degradation of the membrane materials. Prior research work was reviewed first on the development of various membrane materials for extending the membrane performance. Further developments on membrane configuration and process are presented on ion exchange membranes and membrane contactors, and composite hollow fiber membranes where the advantages and problems are stressed. Hydrophilic/hydrophobic blend polymers and block co-polymers have shown much more extended lifetime, which is a potential development direction. In summary, this review provides not only the recent development on membrane materials but also the application process/scheme that can help to improve the performance of membrane extraction, which might be beneficial for a broad audience ranging from academic scientists and industrial engineers who are looking for pioneering alternative solutions for city mining.

### 1. Introduction

#### 1.1. Recycle of metals

Recycle is a short to medium term sustainable solution for metals. The environmental footprint of humankind is unsustainable due to limited natural resources and aggressive human activity on land, water, energy, and materials. To reduce the environmental footprints, it requires a global transformation of the structure of the economy [1]. Challenges and opportunities coexist. Great business opportunity in a century has been envisioned beyond only social impact [2]. As a pioneer, Apple company's closed-loop supply chain is manufacturing products using only renewable resources or recycled material to reduce the need to mining materials from the earth [3].

Metals are infinitely recyclable, however, progress of recycling is hampered by product design, recycling technologies, and the thermodynamics of separation, and sometimes more importantly social behavior [4]. For instance, replacement of copper metal by other metals or

alloy will reduce growth in copper demand; as the resources in mines became scarcer, its price will rise till a value which the economic effect of recycling can compete [5]. Study showed that multimillion tons of metals, Cu (711.6 m ton), Fe (8.1 m ton), Al (37.0 m ton), and Pb (12.1 m ton) could be sourced out from urban mine by 2040 [6]. In Switzerland, valuable metals ( $0.4 \pm 0.2$  mg/kg Au and  $5.3 \pm 0.7$  mg/kg Ag Au, Ag) were found in the incinerated municipal solid waste (MSW) [7]. In practice, frequently utilized metals and metalloids are often not reused at the end of the life cycle, as shown in Fig. 1. For the specialty metals or rare earth metals used in very small amounts in high tech products such as consumer electronics, lightening sources, durable automobile parts, sensors, engines etc., this is uniquely true; the short life time of the consumer products imposes recycling barriers. Collection and purification are thermodynamically unfavorable when metals are mixed with other materials in a small quantity [8].

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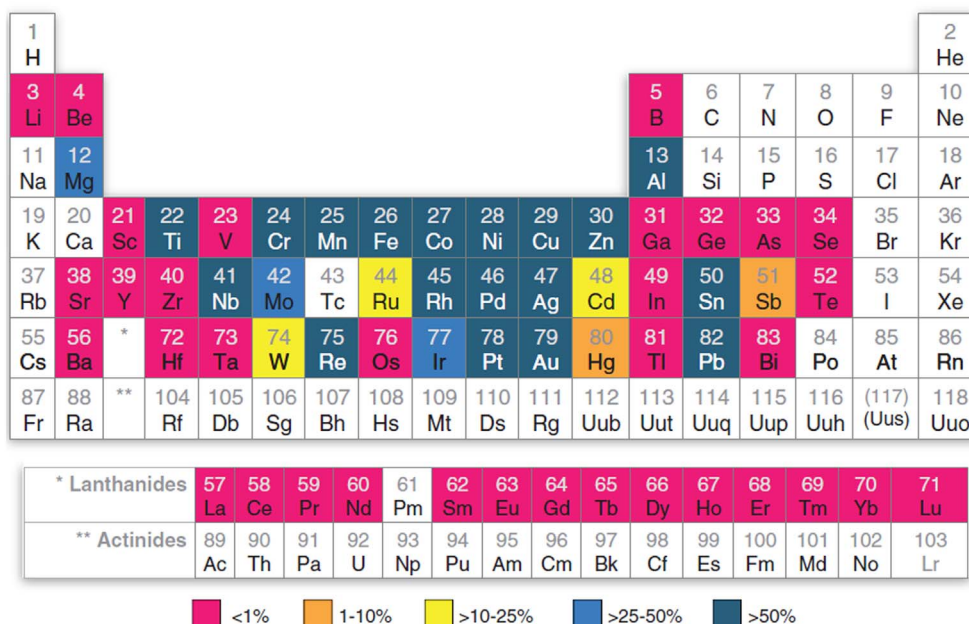


Fig. 1. Global estimates of end-of-life recycling rates for 60 metals and metalloids, circa 2008 [9]; the color legend indicates the recycle rate.

