



Research Paper

A novel polymer inclusion membrane based method for continuous clean-up of thiocyanate from gold mine tailings water



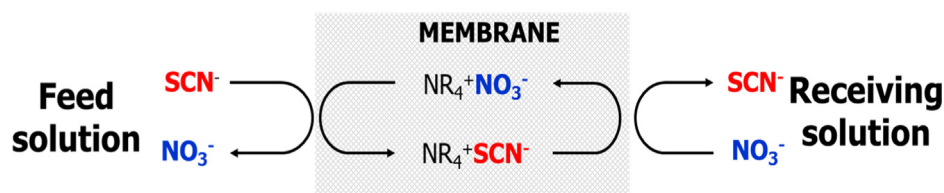
Youngsoo Cho, Robert W. Cattrall, Spas D. Kolev*

School of Chemistry, The University of Melbourne, Victoria 3010, Australia

HIGHLIGHTS

- A polymer inclusion membrane (PIM) for SCN^- clean-up from gold mine tailings waters.
- The PIM contained 20% Aliquat 336, 10% 1-tetradecanol and 70% PVC.
- The PIM separated counter-current feed and receiving streams in a module.
- Complete removal of 1000 mg/L SCN^- in 3 modules connected in-series was achieved.
- The 3-module system operated continuously without any fault for 45 days.

GRAPHICAL ABSTRACT



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ABSTRACT

Thiocyanate is present in gold mine tailings waters in concentrations up to 1000 mg L⁻¹ and this has a serious environmental impact by not allowing water reuse in the flotation of gold ore. This significantly increases the consumption of fresh water and the amount of wastewater discharged in tailings dams. At the same time thiocyanate in tailings waters often leads to groundwater contamination.

A novel continuous membrane-based method for the complete clean-up of thiocyanate in concentrations as high as 1000 mg L⁻¹ from its aqueous solutions has been developed. It employs a flat sheet polymer inclusion membrane (PIM) of composition 70 wt% PVC, 20 wt% Aliquat 336 and 10 wt% 1-tetradecanol which separates counter-current streams of a feed thiocyanate solution and a 1 M NaNO₃ receiving solution. The PIM-based system has been operated continuously for 45 days with 99% separation efficiency. The volume of the receiving solution has been drastically reduced by recirculating it and continuously removing thiocyanate by precipitating it with *in-situ* generated Cu(I).

The newly developed PIM-based thiocyanate clean-up method is environmentally friendly in terms of reagent use and inexpensive with respect to both equipment and running costs.

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1. Introduction

Industrial wastewater is considered an alternative water resource in environmental programs involving water sustainability. Various Environmental Protection Authorities and Agencies

encourage the reuse of industrial wastewater after risk management and appropriate treatments have been considered in accordance with established guidelines [1].

Industrial wastewater may contain numerous chemical species which need to be removed before the water can be reused or recycled. One such species is the thiocyanate anion (SCN^-) which can be present in gold mine tailings water in concentrations as high as 1000 mg L⁻¹ and has been found to interfere with the flotation of gold bearing sulfide minerals if the tailings water is to be recycled

* Corresponding author.

E-mail address: s.kolev@unimelb.edu.au (S.D. Kolev).

[2]. This has led to significant amounts of fresh water being used and then discharged in tailings dams with the associated negative environmental impact. In addition, thiocyanate often contaminates groundwater near mine tailings dams [3] thus leading to potential surface water contamination with its harmful effects on aquatic organisms [4].

Various techniques are available for water treatment but some of them such as reverse osmosis are energy intensive and thus expensive [5]. Less energy intensive techniques for the removal of ionic species from aqueous solutions include solvent extraction [6–8] and ion-exchange [9,10]. However, the use of large volumes of organic diluents in solvent extraction is of considerable environmental and public health concern because most diluents are volatile, flammable and toxic. In addition, the loss of diluents and extractants to the raffinate increases the cost of the solvent extraction based separation process. Ion-exchange, on the other hand, is a commonly used technique for the removal of ionic species from their aqueous solutions. However, the periodic regeneration of the ion-exchange resins used creates difficulties in running the separation process continuously.

An attractive alternative to separation involving solvent extraction or ion-exchange resins can be based on the use of liquid membranes [11]. These membranes incorporate only small amounts of diluents, if any, while at the same time they offer the high selectivity, flexibility and enrichment factors of conventional solvent extraction based separation. In addition, the amounts of extractants used are much smaller compared to conventional solvent extraction applications and this makes the use of expensive but highly selective extractants economically viable. Most of the extractants used have bactericidal properties and the corresponding membranes are virtually immune to biofouling. Liquid membranes also offer faster and simpler separation than solvent extraction when the chemical species extracted into the organic phase must be transferred subsequently into an aqueous phase before further processing. This advantage stems from the fact that the corresponding extraction and back-extraction processes are integrated into a single step, taking place simultaneously on both sides of the membrane which separates the two aqueous phases, one being the feed solution and the other the receiving solution. When conventional extraction and back-extraction processes are used instead, a sequential arrangement of these processes is required. Similarly, when separation is based on the use of ion-exchange resins, the processes of retention of the target ionic species in the resin and its stripping are also conducted sequentially. The possibility of conducting extraction and back-extraction simultaneously makes liquid membranes suitable for developing separation technologies that operate continuously.

