

Synthesis of Unconventional Materials Using Chitosan and Crown Ether for Selective Removal of Precious Metal Ions

Rabindra Prasad Dhakal, Tatsuya Oshima, and Yoshinari Baba

Abstract—The polyfunctional and highly reactive bio-polymer, the chitosan was first regioselectively converted into dialkylated chitosan using dimethyl anionic solution (NaH in DMSO) and bromodecane after protecting amino groups by phthalic anhydride. The dibenzo-18-crown-6-ether, on the other hand, was converted into its carbonyl derivatives via Duff reaction prior to incorporate into chitosan by Schiff base formation. Thus formed diformylated dibenzo-18-crown-6-ether was condensed with lipophilic chitosan to prepare the novel solvent extraction reagent. The products were characterized mainly by IR and ¹H-NMR. Hence, the multidentate crown ether-embedded polyfunctional bio-material was tested for extraction of Pd(II) and Pt(IV) in aqueous solution.

Keywords—Lipophilic chitosan, Duff reaction, crown ether and precious metal ions extraction.

I. INTRODUCTION

CHITOSAN is one of the most abundant biopolymer in nature, benign and biocompatible compound which is generated in a huge amount every year as a renewable resource [1]. However, it is considered as a bio-mass wastes generated from agricultural sectors. Owing to increasing environmental awareness of the population, chitin and chitosan are going to be more and more appealing for the replacement of synthetic compounds. Moreover, in cosmetics and in biopharmaceutical industries, chitosan has exclusive properties, which are not found in other synthetic products [2]-[4]. In contrast, there are growing demands of precious metal ions in jewelry and various industries such as chemical, auto, electrical and electronic industries, which are equally demanding to recover such metal ions from the wastes. For the mutual benefit of managing wastes from two different sectors, we can use chitosan as a precursor for the suitable material preparations. It

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is learnt that most of the effort of using chitosan as an ion-exchanger is basically converting the chitosan into adsorbent either by crosslinking the chitosan or by further chemical modification incorporating other functional moiety of our choice [5].

Separation of metal ions from each other is also very crucial aspect as that of its recovery from the wastes, for which the materials needed to have increasing selectivity for targeted metal ions as reactivity needed for the recovery from the wastes. In this connection, it is anticipated that unconventional conversion of chitosan into different functional materials may bring appropriate selectivity to the materials by introducing novel functionality to the native materials [6]-[8].

To synthesize new and selective functional materials, solubility of the products derived from chitin and chitosan in organic solvent is a key and essential requirement for effecting fine molecular design leading to novel types of functional materials, since intractability of these amino polysaccharides has made regioselective modifications almost impossible [9]. Clearly, one of the reasons for the intractability of chitin and chitosan lies in the rigid crystalline structures, and the acetamido or primary amino groups of (N-acetyl-)D-glucosamine residues have an important role. Thus appeared problem could be mitigated by introduction of phthaloyl group into chitosan, which not only offer the reactive functional group intact after its deprotection but also offer increased solubility for further regioselective insertion of different moiety onto the polymers. However, there are very few, in fact, insignificant research progresses are being observed, which obviously reveals the originality and novelty of the work. Converting such amino group into phthaloyl derivatives to protect the amino functionality prior to O-alkylation followed by deprotection of amino group could convert chitosan into lipophilic reactive materials that can be easily condensed with multidentate ligands such as crown ether to prepare and novel solvent extraction reagent for precious metal ions [10].

