ADVANCES IN ARSENIC (V) SEPARATIONS TECHNOLOGY FROM LIQUID STREAMS.

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ABSTRACT

Arsenic (V), in its (V) oxidation state, is considered as one of the most hazardous metals, thus its removal from the As-bearing streams is of the utmost priority. In liquid streams, As(V) can be presented as H3AsO4, H2AsO4-, HAsO32- and AsO43- species depending upon the pH and being the technologies used for As(V) removal bases in the chemistry of the above species. This work considered three separations technologies that can be used to improve the removal of As(V) from liquid streams before its final precipitation and disposal as a crystalline or non-crystalline arsenic salt. Liquid-liquid extraction is a proven technology for the recovery of a number of metals, and is used in medium and large scale operations and when the solute concentration is high. Liquid membrane technologies which used organic phases can be considered as a more recent development that is used to extend the range of conditions under which liquid-liquid extraction processes are viable. Adsorption and ion-exchange processing are useful to remove species from non-clarified liquid streams and when the concentration of the solute is low.

KEY WORDS: Liquid stream treatment; Liquid-liquid extraction; Liquid membranes; Ion exchange; Adsorption; Arsenic
1. INTRODUCTION

Arsenic is a common constituent of more than 200 minerals and though it is considered to be an essential element, also a lot of arsenic compounds is toxic. The toxicity of this element strongly depends on its binding form, thus, organic arsenic compounds are less toxic than inorganic arsenic ones, whereas As (III) species are essentially less toxic than As (V) compounds. Besides that arsenic can cause a number of illnesses, arsenic is carcinogenic and may cause lung, bladder, liver, renal and skin cancer (Hindmarsh et al., 2002; Bissen & Frimmel, 2003).

The predominant form of inorganic arsenic in aqueousoxic environment is As (V) as $\text{H}_3\text{AsO}_4$, $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$, $\text{AsO}_4^{3-}$ species with $\text{pK}_a$ values of 2.2, 7.0 and 11.5, respectively, whereas the sources of arsenic contamination in waters are classified as natural and anthropogenic. Natural sources of arsenic contaminated included the dissolution of arsenic compounds into the water by several factors (geothermal, bio geochemical, etc.); contamination from human activities includes mining, disposal of waste chemicals, the application of arsenic compounds in a series of materials, etc.

Contamination of waters with this element is a problem in various countries: Argentina, India (West Bengal), Mexico, Germany, Austria (Styria), Chile, United States, etc., and most significantly in Bangladesh, being the recommended maximum contamination level (MCL) of arsenic in drinking waters around 50 $\mu$g/L with the most stringent regulations in i.e. Europe, Australia and USA, targeting the MCL value as 10 $\mu$g/L.

To help to reach these levels, companies are increasingly being forced either by regulations, cost and social pressures to reduce the amount and increase the quality of all the wastes, including liquids, they produce.

Traditionally, arsenic-contaminated liquid streams have been treated by physico-chemical as well as biological processes and though generally they can be considered as effective, these processes often do not provide the selectivity necessary to create valuable product streams in order to their recycle or re-use, moreover, the sludge formed as a by-product of these technologies can become a further disposal problem.

By the conceptual use of the separation technologies the latter objective can be achieved by dividing the liquid streams into the necessary liquid phases that facilitate their final treatment, i.e. precipitation of a more pure arsenic product, recycling of the solution, production of a cleaner liquid effluent, etc.

The present work considered the most recent (2002-2006 years) advances in arsenic (V) separation technologies considering as such: liquid-liquid extraction, liquid membranes and adsorption and ion-exchange operations.

2. LIQUID-LIQUID EXTRACTION

This technology is one of the more established separation technology for wastewater recycling and also it is used with great success for the extraction of copper and other base metals.

In liquid-liquid extraction operation, a, normally liquid, organic extractant is used to remove the desired solute from aqueous solution (i.e. a leach solution or liquid effluent). The extractant is dissolved in an organic diluent to achieve a suitable reagent concentration in the organic phase and also to decrease the viscosity of the extractant. The intimate contact of the organic and aqueous phases, typically during few minutes, allowed the transfer of the solute from the aqueous solution to the organic phase, and after a very few minutes of phase disengagement, the loaded organic phase is then further contacted with a new aqueous strip phase. Then, the solute transfer back into this aqueous stripping solution, from which the solute is recovered by the best suitable procedure, and the unloaded organic phase is back-recycled to a further extraction operation.

