Reactive and Functional Polymers 130 (2018) 90–97

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react

Fabrication of poly (1, 4-dioxa-7, 12-diazacyclotetradecane-8, 11-dione) macrocyclic functionalized hydrogel for high selective adsorption of Cr, Cu and Ni

Brian A. Omondi[a,b,*], Hirotaka Okabe[a,b], Yoshiki Hidaka[a,b], Kazuhiro Hara[a,b]

[a] *Department of Applied Quantum Physics and Nuclear Engineering, Faculty of Engineering, West 2, 922-2, Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan*
[b] *Research Institute of Environment for Sustainability, Faculty of Engineering, Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan*

ARTICLE INFO

Keywords:
Selective adsorption
Macrocyclic hydrogels
Host-guest chelation
Functional adsorbents

ABSTRACT

Synthesis of hydrogel adsorbent for high selectivity and strong chelate removal of transition metals Cr, Cu and Ni was accomplished via sol-gel method using ligand monomers maleic acid and (2, 2′ ethylenedioxy) bis (ethylamine) reagent. We obtained a 14-membered macrocyclic functional unit called poly (1, 4-dioxa-7, 12-diazacyclotetradecane-8, 11-dione) as the main active sites for metal adsorption. The new adsorbent's cross-linked polymer chains was clearly visualized using SEM spectroscopy; whereas the FTIR, ^{13}C NMR and EDX techniques demonstrated its structural and functional groups. With an improved chelating power, this macrocyclic hydrogel was able to ignore non-target substrates, instead showing high specificity for only Cu, Cr and Ni from both single and multi-ion competitive aqueous solutions, in the order Cr > Cu > Ni. Pseudo-second order kinetic model aptly described the adsorption process, revealing chemisorption as the main mechanism which proceeded based on the host-guest chelation principle of metal ions onto the gel's macrocyclic active sites. Thus a high performance, high selectivity adsorbent system was achieved using active sites bearing substrate recognition and isolation properties.

1. Introduction

The design of new or improved materials for adsorption works require a careful balance to ensure high substrate specificity and high efficiency in adsorption process is achieved. Specificity of adsorbents, especially, is an invaluable quality property which determines which adsorbents are finally adopted for actual industrial application, bearing cost effectiveness [1–4].

Specificity requires adsorbents to either possess inherent functionalized active sites which bear properties that promote adsorption specificity and efficiency; or design of wholly new materials with deliberately created functional groups to fulfill this demand [5–10]. Adsorption selectivity is desired in purification works where one metal appears as impurity in the presence of other metals and requires selective removal without affecting the base metal. Additionally, in metal recovery and harvesting where target metal needs to be extracted from high competitive environment by overcoming effects of concentration and sameness of substrate features as ionic charge, size etc. in order that eventually, only the metal of interest is adsorbed. Therefore adsorbent materials that promote selectivity are the most relevant for such kind of works. In our discussion, the target substrates included heavy metal pollutants such as Cu, Cr and Ni which are heavily used in electroplating industries and coating industries. Effluents from these activities contain high concentrations of these metals and require strict decontaminating before the waters could be released. In such cases, adsorbents with high selectivity and efficiency would be a very good candidate of decontamination pathways via aqueous chemistry [11, 12] that would effectively and efficiently remove these contaminants.

Macrocyclic groups are archetypical high sequestering active sites for substrates in selectivity studies [13–15]. They have previously been used for selective capture of cesium [16, 17], palladium [18] and silver [19]. However, except for being mounted onto solid supports which bear no other functionality other than being base material, there had been no development hitherto of these groups into active adsorbents for industrial applications such as heavy metal decontamination of waters [20–22]. But we opine that if proliferation of macrocyclic groups to cover the entire framework of an adsorbent in a three-dimensional manner could be accomplished, this would instead produce a much more potent functionalized material. It would also allow more flexibility for such adsorbent's development and widen the breadth of

---

* Corresponding author at: Department of Applied Quantum Physics and Nuclear Engineering, Faculty of Engineering, West 2, 922-2, Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan.
E-mail address: brio254@athena.ap.kyushu-u.ac.jp (B.A. Omondi).

https://doi.org/10.1016/j.reactfunctpolym.2018.06.006
Received 26 February 2018; Received in revised form 13 June 2018; Accepted 13 June 2018

application.

Therefore, engendered by the gap for such kind of wholly macrocyclized adsorbents, our group attempted to synthesize a functionalized macrocyclic hydrogel for high selectivity adsorption works, exploiting the host-guest chelation principle. Our previous results on poly (1,4-diazocane-5, 8-dione) hydrogel [23] described successful synthesis of such functional adsorbent which demonstrated high specificity metal adsorption. Direct synthesis and polymerization of macrocyclic groups into a solid hydrogel materials ensured that the entire hydrogel surface contains these functional groups.

This material also allowed exciting opportunities whereby the nature of the macrocyclic ring could be altered in order to improve or expand the degree of selectivity and/or efficiency. But this required monomers with capability for water solubility, capacity to react in a condensation process and propensity for polymerization. In the present work therefore, with careful selection of new monomers while still building on the concept of macrocyclic functionalized hydrogels, we attempted synthesis of new adsorbent materials incorporating larger macrocyclic ring with more donor atoms. Our objective anticipates that bigger ring would change the nature of adsorbed metal selectivity, whereas increasing the number of donor atoms would improve ligand power, possibly leading to higher adsorption efficiencies. We describe the synthesis, characterization and performance testing of this new macrocyclic hydrogel.

