Characteristic Properties of Macrocyclic Functional Hydrogels for Selective Heavy Metal Adsorption

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Introduction

Hydrogels are increasingly becoming ubiquitous materials for heavy metal adsorption works. Adsorption selectivity especially, has become a paramount property on adsorbents, and as such recent research efforts on hydrogels sought towards modifying their functional groups and exploit for selective capture metal pollutants in waste solutions. Additionally, hydrogels structure facilitate desorption and recovery of these metals for potential refinement and re-use as a viable by-product in addition to yielding cleaner, recyclable waste water. By using various spectroscopic techniques, our work explores properties of hydrogels functionalized with different types of macrocyclic rings. We also aim to decipher the manner of adsorption selectivity via host-guest capture of target metal ions into the macrocylic rings.

Experimental

Two sets of macrocyclized hydrogels (MAE and EBE) were fabricated using equimolar concentrations of bifunctional monomers comprising maleic acid and ethylene diamine; maleic acid and (2, 2' ethylenedioxy) bis (ethylamine), respectively. The monomers were coupled under high dilution aqueous solution and high temperatures (96 ºC) to facilitate condensation coupling. Pregel-products were obtained, which then underwent polymerization and cross-linking to form the final hydrogels. Extracted and dried hydrogel samples (including the pre-gel product) were analyzed for various properties using scattering technique (WAXS), SEM and EDS analysis, swelling and de-swelling, ^{13}C NMR, FTIR and Raman spectroscopy method. Adsorptive properties of the hydrogels were also attempted using batch technique on various sets of heavy metal ion types and concentrations within a single solution.

Results and Discussion

Scattering experiment showed that there was distinct structural differences between the pre-gel product and the final polymerized and cross-linked gel material. Whereas both products displayed similar functional groups in their FTIR, Raman and NMR analyses, the scattering profile of MAE pre-gel product gave crystalline peaks which then changed to amorphous peak profile in the final hydrogel (Fig. 1). This is a curious property that can be exploited for adsorption selectivity. The pre-gel product is a ringed material of different shape and type in both hydrogel types. It is the unit monomer which would then constitute the main network and functional group of the final polycyclic hydrogel product. Using backscatter electrons, EDS spectroscopic analysis showed for both hydrogels, the main constituent elements which make up the ring of the pre-gel and final gel is C, N and O in various proportions as summarized in Table I.

Table I. Single metal ion adsorption

Elements	MAE		EBE	
	Pre-gel	hydrogel	Pre-gel	hydrogel
C	45.17	56.85	56.72	47.15
N	17.26	10.08	10.06	11.83
O	37.57	33.08	33.22	41.02

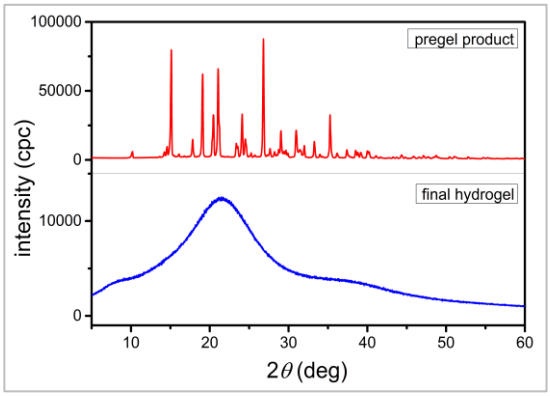

Fig. 1. Scattering profiles of MAE pre-gel and final hydrogel products

When applied against multi-element metal ions solutions of various degrees of competition, both gels showed high extraction (>95% extraction) and each hydrogel demonstrating acute selectivity for only one type of metal ion despite the type of competition.

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