Little efforts about the use of this technology in the treatment of As(V)-bearing liquid streams have been found in the recent literature, and all the investigations were phocused in the removal of arsenic (V) from copper electrowinning solutions.

The use of Cyanex 301, Cyanex 925 extractants and their mixtures dissolved either in toluene or n-octane to extract As(V) from highly acidic solutions (150 g/L sulphuric acid in the feed) is reported in the literature (Iberhan & Wisniewski, 2002, 2003).
As can be seen from results presented in Table 1, the use of the extractants mixture improves the extraction of arsenic (V) when it is compared with the obtained with each reagent separately.

<table>
<thead>
<tr>
<th>Reagent Type</th>
<th>Diluent</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanex 301 dTPA</td>
<td>Toluene</td>
<td>45.6</td>
</tr>
<tr>
<td>Cyanex 925 PO</td>
<td>Toluene</td>
<td>60.6</td>
</tr>
<tr>
<td>Mixture dTPA+PO</td>
<td>Toluene</td>
<td>94.0</td>
</tr>
<tr>
<td>Cyanex 301 dTPA</td>
<td>n-Octane</td>
<td>43.0</td>
</tr>
<tr>
<td>Cyanex 925 PO</td>
<td>n-Octane</td>
<td>48.0</td>
</tr>
<tr>
<td>Mixture dTPA+PO</td>
<td>n-Octane</td>
<td>98.0</td>
</tr>
</tbody>
</table>

dTPA : dithiophosphinic acid; PO : phosphine oxide

Also the effect of the organic diluent is small or even negligible for Cyanex 301 and Cyanex 925 mixtures but becomes important for Cyanex 925. However, and since the formation of a third phase was observed in the system containing n-octane and the mixture of Cyanex 301 and Cyanex 925, this would precluded its practical use.

The extraction of arsenic (V) by the phosphine oxide can be related to a solvation extraction:

$$\text{H}_2\text{AsO}_4^{aq} + \text{H}^+ + \text{HSO}_4^{aq} + \text{PO}_{org} \rightleftharpoons \text{H}_2\text{AsO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{PO}_{org}$$ (1)

with the probable co-extraction of water. In the above equation the subscripts aq and org referred to the respective aqueous and organic phases.

Extractants dibutyl butyl phosphonate (DBBP) and bis(2-ethylhexyl) phosphoric acid (D2EHPA) have been investigated for arsenic removal in a copper electrolyte solution (Ballinas et al., 2003). By the use of the correct operational parameters, the concentration of As(V) in the liquid effluent can be reduced from 7.3 to 2.0 g/L, whereas for mixtures of DBBP and D2EHPA, there is an increase in the arsenic extraction (synergism) compared to DBBP alone.

In all of the above systems, arsenic (V) (and co-extracted H₂SO₄) can be stripped by the use of water, and since the arsenic content in the copper solution is reduced to an acceptable level, this As-depleted electrolyte can be recycled to the copper electrorefining cells.

### 3. LIQUID MEMBRANES

Under the term of liquid membranes, a separation process which does not rely on inherent chemical characteristics of a thin, solid (semipermeable) barrier, is described. Liquid membranes can be put into two classifications: a) Non-supported liquid membranes, which includes bulk liquid membranes (BLMs) and emulsion liquid membranes (ELMs), b) Supported liquid membranes (SLM), which presented several operational configurations, i.e. flat-sheet, hollow fiber and spiral wound. Not really included in either of the two above types, other membrane configurations, all of them using a solid support to separate the phases, are gaining a great interest such polymer inclusion membranes (PIMs), non-dispersive solvent extraction (NDSX) and emulsion pertraction technology (EPERT).

Though the characteristics of each type of membranes had been described elsewhere (Alguacil & Villegas, 2002), it is worth to give here a brief comment about the performance of the most common types of liquid membranes used in the treatment of effluents.

In BLMs, two miscible aqueous solutions (donor and acceptor) are separated via a third immiscible phase (carrier or organic phase). The mass transfer from the donor to the acceptor phase is carried out via the carrier, and because transport through the bulk takes place by convection, the unstirred boundary layers between the immiscible phases form the largest transport resistance.

ELMs are three phase systems in which the liquid membrane in the form of relatively large droplets (0.1-1 mm diameter) encapsulates the acceptor solution which is a fine dispersion of smaller drops (1-10 μm). This emulsion is stable due to the size of the drops and the content of emulsifiers or surfactants. In operation, this membrane emulsion phase is dispersed into the donor aqueous solution and the process of mass transfer takes place.
SLMs are based in the use of a porous solid membrane which supports or retain the liquid membrane phase, and this support separates the donor and acceptor phases, being the solute transported from the donor to the acceptor phase through the organic solution retained in the micropores of the solid support.

