Poly (1, 4-diazocane-5, 8-dione) macrocyclic-functionalized hydrogel for high selectivity transition metal ion adsorption

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ABSTRACT

We present a method of synthesizing macrocyclic hydrogel systems using sol-gel polymerization and for high selectivity adsorption works. The hydrogel was fabricated using maleic acid and ethylene diamine ligand and characterized using FTIR, Raman, SEM/EDX, ^{13}C NMR and SAXS techniques. It was revealed that 1, 4-diazocane-5, 8-dione were the principal active sites of this adsorbent. These macrocyclic sites provided defined zones which limited capture and chelation of transition metal ions such that from single ion solutions, only ion substrates of between 1.23 and 1.29 Å ionic size were mainly adsorbed; whereas in case of metal-metal competitive solutions, then only 1.29 Å sized substrates would be adsorbed. This adsorption specificity required that aqua metals of these sizes be of octahedral configurations for more optimum host-gest chelation with the gel active sites. Since $Fe_{(aq)}$ effectively met these criteria, the gel adsorbent displayed outstanding specificity for $Fe_{(aq)}$ adsorption from different levels of competitive environments. Present adsorbent showed that macrocyclic chelate sites can be infused directly into the hydrogel network without any grafting, and facilitates a shape-based, size-limited adsorption. This hydrogel is a promising candidate for applications in heavy metal pollution remediation, drug development and fuel cell catalysts, where high specificity adsorptions are desirable.

1. Introduction

High selectivity in metal-ion separation techniques has increasingly become a paramount criterion in the design of materials for hydrometallurgy, adsorbents for heavy metal-polluted waste water treatment and even in drug development. This is because target substrates often exist in competitive environments with other similar but less harmful fractions. Therefore materials for these purposes need critical design in order to exploit the specific and distinguishing properties of targeted groups over the shielding and overlaying properties of the other undesired ions existing within the same environment. Materials with such properties have recently included SuperLig [1,2] biochemical chelatase [3,4] or even natural-sourced adsorbents [5–7].

Chelates have always stood out for their high sorptive power depending on type and number of donor atoms; whereas macrocyclic groups provide closed zones for capture of substrates. Various studies have therefore focused on how to combine these two properties into more potent adsorbent that can exhibit high capture and selectivity. Earlier works started with the Pedersen crown ethers [8] and more recently into active crown ether adsorbents for heavy metal removal [9,10]. However, crown ethers' complexing ability has tended to be strong only against alkali/alkaline earth metals, but weak on transition metals. Yet transition metals form the bulk of target ions due to their prevalent use and consequently high toxicity as pollutants. As a result, new polydentate cyclic ligands for this latter group have become the subject of various researches, leading to many attempts on supramolecular polymers [11–14] and catenanes [15]. These efforts have still fallen short, since except by being grafted onto solid support structures, these macrocyclic groups have yet to be developed into single effective adsorbent.

Among the types of synthetic macrocycles, diamide based macrocyclic rings gained popularity due to their relative ease of synthesis. Initially advanced by Stetter et al. [16], acyl chloride and diamine fractions are coupled in a double amidation process to form a cyclic ring in a two-step irreversible reaction involving conversion of carboxylic acid to an acyl chloride before eventual coupling with a diamine. More recent methods have included the use of esters instead of acyl chlorides in amines coupling [14]. Since by using acyl chlorides, despite being more reactive and providing faster coupling at ambient conditions, they have solvent limitation since water could not be used as dilution media

because they react with water. It renders this method only suitable for creating small macrocyclic rings in organic media, but unsuitable for development into active solid adsorbents like hydrogels which require aqueous environment.

Therefore it is on this premise of seeking alternate adsorbents and methods of infusing macrocyclic groups into a solid structure network without any grafting but for high metal ion adsorption specificity, that hydrogels were considered. Hydrogels are three dimensional cross-linked polymers whose stand-out features include porosity, ease of formation and structural flexibility [17,18]. However, they have repetitively lacked adsorption specificity because they have largely employed ion exchange as the primary mechanism of adsorption [19–22]. This way most hydrogels are carboxylate based in order to facilitate cation exchange. However, since all metal ions bear positive charge, ion exchange is not a very restrictive mechanism regarding which types of metal ions can be preferentially adsorbed [23,24]. Ultimately, this created an undesired generality in hydrogels work.

In view of these, our present work focused on designing hydrogel adsorbent materials for high selectivity, high efficiency applications. We sought a synthesis method that enables creating, infusing and propagating macrocyclic chelate rings throughout the gel structure. Our work anticipates that if the active sites (which are also zones for adsorption) are macrocyclic rings, whose structure have defined shapes and sizes with chelate properties, then adsorption would be restricted to only a few substrates that could be accommodated therein. This way selectivity would be enhanced. Monomers for this work should be ligands and need high solubility in the choice solvent for initial coupling. This therefore highly restricts the type of materials that could be used. Herein, using maleic acid and ethylene diamine monomers, we report the synthesis, structural and functional characterization; and application of macrocyclic hydrogel system.