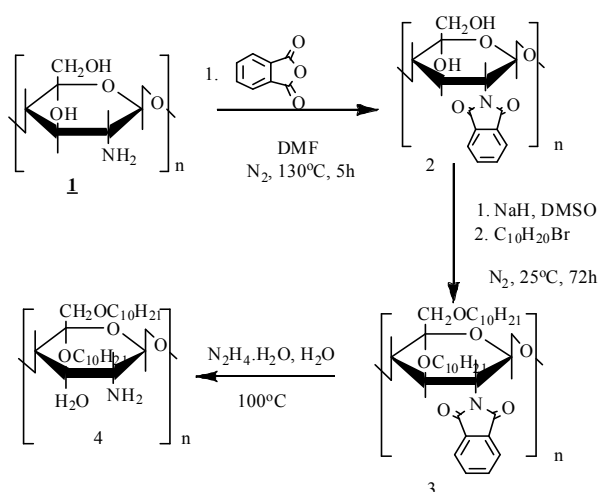
On the other hand, the crown ether alone being used as a solvent extraction reagent with additional counter anion, generally for extraction of alkali metal ions, however, there are some efforts on extraction of precious metal ions [11]. However, the problems associated with increased solubility of extractant towards aqueous phase and counter anions generally added for effective extraction usually impedes the stripping process, there by posing a limitation on its application for solvent extraction

with crown ether. To overcome such problem, we have condensed both macromolecules together to offer more selective site on the materials. We assumed that the selective extraction of precious metal ions would be possible on synergistic approach. We have synthesized a novel but unconventional functional materials as solvent extraction reagent by using the chitosan and formyl derivative of benzocrown ether through Schiff's base formation and tested for Pd(II) and Pt(IV) extraction from aqueous solution using chloroform as diluents.

II. EXPERIMENTAL

The syntheses of the materials were carried out as depicted in Schemes 1, 2 and 3.

A. Synthesis of Lipophilic Chitosan (3,6,-O,O-didecyl-chitosan



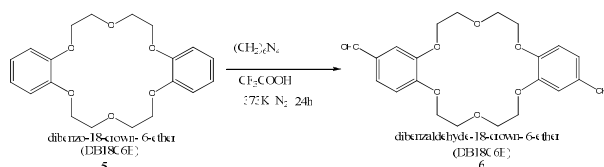
Scheme 1 Synthesis of lipophilic chitosan derivative starting from chitosan.

The chitosan, **1**, (DD>95%) (5g.) purchased from Kimica was dispersed in DMF(100ml) and subsequently phthalicanhydride (9g., 2 equivalent with respect to chitosan) was added and stirred vigorously at 130°C for 5h under inert atmosphere as shown in Scheme 1. After completion of the reaction, the reaction mixture was precipitated out by ethanol, filtered out, repeatedly washed with ethanol and finally dried *in vacuo* to obtain brownish white product, 7.5g. Thus obtained phthaloyl chitosan, **2**(5g) was vigorously dispersed into DMSO (200ml) at elevated temperature for 2h, which was followed by addition of dimsyl anion solution prepared by dissolving NaH(3.9g) in DMSO and kept stirred for 30 min. It was followed by addition of n-bromodecane (115ml) in drop wise manner and the reaction mixture was kept stirring at 200rpm at 25°C for 3 days under the inert atmosphere to obtain highly viscous reaction mixture of tanned color. The crude was precipitated out with ethanol, filtered and washed with ethanol several times so as to obtain clear filtrate passing out of it and dried *in vacuo* to obtain 8.5g. The alkylated chitosan (**8**) was then dissolved in pyridine (50ml) at elevated temperature,

followed by addition of water (100ml) and hydrazine monohydrate (5g) under inert condition at 80°C for 24h. The crude was precipitated out by ethanol, filtered, washed several times again with ethanol and finally dried *in vacuo* to obtain 6.0g dialkylated and deprotected chitosan.

B. Synthesis of Diformylated Dibenzo Crown Ether

This compound was prepared according to modified method of Duff reaction as depicted in Scheme 2.