Being of a broad interest from the academia, scientist and even the industry, the use of liquid membranes had yet not know a great degree of practical application due to problems to maintain its stability under larger operational times (SLMs) and problems related to the emulsion stability (ELMs). This is because the other liquid membranes operational modes are gaining a particular importance in the field of treatment of liquid effluents.

Transport of metallic species through a liquid membrane is usually done by facilitated transfer sometimes referred as carrier mediated transport. Since the liquid membrane contained an organic phase, which composition is similar to these used in liquid-liquid extraction practice, the permeating species reacts selectively and reversibly with the extractant contained in the membrane, i.e.

\[
H_2\text{AsO}_4^- + \text{H}^+ + nL_{\text{membrane}} \leftrightarrow H_3\text{AsO}_4 \cdot nL_{\text{membrane}}
\]

where \( L \) represent a neutral type organic extractant. Thus, the carrier shuttles the arsenic species from the donor phase where conditions are such that the equilibrium of the reaction shifts to the right and the solute is released into the acceptor phase and the unloaded organic solution return to the donor-membrane side and reacts again with the arsenic species. Moreover, the transport of the arsenic species is helped by the co-transport of a counter ion, \( \text{H}^+ \) in this case, being this the driving force for the arsenic transport, and this is because this type of mechanism is called facilitated cotransport, which is typical of basic and solvation extractants. Since arsenic (V) species are mainly anionic in nature, this is the type of mechanism normally associated with the transport of arsenic (V) compounds.

Though the use of LMs has received much attention in the literature, the technology had been surprisingly scarcely investigate to remove As (V) from wastewaters or liquid effluents.

Polymer inclusion membranes based on cellulose triacetate (CTA) and DBBP extractant were investigated for arsenic (V) separation from sulphuric acid for its recovery from copper electrolytes (Ballinas et al., 2004). In these highly acidic solutions the mixed species \( \text{H}_2\text{AsO}_4^- \text{DBBP-H}_2\text{SO}_4 \), together with \( \text{H}_2\text{AsO}_4^- \text{DBBP-H}_2\text{SO}_4 \), are responsible for the transport of the solutes, whereas a very high As (V) selectivity over Cu(II) was attained.

Being a promising technology, PIMs had apparently not known further use in arsenic removal from aqueous streams (Nghiem et al., 2006).

4. ADSORPTION AND ION-EXCHANGE

Being two different processes, they are often considered together probably due to that the solute to be removed from the liquid stream is retained in a solid matrix.

The use of carbon or charcoal for drinking water filtration dated-back for more than 3500 years ago, however the use of activated carbon in the industry is a technology with a mere two centuries old. Activated carbon can be prepared from various resources, being wood, coal, lignite, coconut shell and peat the most commonly used.

Activated carbon adsorption was investigated in arsenic and antimony removal from copper electrorefinning solutions (Navarro & Alguacil, 2002), with a huge arsenic adsorption capacity of near 2.9 g As(V)/g activated carbon.

Besides the above, several types of activated carbon were synthesized and used for the removal of arsenic from wastewaters.

Iron-containing granular activated carbon adsorbents were developed to remove arsenic from water (Gu et al., 2005). The removal of As(V) occurred in a wide pH range (4.4-11), though arsenate adsorption decreased at pH values higher than 9.0.

Oat hulls activated by steam produced an activated carbon with adsorption capacities ranging 3.1 to 1.6 mg As(V)/g carbon for initial pH values of 5.0 to 8.0, respectively (Chuang et al., 2005).
Considering as low cost adsorbents, various types of materials or products were also used to investigate their performance in the removal of As(V) from various liquid environments. A number of these were summarized in Table 2.

