

Executive summary

Back ground

A new technique to purify waste water from SA mines and factories was developed. The importance of a solution to the general world wide problem to purify water cheaply, and effectively, is highlighted by the fact that UNESCO has identified contamination of earth's fresh water supplies as the biggest threat to man's survival on earth. This is put in perspective when one realises that UNESCO estimates that only 0.007 % of water on earth is still capable and simultaneously available (i.e. not too deep underground, not frozen on polar ice caps etc.) to support human life. The remainder is too contaminated with salts and metals to support human life (quoted from UNESCO'S web page: <http://www.unesco.org>). It is, therefore, important to maintain existing fresh water supplies and to purify large industrial volumes of waste water. Purification of industrial waste water, however, presents a large problem. Reverse osmosis, or other technologies are currently used to *partially* remove sulphate, chloride, sodium, calcium, phosphate and other ions from industrial effluents by fractionating the water into a clean portion and one in which the contaminants are concentrated to 10% or more. Either the contaminated fraction is stored in sludge dams or dams with a high salt content to slowly evaporate, or more expensive purification processes (e.g. distillation) are used. Eventually, contaminated water from the waste water reservoirs seeps into the ground, and contaminates underground water reservoirs. Such underground water reservoirs eventually become unfit for human consumption or to support life in general (i.e. bore holes become useless). The poisonous nature of the water in the sludge dams also poses a major threat to the entire ecological system in which they are situated. For example, no fish will live in it. Birds and small mammals become poisoned when they drink it, they die, and an entire life chain is disturbed. Trees and vegetation will die. A technology which can remove all contaminants from wastewater after techniques such as reverse osmosis, membrane technology partially cleaned it, is highly desirable.

We began developing such a technology and funding to develop it further should be top priority. Our strategy involves identification of a suitable ligand that can bind a target metallic cation, in this study the sodium cation, strongly but reversibly. To bind sodium cations, the crown ether family of ligands was identified. In order to handle this sodium cation scavenging moiety in a convenient way during the purification of water, the crown ether was anchored on a suitable support system, here an elastomeric (rubber-like) polymer. To make this material work as sodium cation scavenging device it needs to be circulated through contaminated water, given

enough time to bind the contaminant cations, and then it must be transported to a collecting vessel where the contaminating cations must be released and recovered from the support. If this process can be achieved in a cyclic way economically, it will complement existing membrane technology by taking over the cleaning of polluted waste water after membrane technology concentrated impurities into a smaller volume of water. It provides for the eventual recovery of all water contaminated in industrial processes. When such technology becomes fully operational, greatly improved opportunities will be created, many of these economic.

Aims of study

To achieve this goal, the aims of this study was as shown below. All the aims were realised.

1. Synthesis and modification of crown ethers and other macrocycles.

Since crown ethers are the molecules that was chosen to bind the sodium cation contaminants in waste water, they were chemically modified to allow polymer anchoring.

2. Test the effectivity of synthesised crown ethers as contaminant scavengers

This task was done routinely to establish if a newly synthesised compound was an effective contaminant scavenger.

3. Develop suitable polymers on which the crown ethers may be anchored

A polymeric solid support was chosen as the tool required to transport the contaminants from the contaminated water reservoir to a suitable site for precipitation.

4. Anchor the crown ethers on the polymers

Suitable methods to bind the crown ethers to the polymeric solid support were developed

5. Develop techniques to allow release of the contaminants from the polymeric carriers.

Once the contaminants have been trapped by the polymer bound crown ethers, they need to be release again under controlled conditions at a previously determined site. Factors that may be used to influence the release of the contaminants are heat (up to 60 C), UV light irradiation and pH changes. Precisely how pH control may be utilised to induce release of the contaminants from the polymers were researched.

Methodology

In order to modify crown ethers to allow it to be anchored onto a solid support benzo-15-crown-5 derivatives were synthesised and functionalised to have an aldehyde, nitro, amino, alcohol, halide or carboxylic acid group on them. This provided a handle to anchor it on the polymer.

The effectivity of selected crown ethers as sodium cation scavenging devices were tested by measuring the amount of sodium cations it could remove from a standard stock solution utilising analytical techniques such as flame photometry. The solid support required to anchor the crown ether sodium cation scavengers on, involved developing techniques to polymerise hydroxy-terminated polybutadiene into a rubber-like elastomer via diisocyanate curing. The polymerisation of epichlorohydrin, and its functionalisation to have amino, isocyanate and carboxylated side chains were also explored. This provided us with handles to which the crown ethers may be anchored. Methods to chemically bind the crown ethers to the polymers involved the reactions between amines and isocyanates, amines and carboxylic acids, alcohols and isocyanates, amines and halogens. In essence the crown ethers was attached to the solid support via linking units of monomeric (e.g. isophorone diisocyanate) or polymeric (e.g. polyvinyl alcohol) nature. Finally, the effectiveness of sodium release from the polymer-anchored crown ether device under different acid conditions were researched by determining how much cations was released from the cation scavenging device under specific acidic conditions. The method of detecting sodium cations was again flame photometry.

Results

All the above aims were successfully explored. The best sodium cation scavenging devices were found to be those that had polymeric linking groups between solid support and crown ether. Systems that allowed dendrimer technology of the third order to exponentially increase the loading capacity of crown ethers on the solid support were especially effective. Specifically, when the linking groups were a dendrimer constructed from a di-isocyanate coupled to polyvinyl alcohol, which was in turn coupled to an isocyanate-containing polymer, 92% removal of all sodium cations from a 10 cm³ sample of 200 ppm stock solution was achieved in a single extraction experiment. The device performed optimally at ca 50-60 °C. Repetitive experiments showed that the device did not loose activity after 10 extraction cycles. The capacity of the present device is approximately 1.5g/m² surface area of the scavenging device.

Conclusions and Recommendations for Further Research

During the period 2000 –2002 we have set ourselves the goal of developing the science required to develop a new means of cleaning factory wastewater. This new process is distinctly different from current state of the art ion exchange or membrane technology. We have developed

procedures to synthesise an elastomeric polymeric support, synthesise Na^+ scavenging devices in the form of crown ether derivatives, and we developed the science required to heavily coat the surface of the solid support with the crown ether Na^+ scavenging molecules. In particular we used dendrimer technology adapted to polymer systems and we called these starburst molecules. The design of our device is provided in schematic form providing details of the system on page 41, **Figure 12**.

Although this research program succeeded to develop the science required to manufacture a device that is capable of transferring 76-92% of the available Na^+ cations from a 200 ppm Na^+ solution, and release half of this amount again in a previously determined reservoir in a single cycle, the density of Na^+ cations on the solid support is still low: only about $1.5 \text{ g} / \text{m}^2$. Also, the present technology only supports Na^+ removal from water. To improve the loading capacity, and to expand the technology to also include other cations including heavy metals, it is recommended that

- 1) Funding be made available to develop the technology to increase the density of Na^+ loading by expanding the order of the existing starburst structure from 3 to 6.
- 2) Devices be developed that can remove (and selectively recover) other metals from aqueous solution including magnesium (pollutant), lead (poison), platinum and silver (precious metals), copper and cobalt (economically important but scarce metals in South Africa) cations.
- 3) The present technology be expanded to include inputs from engineering institutions to test and develop this new technology on pilot plant scale and beyond.