Molecularly imprinted polymers for indium using a novel functional monomer

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Introduction

- The need for rapid extraction methods of high value metals has increased in recent years as demand has exceeded supply
- The global trend towards sustainable energycould be answered by solar panels; however, Indium(III) and other metals used in their construction are very expensive mainly due to high demand
- In(III) is present in large amounts in geothermal waters, but no reported attempt to extract, due to the high acidity and temperature of the known sources
- Molecularly imprinted polymers (MIPs) are materials known to uptake target molecules from harsh media, making them ideal candidates as an extraction tool
- Bilirubin (Fig 1) complexes strongly with transitional metals due its wide range of functional groups, and its ability to exhibit keto-enol tautomerism. This makes it suitable as a functional monomer in a MIP
- The current study reports complexation constants for the In(III)-bilirubin complex, the development of a polymer and its uptake characteristics in highly acidic media

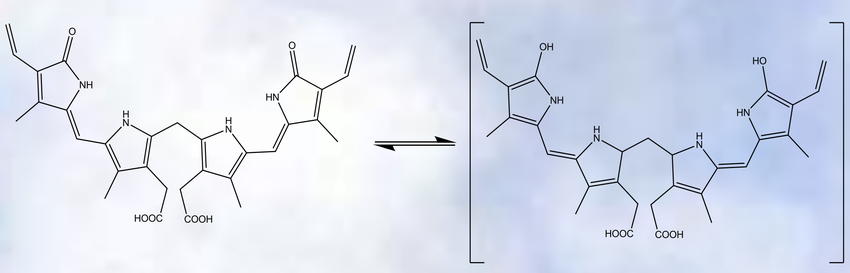

Fig 1- **Bilirubin in its enol-keto forms**

Experimental

- Bilirubin-indium (III) titrations:
  - Performed in methanol and aqueous media (bilirubin dissolved in slightly basic solutions)
  - UV-Vis and fluorescence of the solutions monitored- UV-Vis at 500 nm, fluorescence emission at 560 and 660 nm
  - Presence of new fluorescence emission peaks associated with formation of complex
  - Enhancement of absorbance or fluorescence correlated with monomer-template ratio
- Polymers synthesized using a In(III)-bilirubin ratio determined from the template-functional monomer titration (unusual complex 1:10, confirmed IR)
- Tests performed to determine uptake of In(III) by polymers
- Binding tests were performed by passing In(III)-containing solution at a rate of 10 mL/min through 100 mg polymer

Discussion

In(III)-bilirubin complexes

Titrations (Figure 2) demonstrate two different complexes forming:

- 4:1 In(III)-bilirubin complex is observed in fluorescence studies
- 10:1 In(III)-bilirubin complex is observed in UV-Vis studies (absorbance too low to observe 1:4)
- Both complexes are characterised by strong absorbance/fluorescence enhancement; calculations show 1:4 and 1:10 complex formation
- Same type of complexes were observed both in methanolic and aqueous solutions
- Bilirubin is able to interact via nitrogens- In(III) known to form complexes with N ligands

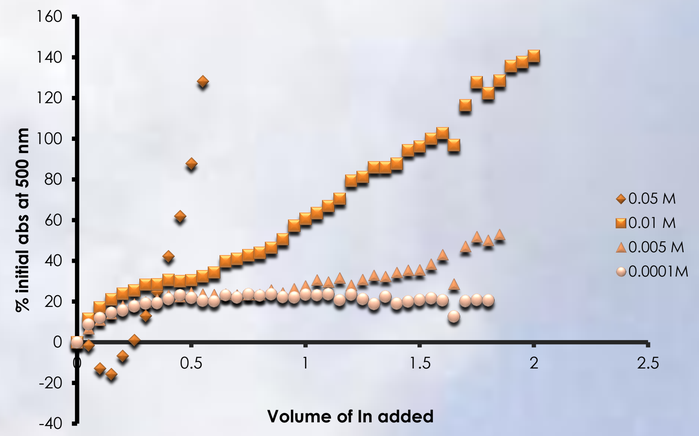

Fig 2- **UV-Vis titrations with a range of Indium solutions**

Polymer synthesis and characterisation

- Combinatorial approach used, In(III) uptake characterised only from aqueous environments
- Optimum polymer composition determined
- Polymer uptake characterised from acidic media, response time of under 1 min was observed (Figure 3), polymer response linear over concentrations similar to the ones found in geothermal waters

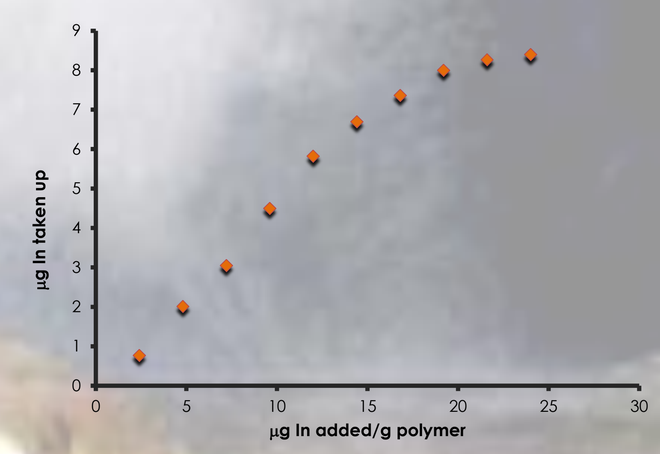

Fig 3: **Uptake of In(III) from solution**

Conclusion

The polymer performs well in acidic media mimicking geothermal waters. This has the potential to develop into a sensor or filter for extracting indium from geothermal waters.

Acknowledgments

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