2. Materials and methods

2.1. Materials

Maleic acid and polymerization agents: ammonium persulfate, *N, N′* Methylenebisacrylamide and tetramethylenediamine were all obtained from Sigma Aldrich, Japan. Ethylene diamine was sourced from Tokyo chemicals, Japan. Standard solutions of Cr^{3+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+} and a multi-element metal ion solution (high purity ICP/MS standards) were purchased from Sigma Aldrich, Japan. All chemicals were of high analytical grade quality and used as received. References to water shall refer to ultrapure deionized water.

2.2. Hydrogel synthesis

Hydrogel adsorbent was prepared via standard radical polymerization method, carried out in a 50 mL reacting beaker fitted with magnetic stirrer and drop funnels. The main monomers, a di-acid and diamine were coupled in high dilution environment in a similar manner to the proven synthesis of macrocycles by Stetter et al. [16]. Accordingly, equimolar concentrations (700 mM) of maleic acid and ethylene diamine were added drop-wise into an aqueous solution and stirred until complete dissolution. The two monomers were allowed complete coupling in a preliminary condensation reaction under mild stirring for 8 min. The reaction was carried out under fume chamber and 40 °C constant temperature heating water bath. Thereafter, a catalytic amount of acrylic acid was added to this monomer solution as an additional source of free radicals in order to instigate linear polymerization. Other polymerization agents: *N, N′* –methylene bisacrylamide (for chain cross-linking) and ammonium persulfate (APS) were added in 50 mM and 5 mM concentrations respectively, to make the final pregel solution. APS was a free-radical initiator for the polymerization process. The reacting beakers with pregel solution were purged with nitrogen gas, sealed and the reaction temperature maintained at an isothermal level of 60 °C for polymerization and cross-linking until complete gelation. Gel formation was successfully accomplished within 4 h and allowed a further 2 h for curing.

In the post synthesis processing (otherwise known as adsorbent activation), the hydrogel material was extracted, cut into predetermined cubic fractions and washed in water extensively for 36 h to dissolve and elute any excess un-reacted precursors and oligomers. The cubic fragments were then dried at ambient conditions to obtain the final dry, cross-linked and insoluble fraction. This dry hydrogel was characterized variously for its intrinsic properties and tested against selective adsorption of transition metal ions.

3. Physico-chemical characterizations

3.1. Functional group, geometry of the hydrogel

Analysis for primary functional groups and structural arrangement was done using Jasco 4100 FTIR spectroscopy in the attenuated total reflectance (ATR) mode. Meanwhile Raman spectrum for solid hydrogel samples was acquired using the HORIBA LabRam Aramis spectrometer, utilizing the 785 nm laser and D0.03 filter lens within a scan range of 700–1400 cm^{-1}. However, since Raman and FTIR cannot conclusively predict the arrangement of functional groups isolated, we performed ^{13}C NMR analysis employing the Cross Polarization Magic- Angle Spinning (CPMAS) technique in order to determine the types of carbon their location and environment in the newly fabricated hydrogel sample. CPMAS is a high resolution solid state technique used to minimize large anisotropic NMR interactions and improve the S/N ratio in rare spin (i.e.^{13}C nuclei) NMR spectra.

3.2. Small angle X-ray spectroscopy (SAXS)

The SAXS experiments for hydrogel structural properties were carried out at the SAGA Light Source Beam Line (BL) 11 in Kyushu area, Japan. Using a double crystal monochromator and a bent cylindrical focusing mirror composing of Rh-coated fused quartz, an incident X-ray beam from synchrotron radiation of wavelength (λ) of 1.378 Å was irradiated to the hydrogel samples mounted onto flat cell holders. The exposure time was kept within 600–1200 s, which increased relative to the changing/diminishing beam intensity. The sample to detector distance was set at 1676.3 mm whereas collimation effects were negligible for this setup. The experimental data were corrected for background scattering radiation and sample transmission flux variation, using an ion chamber detector. Results from scattering experiments were utilized to discover structural information of the synthesized hydrogel material.

By applying monochromatic synchrotron beams scattered through an angle $2\theta < 2^{\circ}$, spectral results of scattering intensity versus the scattering vector were interpreted using Guinier plot expansions based on Eqs. 3 and 4

$$I(Q) = I_0 \exp\left[-\frac{Q^2 R_g^2}{3}\right] \tag{1}$$

$$Ln[I(Q)] = Ln[I_0] - \frac{Q^2 R_g^2}{3} \tag{2}$$

where $I(Q)$ is the scattering intensity, I_0 is the forward (zero angle) scattering intensity, Q is the scattering vector and R_g the radius of gyration. Guinier law proposes that in case of very small scattering angles, or where the wavelength of the scattered wave ($qR_g \ll 1$), then a linear fit will be obtainable when plotting $Ln[I(Q)]$ *vs.* Q^2.

3.3. Thermo physical properties

Differential Scanning Calorimetry (DSC) measurements were performed under nitrogen flow using the NETZSCH DSC 200 F3 instruments, in the temperature range 20–600 °C with a heating rate of 5 °C/