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Influence of the modification method on the immobilization ratio of crown ethers on the chitosan resin

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Abstract – In the presented study, a chitosan resin was modified by hydroxydibenzo-14-crown-4 ether, which is a highly selective complexing agent, often used in lithium extraction processes. Three immobilization methods of the analyzed ether were investigated: surface modification of dry chitosan beds, modification of fresh, wet resin, and pre-polymerization modification in solution. The immobilization efficiency was evaluated by analyzing organic residues in post-modification and storage solutions, while structural and morphological changes were assessed using SEM imaging. The pre-polymerization method resulted in the highest immobilization efficiency (over 90%), likely due to the incorporation of the crown ether into the resin matrix. The second highest immobilization ratio was observed for a fresh resin modification, obtaining over 30% immobilization of crown ether on the surface of chitosan beds. One of the possible explanations for these results is that the hydration state significantly affects reagent diffusion and surface coverage. SEM analysis revealed that each method induced distinct microstructural transformations, with pre-polymerization modification, giving the most porous and irregular surface morphology. These results demonstrate that the modification technique critically influences both the functional and structural properties of the chitosan resin, which may impact its future applications in different kinds of metal recovery processes.

Key Words**:** Chitosan resin, Resin modification, Crown ethers, Adsorption, Immobilization, SEM analysis

1. INTRODUCTION

Chitosan is a well-known resin type, popular mostly because of its biodegradability, non-toxicity and antimicrobial activity. It has become the center of interest in many studies in the fields of biomedical materials, drug delivery, wastewater treatment, and others (Sivanesan et al., 2022; Tan et al., 2013; Wang et al., 2020).

Another important compound related to the presented study is crown ethers, organic compounds capable of complexing different metals in a highly selective way. Due to their unique cyclic structure, crown ethers can effectively bind alkali metal cations, reducing their ion pairing strength (Gao et al., 2015; Junk, 2008). In the scientific literature, there are many reports showing that crown ethers, such as 18-crown-6, can have a high efficiency in stabilizing cations in solutions, which makes them important compounds in many chemical and material applications (Endicott and Strauss, 2007; Hilderbrand et al., 2006).

That is why, in the context of chitosan resin modification, using crown ethers to modify the surface of chitosan resin beds can help to increase the selectivity and efficiency of the adsorption processes, especially in terms of lithium selective binding. Studies have shown that chitosan modified with crown ethers shows a better ability to adsorb various cations, including Pb^{2+}, Cd^{2+} and Hg^{2+} compared to pure chitosan, indicating a clear synergistic effect (Changhong et al., 2003; Radwan et al., 2010; Yang et al., 2000).

However, the complexity of the interaction between chitosan resins and crown ethers leads to the necessity of analyzing the best immobilization method, to avoid loss of the crown ether compounds. That is why in this article, the authors aim to explore and analyze the influence of chitosan resin modification methods using hydroxydibenzo-14-crown-4 ether, on their surface properties and efficiency of the immobilization process itself.

2. MATERIALS AND METHODS

2.1. Synthesis of hydroxydibenzo-14-crown-4 ether

The selection of crown ethers was based on the results of preliminary studies based on existing literature reports (Kobiro, 1996; Pálsdóttir et al., 2021; Torrejos et al., 2016, 2015). The crown ether used in the study to modify the chitosan resin was hydroxydibenzo-14-crown-4 ether. Due to the free hydroxyl group, in this form, this ether is characterized by better binding properties to the surfaces of solids such as resins or selected sorbents, thus enabling their easier identification. The synthesis of hydroxydibenzo-14-crown-4 ether was carried out as part of earlier studies, obtaining a high-purity product by multiple crystallization, without the need to purify the product on columns. The purity and quality of the obtained product were confirmed using liquid chromatography (LC-MS) as well as ^{1}H and ^{13}C NMR H1 (1H

NMR (600 MHz, $CDCl_3$): δ (ppm) 2.25 (q, 4H, J = 5.5 Hz, –CH2–), 4.22 (t, 8H, J = 5.4 Hz, –CH2–), 6.87–6.89 (m, 8H, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 29.3, 67.2, 115.7, 121.6, 149.3.). All reagents used during the syntheses were of analytical purity and were purchased from Sigma Aldrich or VWR depending on the specific reagent. After obtaining the crown ethers in the form of a white powder, they were stored at room temperature in a desiccator until the actual immobilization process of the obtained product on the chitosan resin was carried out.

