

## **EXECUTIVE SUMMARY**

### **BACKGROUND AND MOTIVATION**

A clean supply of water is an essential requirement for the establishment of a healthy community. It acts not only as a source of potable water, but also supports the growth of aquatic life, thereby providing valuable food supplements. Nowadays, despite its importance, water throughout South Africa is polluted and a particular area of concern is the release of heavy metals by the industrial sector into sewage streams and natural waters. Impure water, containing excessive levels of metals such as copper, zinc, nickel and mercury, is hazardous to human, animal, aquatic and plant life. Due to their toxic and often carcinogenic nature, as well as the careless disposal of large quantities into the environment, heavy metals have been prioritised as leading contaminants in South Africa. Since heavy metal ions are often even toxic at low concentrations and are not biodegradable, they must be removed from the contaminated water. Due to the financial value of some heavy metals it is also important to recover these metals from wastewater. In this study, the removal and recovery of heavy metals using the biosorbent chitosan is investigated

### **EXPERIMENTAL APPROACH**

In this study, different forms of chitosan have been prepared from chitin flakes, obtained from rock lobster waste from the seafood processing industry by BioSpec (Cape Town), in order to use the chitosan material for the adsorption of heavy metals from wastewater. Firstly, the chitin flakes were converted to chitosan flakes, and after characterisation of the material, large similarities with commercial chitosan (biopolymer engineering) were found. Since flakes do not have good adsorption characteristics and are difficult to use in large equipment, other configurations (beads, membranes and immobilised chitosan) were prepared for the experimental adsorption studies. All configuration techniques used, were based on the phase inversion method, in which chitosan is dissolved in acetic acid and later precipitated in a caustic soda bath. The adsorption experiments were carried out at a laboratory scale.

### **RESULTS**

#### **Technical results**

Using the phase inversion method, a gel type of material is formed, which contains predominantly water (93-96%) and the balance chitosan (4 – 7%). Initial experiments showed, that chitosan in the gel form has much better adsorption characteristics than chitosan flakes (affinity parameter is at least a factor 10 higher for beads compared to flakes).

### Beads

When using beads, a high adsorption capacity of 160 mg/g for copper was obtained, and the affinity parameter was 0.07 L/mg, values that are larger than reported values for activated carbon and measured values for ion exchange resins (in this study Amberlite 200C was used as reference). During adsorption column experiments using a 10 ppm copper solution, at least 550 Bed-volumes were processed to a < 1 ppm (WHO limit) effluent solution, in three cycles of adsorption and desorption. The copper could be recovered using an acid of pH = 1, obtaining a copper solution of 1200 ppm, which could be processed further to recover the metal in its pure form. The beads were stable to only 5 cycles, using the high acid concentration. When milder desorption conditions (pH = 2), the effluent copper solution only contained about 100 mg/g, making further processing more difficult. During the adsorption process, the diffusion inside the beads played an important role in the total mass transfer. An effort was therefore undertaken to reduce the size of the beads, which resulted in beads with an average diameter of 1.8 mm, a size that still results in a negligible pressure difference over the column.

For the chitosan beads, a novel adsorption model has been developed, which takes the acid base characteristics of the chitosan into account. The new model can therefore be used at any pH, for both adsorption and desorption. From this model, it could be concluded that the chitosan has the largest affinity to copper, followed by lead, nickel, zinc and cadmium

### Membranes

Chitosan membranes have been prepared according to a method quite similar to the production of beads. The membranes were characterised and it was found that the membranes could be modelled as a porous hydrated membrane and showed large similarities with ultrafiltration membranes, both for the flux of clean water and salt solutions. The membranes showed large affinities to Zn (maximum adsorption capacity 135 mg/g and affinity parameter of 0.02 mg/L at a pH of 6). The adsorption could well be described with a Langmuir isotherm in the region from 20 – 40 °C. The adsorption capacity increased from 20 – 30 °C and remained constant between 30 and 40 °C. The increase of the capacity could be due to a better accessibility of sites, caused by an increase in free volume of the biopolymer. The affinity parameter also increased in temperature, indicating an exothermic adsorption process. The membranes could be recycled effectively (>95%) using sulphuric acid (pH = 2), but after 2 cycles of adsorption and desorption the membranes were damaged and could not be used anymore. This was possibly caused by the acid, which was pumped through the membrane during desorption (SEM analysis revealed that after crosslinking the edges of the membrane were more cross-linked than in the centre of the membrane).

### Immobilised chitosan

Immobilised beads were prepared by the coating of a thin chitosan layer (around 20  $\mu\text{m}$ ) on an alumina support. Very high adsorption capacities ( $> 200 \text{ mg Cu/g}$ ) were obtained when a porogen was used. The porogen makes the active sides easily available.

### **Non - technical results**

Since chitosan is only produced at a small scale, the prices on the world market are relatively high (\$ 35/kg). Since the market for chitosan is rapidly growing (mainly for the application of fat absorber), price decreases are expected in the future. The production costs for the preparation of chitosan are largely determined by the conversion of chitin to chitosan; a process that uses an excess of caustic soda. Without reuse of the soda, a price of around \$6/kg is estimated. This price can be reduced to an approximated \$ 0.6/kg if the caustic soda is recycled effectively. The cost for cleaning contaminated water is then about \$ 0.06/ $\text{m}^3$ , not taking into account the investment for an adsorption/desorption plant. Although excellent adsorption characteristics have been obtained for immobilised chitosan, the production of the ceramic support is still very expensive ( $> \$ 200 / \text{m}^2$ ), which makes this technique less applicable for water purification.

### **ADVANTAGES AND DISADVANTAGES**

*In general, we can conclude that chitosan (in the gel form) is a very effective adsorbent. It can adsorb the studied metals Cu, Zn, Pb, Ni and Cd to a very high degree, higher than their economical counterparts, such as activated carbon and ion exchange resins. A general disadvantage of chitosan is that the stability is not very good. In the case of beads, chitosan could be recycled 5 times and for membranes only 2 times, which makes a long-term use of the biopolymer impossible. The harsh conditions, under which the desorption process takes place, is the main reason for this. Milder desorption conditions, however, would result in a more dilute metal stream, which again is unfavourable for further processing and recovery of the metal.*

In comparing the three configurations studied in this project, the following table can be presented, in which the three different configurations are compared on adsorption, flux, stability characteristics and costs.

	Beads	Membranes	Immobilised on alumina
Adsorption	+	+	++
Flux	+ / -	+	+
Stability	+ / -	-	Not studied
Costs	+	+	--

Chitosan immobilised on alumina shows excellent adsorption characteristics above beads and membranes, but is rather expensive because of the high production costs involved in the preparation of the ceramic supports; also the low capacity per volume requires large equipment (only a thin layer of chitosan is deposited). Comparing chitosan membranes with beads, it can be concluded that beads are more stable than membranes. However, the advantage of using chitosan membranes is that a pressure difference is used to induce convective flow through the membrane, which in turn results in a higher throughput, compared to the diffusive transport inside the bead, which is the rate determining step in the adsorption column. (Also, slightly higher adsorption capacities could be obtained with membranes, compared to beads).

### **RECOMMENDATIONS**

An improved crosslinking technique for membranes should be found in order to solve the stability problems. If such a technique could not be found, the use of adsorption beads in an adsorption/desorption column would be the recommended process, which can process metal contaminated wastewater at relative low concentrations (< 10 ppm) to disposal water, meeting the most stringent legislation, against a price of about \$ 0.06/m<sup>3</sup>.

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