2. Materials and methods

2.1. Materials

The following synthesis reagents were sourced from Sigma Aldrich (USA): 14-metal multi-element solution; Cr^{3+}, Cu^{2+} and Ni^{2+} stock solutions; *N, N′* Methylenebisacrylamide and ammonium persulfate polymerization agents; and (2, 2′ ethylenedioxy) bis (ethylamine) ligand monomer. Whereas acrylic acid and maleic acid were sourced from Wako chemicals (Japan) and Kanto chemicals (Japan), respectively. All materials were of pure analytical grade and were used as received without any further purification. All references to water shall refer to the ultrapure deionized water from Puric-ω purifier (Organo, Japan).

2.2. Synthesis process

Repetitive hydrogel fabrications showed that good mechanical and swelling properties are usually achievable at monomer concentrations between 0.5 and 1 M. In the present work, 1 M concentration was found most suitable and applied in all synthesis procedures. The monomers for this work were designed to interact in a condensation reaction, hence it was imperative that a 1:1 ratio be strictly maintained.

The first step involved dissolving 1 M concentration of maleic acid in water under high dilution. Thereafter, an equimolar concentration of (2, 2′ ethylenedioxy) bis (ethylamine) reagent was added to this mixture in a glass beaker under constant stirring. The mix monomer solution was transferred to a preheated hot water bath for 7 min sustained isothermal heating at 95 °C. This was in order to facilitate condensation coupling between the two monomers. Following, the polymerization agents: 0.2 M acrylic acid, 50 mM BIS and 5 mM of APS were added to this solution, making the final pregel solution mixture. The beaker with pregel contents was sealed and incubated at 40 °C isothermal bath for 24 h until complete gelation. Hydrogel fabrication was achieved within 12 h and designated as EBE hydrogel.

The newly fabricated gels were extracted, cut into predetermined cube sizes and washed in water for 48 h to dissolve and elute all unreacted chemicals and oligomers. The purified samples, now containing only the dense undissolved and cross-linked polymer chains making up the gel, were allowed to dry until a constant weight. Dried samples were characterized and tested for sorption properties.

3. Physico-chemical characterizations

3.1. Functional group and geometry

To investigate the presence and types of functional groups, the Fourier transform infra-red (FTIR) spectroscopy was undertaken using Jasco 4100 machine using the attenuated total reflectance (ATR) mode for the dried solid samples. Meanwhile, since EBE hydrogel was a functional polymeric material, there would only be a given number of equivalent carbons making up its structure. In order to determine the nature, types and location of actual carbons making up the hydrogel's active groups, ^{13}CNMR spectral measurements using the cross polymerization magic angle spinning (CPMAS) technique were recorded and analyzed.

3.2. SEM/EDX measurements

The SEM Superscan SS-550 model (Shimazu, Japan) was used in analyzing the surface features of the hydrogel adsorbent. This analytical tool exploits the secondary electrons ejected from the material to map out the characteristic properties of its surface. Measurements of pristine hydrogel were recorded at 20 kV accelerating voltages and probe sizes between 50 and 60 mm to ensure CPS count > 1000. Different magnifications were used until clear spectrums could be obtained.

SEM method also enabled concurrent electron dispersive spectroscopic (EDX) analysis, which was used to determine the actual elemental composition of the synthesized hydrogel. EDX measurements were simultaneously recorded for both the pristine and the metal-adsorbed hydrogel samples utilizing the same parameters as the SEM measurements.

4. Adsorption studies

4.1. Preliminary adsorption from multi-element solution

The first stage involved determining which metal(s) the EBE hydrogel had the most preference for adsorption. Accordingly, we used an integrated test solution containing 14-metals of equal concentration. Samples from original stock solution were diluted ten-fold with water to make working standard volumes whereby each metal within the multi-element solution had a final concentration of approx. 1 mg/L. Thereafter, EBE hydrogel adsorbent of mass 0.02 g were immersed into 0.02 L of this working standard test solution in batch adsorption experiments, investigated for up to 36 h. Changes in concentration of the working standard solution were monitored and recorded using ICP/MS instrument (Agilent 7700 s, Japan).

The results showed that whereas the concentration of other 11 metals remained unchanged, there was significant adsorption of only Cr^{3+}, Cu^{2+} and Ni^{2+} from this competitive solution.

Consequently, subsequent works of our study hereon focused on adsorption of these three metal ions from aqueous solutions, using EBE hydrogel.

4.2. Equilibrium adsorption of Cr, Cu, Ni

In the adsorption experiments, working standard solutions of the three metals were prepared in different concentrations as summarized in Table 1. Onto each of these concentrated test solutions, dry EBE hydrogel adsorbent masses of 0.02 g were immersed for batch adsorption process at ambient conditions under constant agitation of 110 rpm. The adsorption assays were repeated by changing parameters such as: initial concentration of metal ion solutions, level of competition, pH of solutions, adsorbent mass and adsorption time.

To analyze the degree of metal uptake and adsorption onto EBE hydrogel, we monitored changes in concentration of the respective solutions using the ICP/MS instrument and applied Eqs. (1) & (2):