2.2. Synthesis of chitosan resins and their modification

The selected method of immobilization of crown ethers was their binding to the ethers of the chitosan resin surface, which was chosen as a potential carrier of the extractant due to its ecological nature and lack of toxicity to aquatic organisms in the event of decomposition. The preparation of chitosan resins was carried out by the drop method, in accordance with the commonly used methodology, in which 10 grams of the chitosan flasks were added to 300 ml of a 1%v/v solution of acetic acid in water. Next, the solution was stirred for 24 hours to a complete dissolution of the chitosan flask. Next, a crosslinking process was performed by adding a 15 g of epichlorohydrin, to 285 g of previously prepared chitosan solution. The obtained chitosan mixture was once again stirred, and after 2 hours it was added dropwise to a 2.5 molar solution of sodium hydroxide in distilled water. After addition, a white round beds of chitosan resin was formed and left in the NaOH solution for the next 12 hours to stabilize the resin structure. Obtained chitosan beds were then washed with distilled water until the full neutralization of the rinsing water was achieved. After this time, the resin was either dried or used for the crown ether modification, depending on the specific form of analysed modification. The drying process was conducted either before or after the crown ether modification. Nevertheless drying was always conducted at room temperature, in a desiccator, until a constant mass was obtained, but not shorter than 72 hours. Slow drying of the resins prevented their cracking and structural damage that could occur if they were dried at high temperatures.

Two methods of modification on the already polymerized chitosan resin were used on either dry or fresh chitosan resin beds. Dry resin modification (DM) was conducted by the addition of 9,5 g of the dried resin to the flask containing 100 ml of previously prepared solution of 0,5g hydroxydibenzo-14-crown-4 ether added to distilled water and heated to 75 °C until a full dissolution of crown ether was obtained. Next chitosan beds were mixed in that solution for the next 24 hours, keeping 75 °C temperature. After this time the water solution was analysed for the presence of un-immobilized crown ether concentration, while modified chitosan beds were washed several times in distilled water and stored for the next 5 days in 200 ml of demineralized water. Modification of fresh chitosan resin (FM) was conducted in a similar way, the only difference was the use of fresh chitosan beds instead of dry ones (the mass of the wet chitosan resin was adjusted to be equal to 9.5 g of dry mass).

The third method (solution modification - SM) of modification that was used during the study, was a modification of the resins before the polymerization process. In that case, modification was conducted directly at the initial 3,33% crosslinked chitosan solution, before the formation of the beds. To do so, 0,5g of previously prepared solid crown ether was added to 9,5 g of chitosan solution. Next, the mixture was grounded in a mortar until a uniform structure without lumps and larger crystals was obtained. The next steps of modified chitosan beds were conducted according to the previously mentioned methodology.

2.3. Analysis of the immobilization efficiency and Surface analysis

The analysis of the degree of immobilization of ethers on chitosan resins was carried out based on the analyses of organic residue mass in the water solution after the immobilization process (in the modification solution) and after proper conditioning of the modified resins in demineralized water after 5 days. The dry mass of the organic residues was calculated after the full evaporation of water on the rotary evaporator (50 °C and 0.01 atm). Next, dry organic residues were analysed on LC-MS and ^1H and ^{13}C NMR to confirm if it was consisting only of the unreacted hydroxydibenzo-14-crown-4 ether. Next, the modified and dried chitosan beds were analysed by using SEM methods to confirm differences in the surface of resins modified in different ways.