Scheme 2 Synthesis of diformyl dibenzo-18-crown-6-ether by Duff reaction

A mixture of dibenzo-18-crown-6 (**DBC**) (5g, 15mmol), trifluoroacetic acid (0.10mol) and hexamethylenetetramine (4.4 g, 0.01 mol) was stirred at 90°C under nitrogen for 24h. The mixture was cooled down and scavenging the remaining acid by addition of 25 ml of concentrated KOH and 100 ml of water were successively added. The product was precipitated as a brown solid. The crude product was then collected by suction filtration and washed with acetone several times, resulting in brownish powder. The crude was again dissolved in chloroform and precipitated out by acetone to obtain the targeted product, filtered, washed with acetone and dried *in vacuo* to obtain 1.0g of diformylated dibenzo crown ether.

C. Synthesis of Crown-Ether Incorporated Lipophilic Chitosan Derivative

Hence, the newly synthesized two compounds **4** and **6**, as shown in Schemes 1 and 2, were condensed to obtain Schiff base as depicted in Scheme 3.

Dialkylated chitosan, **4**, (0.5) was dispersed in DMF (50ml) and treated with formylated dibenzo crown ether, **6**, (0.73g) at 90°C under N₂ for 24h. The product was then precipitated out by ethanol, filtered washed several times with ethanol and finally dried *in vacuo* to obtain 0.9g Schiff base of lipophilic chitosan. It was further dissolved in DMF and was subsequently reduced by NaBH₄ to obtain a novel material, **8** as shown in Scheme 3.

of diformylated dibenzo crown-ether of total product formed. Thus synthesized lipophilic chitosan and diformyldibenzo crown ether was condensed by Schiff base formation which was subsequently reduced with NaBH_4 into 8, a novel solvent extraction reagent of biopolymer origin. The IR-spectra and $^1\text{H-NMR}$ spectra of the product evidently supported the final conversion into desired product as we have observed intensified peak for etheric linkage, aromatic bending vibration, and rocking vibration at corresponding site.

B. Solubility of the Materials

The chitosan having $\text{p}K_a$ value ~ 6.5 makes it soluble in acidic solution, which can be avoided by either crosslinking the materials or introducing suitable functional group onto it so as to make the materials effective for metal ions adsorption. There are many efforts were maneuvered on alkylation of amino group to make it lipophilic but there is very insignificant almost non existence of O-alkylation process so as to make the chitosan lipophilic. The phthaloylated chitosan was soluble in DMSO, pyridine and DMF at elevated temperature. After successful alkylation onto chitosan, the material was found dissolved easily on aforementioned solvent at low temperature as well. After insertion of crown ether into chitosan, the material was observed highly compatible with chloroform and remains dispersant for several hours as of homogenous solution. It was also clear that the material was not dissolved in acidic solution as the native materials do. Hence, the material can be used as a solvent extraction reagent for selective removal of precious metal ions, in general, as we have expected. There is conventional trend of using low molecular weight reagents for solvent extraction technique to lessen the viscosity of the solution. However, considering our pursuance to make the novel materials with increased selectivity out of biopolymers, we have synthesized much more lipophilic materials, which are unexpectedly soluble in organic solvent. It is believed that on using such macro molecule may help to reduce the compatibility to the aqueous phase of the extraction solution even we have used crown moiety as a reagent.

C. Solvent Extraction Tests for Some Precious Metal Ions

We have tested the novel functional materials for Pd(II) and Pt(IV) extraction in chloroform as diluents as a function of $[\text{HCl}]$ to observe whether there is selectivity enhancement towards these precious metal ions or not. It revealed that at lower acid concentration both metal ions extraction was higher which was declined with increasing acid concentration suggesting the increased competition with H^+ for both metal ions as depicted in Fig. 4. It is worthy to consider the differences in affinity of the materials towards similar type of metal ions, namely, Pd(II) and Pt(IV) which is unlikely to be observed with chitosan. The chitosan, which has amino functional moiety, is believed to be efficient enough for up taking of precious metal ions mostly by ion pair formation. On contrary, we could assume that the crown ether is believed to involve on the metal ions up taking, basically, by size fitting mechanism for smaller metal ions, whereas larger metal ions are capping/cushioning onto the ring together with ion pair formation with coexisting counter anion. However, once the

crown ether is incorporated onto chitosan polymeric matrices, we can presume that something different phenomena do prevail the complex formation mechanism for metal ions extraction like capping mechanism or sandwiching between bifunctional ligands. This phenomenon also reduce the entropy of the complex, hence, it is attributing for the slight increment of the selectivity towards the Pd(II) over Pt(IV) metal ions.