The liquid membranes most often employed in industrial separation are: bulk liquid membranes (BLMs) [12], emulsion liquid membranes (ELMs) [13–15], supported liquid membranes (SLMs) [16–20], and polymer inclusion membranes (PIMs) [21–26]. However, some of them suffer from substantial drawbacks [27]. SLMs are arguably the most popular liquid membranes used at present. However, their main disadvantage is the slow leaching of the membrane liquid phase, consisting of an extractant and diluent, into the aqueous receiving and feed solutions, thus reducing significantly the membrane lifetime. While offering the same advantages as SLMs over BLMs and ELMs in terms of simplicity of use, PIMs are characterized by better stability and longer lifetime than SLMs [21–23]. A PIM is usually prepared by solvent evaporation casting from a homogeneous solution of a polymer (e.g. poly(vinyl chloride) (PVC) or cellulose triacetate (CTA)) and an extractant (e.g. Aliquat 336, Cyanex 272, di-(2-ethylhexyl) phosphoric acid), often referred to as the carrier, in a suitable solvent (e.g. tetrahydro-

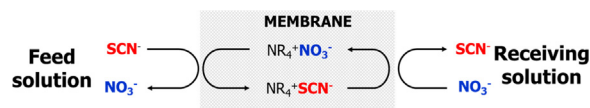
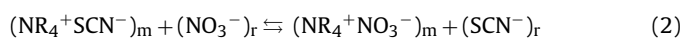
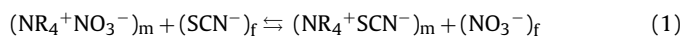


Fig. 1. Schematic of the transport of SCN^- across a PIM incorporating a quaternary alkylammonium nitrate (NR_4NO_3) as the carrier into a receiving solution containing NO_3^- as the stripping reagent.

furan (THF) for PVC based PIMs and chloroform for CTA-based PIMs). In some cases the incorporation of a plasticizer or modifier (e.g. dioctylphthalate, *o*-nitrophenyloctyl ether, 1-dodecanol) is required to achieve homogeneity and sufficient flexibility of the membrane or to increase the solubility of the extracted species in the membrane liquid phase (i.e. carrier and modifier), respectively. PIMs have been used successfully for selective separation of both inorganic and organic chemical species [21–23]. We have developed a PIM, consisting of 20 wt% Aliquat 336 as the carrier, 10 wt% 1-tetradecanol as the modifier and 70 wt% PVC as the polymer, capable of efficiently extracting thiocyanate from weakly alkaline solutions which can be quantitatively back-extracted using NaNO_3 as the stripping reagent [28]. Aliquat 336 is an inexpensive commercial extractant which consists of a mixture of quaternary alkylammonium chlorides (NR_4Cl) and small quantities of octanol and decanol. Fig. 1 shows schematically the transport of SCN^- across the PIM mentioned above after its preconditioning in a NO_3^- solution to allow the replacement of Cl^- in Aliquat 336 (NR_4Cl) with NO_3^- .

The processes involved are: (1) ion-exchange of thiocyanate with the nitrate anion of the Aliquat 336 cation-nitrate anion ion-pair at the membrane/feed solution interface (Eq. (1)), leading to the membrane extraction of thiocyanate; (2) diffusion of the newly formed Aliquat 336 cation-thiocyanate anion ion-pair across the membrane; and (3) ion-exchange of nitrate with the thiocyanate of the Aliquat 336 cation-thiocyanate anion ion-pair at the membrane/receiving solution interface (Eq. (2)) which results in the stripping of thiocyanate into the receiving solution containing NaNO_3 and the regeneration of the original Aliquat 336 cation-nitrate anion ion-pair and its subsequent diffusion towards the membrane/feed solution interface to transport another thiocyanate anion.



where *f* and *r* refer to the feed and receiving solutions, respectively, and *m* refers to the membrane phase.

This type of membrane transport is known as facilitated transport [23]. The concentration of the stripping reagent in the receiving solution (i.e. NO_3^-) is significantly higher than that of the target chemical species (i.e. SCN^-) in the feed solution and as a result the target chemical species can be quantitatively transported from the feed into the receiving solution.

This study describes the use of a flat sheet PIM with the composition mentioned above in a separation module and a system of such modules connected in series for the continuous removal of thiocyanate from an aqueous feed solution into a receiving solution containing $1.0 \text{ mol L}^{-1} \text{ NaNO}_3$. The various parameters influencing the efficiency of the removal of thiocyanate such as its feed solution concentration, the flow rates of the feed and receiving solutions, the flow configuration and the PIM surface area exposed to the aqueous solutions are discussed. In addition, an approach is proposed where thiocyanate is removed chemically from the receiving solution thus allowing the use of a much smaller volume of a receiving solution

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