## 1.2. Mining from city

Mining from city is becoming an indispensable choice. Waste materials from mining, infrastructure and products are now becoming valuable 'above-ground' mineral resources. Previous studies have indicated that urban mining for metals recycling can decrease energy consumption and pollutants emission compared to the extraction of metals from natural minerals [10]. Waste electrical and electronic equipment (WEEE) has become increasingly important over the last years. CSIRO Flagship Collaboration Fund identified that the value of metals in end-of-life products is more than AUD6.0 billion per year [11]. For Belgium, 80 and 87% less resource consumption is achieved for desktops and laptops respectively in 2013; the natural resource consumption of the recycling scenario is much smaller than land filling the WEEE [12]. High values of the resource index indicate that the waste is important to the European Union (EU) economy and hence has significant potential for recycling as a resource [13]. Recovery opportunity is widely accessible for metals [14] and phosphorous [15, 16] from sewage sludge, and uranium and rare earth metals from copper mine waste streams [17].

Since city mines covers a large spectrum of metals or metal ions, we will focus on only the widely dispersed metals which are suitable for extraction and purification in a liquid form rather than in a bulky solid form. Wastewaters containing precious and heavy metal ions are located at the vicinity of the large cities such as Shanghai, Shenzheng, and many small and medium cities around China. They are the main concerns of the Chinese environment protection plan. Due to the past short-term industry development of Chinese economy, many industries discharging large amount of waste streams are facing stringent environmental regulations. There is a strong incentive for them to adopt a new sustainable development plan to survive. As a retrofit to the existing industry parks, the extraction of the precious and heavy metals ions from their waste streams would be beneficial to both the environment and the economics of the individual industry. Water reuse and mineral recovery could be combined to reduce the cost [18]. Operational cost for an ultrafiltration-nanofiltration membrane processes for gold acid mine drainage was estimated to be 0.263 US\$/m<sup>3</sup> of effluent [19]. Extraction of the metals from the concentrate is expected to generate extra cash revenue which may cover the operational cost or potentially the capital cost.

## 1.3. Separation and purification technologies for metals

Bulk metal materials separated mechanically are responsible for the majority of the common minerals. However, different methods are needed for precious and valuable metals of low content and widely distributed in alloys. To collect, transport and mechanically treat these materials is not the focus of this review. Downstream of this supply chain, separation and purification of the single element from a complicated mixture is difficult and energy intensive. Therefore, an efficient and highly selective separation technique is necessary to extract, separate and purify the metals from a mixture. Table 1 lists the separation and purification approaches currently employed in practice. Obviously, the characteristics of these technologies dictates that no single process is all-purpose to yield products of a high purity. For example, incineration/combustion is suitable for the upstream treatment prior to downstream purification processes; chemical precipitation, nanofiltration, electro dialysis, ion exchange, and adsorption technologies, except for some limited cases, are generally not used for the final purification stage. Chemical precipitation has been used for production of lithium carbonate in salt lake brine in South America, but not suitable for the brine in Northwest China where the salt lake brine is of high magnesium/lithium ratio [20]. The most frequently utilized purification approach is liquid-liquid extraction for obtaining a highly purified form of the metal element, which will be the focus of present review.

The chemistry and the processes to attain the targeted purity of liquid-liquid extraction have been extensively understood. For different mixtures, the extractant and separation processes will be largely different, the variety and complicity is beyond the discussion of this review. Therefore, this review focuses on the core equipment or facilities to realize the extraction processes, particularly, the membrane based liquid-liquid extraction, or membrane extraction. The state-of-the-art of membrane based liquid-liquid extraction will be introduced. The development in this area and the key issues will be analyzed.

## 2. Membrane extraction: highly efficient purification technology for metal ions

### 2.1. Equipment for liquid-liquid extraction

Four types of industrial scale extraction equipment are identified as mix-settler, column, centrifugal machine and membrane. Except for

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