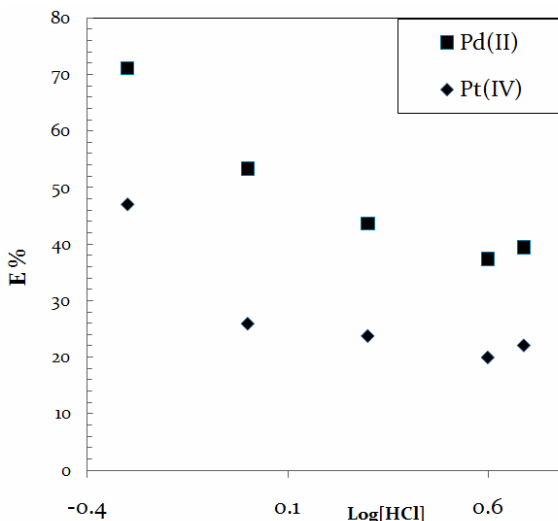


Fig. 4 Extraction tests of precious metal ions onto crown ether added lipophilic chitosan as a function of acid concentration

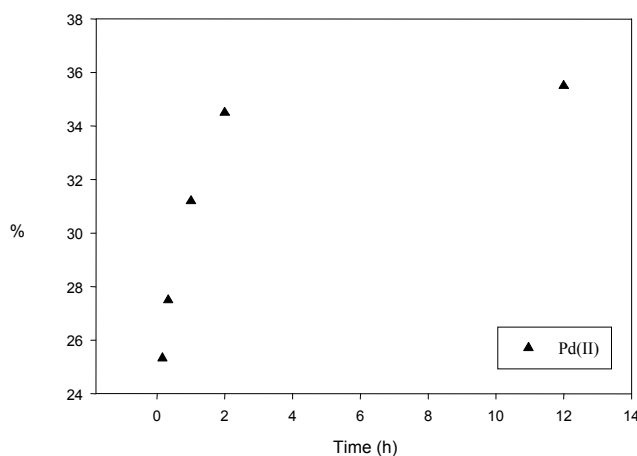


Fig. 5 Extraction tests of Pd(II) ions onto crown ether added lipophilic chitosan as a function of time

Furthermore, we have also tested the preliminary kinetics of extraction of Pd(II) with reagent, 8 anticipating its slow reaction because of molecular size of the materials. Fig.5. Shows the kinetics of Pd(II) extraction isotherms at 1M HCl where equilibrium was found after 2h which is indeed late in comparison to conventional solvent extraction reagent. It is believed that the macromolecular nature of the materials and plausible sandwiching process hereby decreasing the entropy of resulting complexes, is responsible for this effect.

IV. CONCLUSION

Chitosan, a biopolymer which is highly abundant and produced as renewable resources and a biocompatible and generated as a agricultural waste can be used for novel cause for waste management of various chemical industries. Incorporating suitable ligands, we either may increase the reactivity for effective recovery of various metal ions from wastes or enhance its selective by incorporating more selective ligands onto chitosan for separation of metal ions having similar chemical properties. Moreover, making the polymer with reactive moiety intact, we may proceed to opt for membrane filtration using such lipophilic biopolymers which may have more elusive application in the field of ion exchange and separation of wastes.

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Present Research Area:

Metal and Protein separation with adsorbents and extractants, Molecular assembly, Imprint techniques, Solvent extraction Publications

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