<table>
<thead>
<tr>
<th>Type</th>
<th>Subtype</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Industrial by-products</td>
<td>Chars and coals</td>
<td>Sneddon et al., 2005</td>
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<tr>
<td></td>
<td>Red mud</td>
<td>Genç-Fuhrman et al. 2005</td>
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<tr>
<td></td>
<td>Blast furnace slag</td>
<td>Zhang &amp; Itoh, 2005</td>
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<tr>
<td></td>
<td>Fly ash</td>
<td>Rahman et al., 2004</td>
</tr>
<tr>
<td>Soils</td>
<td>Soils</td>
<td>Zhang &amp; Selim, 2005</td>
</tr>
<tr>
<td></td>
<td>Sand</td>
<td>Nguyen et al., 2006</td>
</tr>
<tr>
<td></td>
<td>Clay minerals</td>
<td>Goldberg, 2002; Dousova et al., 2006</td>
</tr>
<tr>
<td></td>
<td>Zeolites</td>
<td>Xu et al., 2002; Payne &amp; Abdel-Fattah, 2005</td>
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<tr>
<td>Oxides</td>
<td>Single oxides</td>
<td>Ouvrad et al., 2002; Dambies 2004;</td>
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<tr>
<td></td>
<td>Mixed oxides</td>
<td>Kunzer &amp; Chaudhuri, 2005</td>
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<td></td>
<td></td>
<td>Ladeira &amp; Ciminelli, 2004</td>
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<tr>
<td>Hydrotalcites</td>
<td></td>
<td>申花ik et al., 2005</td>
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<tr>
<td>Phosphates</td>
<td></td>
<td>Lenoble et al., 2005</td>
</tr>
<tr>
<td>Metallic iron</td>
<td></td>
<td>Su &amp; Puls, 2003; Bang et al., 2005</td>
</tr>
<tr>
<td>Synthetic adsorbants</td>
<td>Bimetallic adsorbents</td>
<td>Zhang et al., 2005</td>
</tr>
<tr>
<td></td>
<td>Metal-chelated ligands</td>
<td>Dambies, 2004; An et al., 2005</td>
</tr>
<tr>
<td></td>
<td>Metal-loaded polymers</td>
<td>Dambies, 2004; Balaji et al., 2005</td>
</tr>
<tr>
<td></td>
<td>Anion-exchange resins</td>
<td>Dambies, 2004; Alguacil et al., 2005</td>
</tr>
<tr>
<td>Biosorbents</td>
<td>Including: Phytoremediation and</td>
<td>Ruiz &amp; Romero, 2002; Loukidov et al., 2003;</td>
</tr>
<tr>
<td></td>
<td>Biological treatment with living</td>
<td>Ghimine et al., 2003; Kostal et al., 2004;</td>
</tr>
<tr>
<td></td>
<td>microbes/bio-filtration</td>
<td>Guo &amp; Chen, 2005; Shaban et al., 2005; Krämer,</td>
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<tr>
<td></td>
<td></td>
<td>2005; Chen &amp; Chung, 2006; Srivastava et al., 2006;</td>
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<tr>
<td></td>
<td></td>
<td>Pokhrel &amp; Viraraghavan, 2006</td>
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Including above, anion exchange and adsorption onto activated alumina are considered among the best available technologies (BAT) for arsenic removal (Mondal et al., 2006).

5. CONCLUSIONS

Though it is difficult to compare the various technologies considered in this paper due to that experimental conditions are by far not the same, it can conclude a strategy in arsenic (V) separations technology based in a number of premises, i.e.

- Based in arsenic concentration in the liquid stream: liquid-liquid extraction > liquid membranes > adsorption=ion-exchange. That means that liquid-liquid extraction is suitable for the treatment of solutions which contained a higher concentration (in the order of g/L) of the element, whereas adsorption and ion-exchange are the technologies to be used when the arsenic concentration is very low (very few mg/L and even μg/L).

- Based in arsenic purification: liquid-liquid extraction=liquid membranes > adsorption=ion-exchange. In this case, the classification is based in how the final solution (stripping solution or eluate) is more purified with respect to arsenic; accordingly to the above, either with liquid-liquid extraction and liquid membranes the most pure arsenic solutions can be obtained after the treatment of a given wastewater or liquid effluent.
Based in the liquid stream characteristics (i.e. presence of solids): adsorption > ion-exchange > liquid-liquid extraction > liquid membranes. Based in this classification, adsorption and ion-exchange are the technologies to be first selected in the removal of arsenic (V) from non-clarified aqueous streams.

A perspective of the uses and maturity of selected arsenic (V) separation technologies is shown in Figure 1.

Finally, it may considered that many of the above mentioned technologies or processes are not easily affordable by either industries and common people of a large number of countries, thus, the MCL value in these locations stands at 50 µg/L, or greater, for a unknown future and a large number of inhabitants in the world will live under the threat of arsenic poisoning.

6. ACKNOWLEDGEMENTS

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7. REFERENCES


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