3. RESULTS AND DISCUSSION

Thanks to the modification of the chitosan resin, it was possible to immobilize the hydroxydibenzo-14-crown-4 ether on the surface of the chitosan resin. In the figure below pictures of the chitosan resins were presented.

Fig -1: Unmodified and modified chitosan resin beds. A-Unmodified; B – Modified beds FM; before drying; C – DM beds after drying.

As it was presented in Figure -1, after the modification process a slight difference in the resin color has also occurred. Chitosan beds became more yellowish after the modification and even after the drying, the color did not change back to a previous snow white. Based on that it can be also confirmed that crown ethers used during the modification process are definitely present on the surface of the resin after modification. However, to better show the efficiency of the immobilization process, a percentage of the immobilized crown ether for each of the modification processes was summarized in the table below.

Table -1: Immobilization rate of hydroxy dibenzo-14-crown-4 ether by using different modification methods

Modification type	After 24 hours	After 5 days
Dry – DM	31%	27%
Fresh – FM	52%	31%
Solution – SM	94%	92%

As can be seen in the table, the best results were obtained in the case of resin modification before its polymerization (SM). In that case, more than 90% of hydroxydibenzo-14-crown-4 ether were immobilized. However, it is worth remembering that in this case, immobilization took place not only at the surface of the resins but also at a lot of the crown ether mass was probably incorporated inside the chitosan beds structure after the polymerization process. Thus, if the modified resin is used in the future for the extraction of lithium, the efficiency of this kind of modified resin can be much lower, compared to the crown ether content in the overall mass of the resins. However, further usage of the modified resin was not analysed during this study, so at this step, it is hard to conclude if such a high level of immobilization is in fact a desired result in the case of the selective lithium separation.

Another important observation that can be made, based on the results presented in the table is that a much higher efficiency of the immobilization process was obtained for the resins modified in the fresh method (FM), compared to the dry method (DM). This is even more important due to the fact, that the nature of those two kinds of modification methods is very similar and all of the adsorbed crown ether particles, should be immobilized only at the surface of the resin, not inside of it. The possible difference in the immobilization efficiency, in that case, may be related to the different working volumes of the chitosan beds before and after drying. After the drying process, the volume of the chitosan beds was drastically decreased and thus, transportation of the crown ether particles inside the micropores of the beds could be more difficult, compared to the fresh resin beds.

The last step of the presented studies was to make the SEM analysis of the surface, to see if different modification methods had a different influence on the microstructure of the surface of the chitosan beds. SEM results were presented in the figures below (figure -2 and 3).

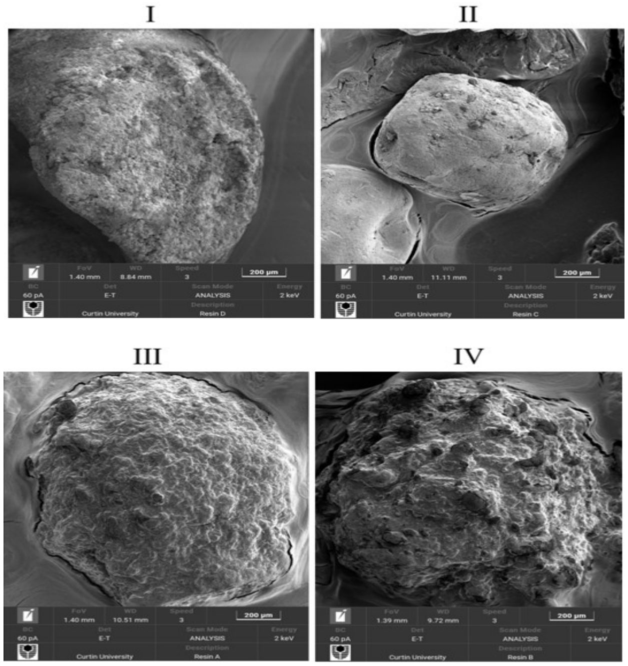

Fig -2: SEM analysis (200x magnification) of chitosan resin beds after each type of modification I- unmodified; II – DM; III – FM; IV – SM

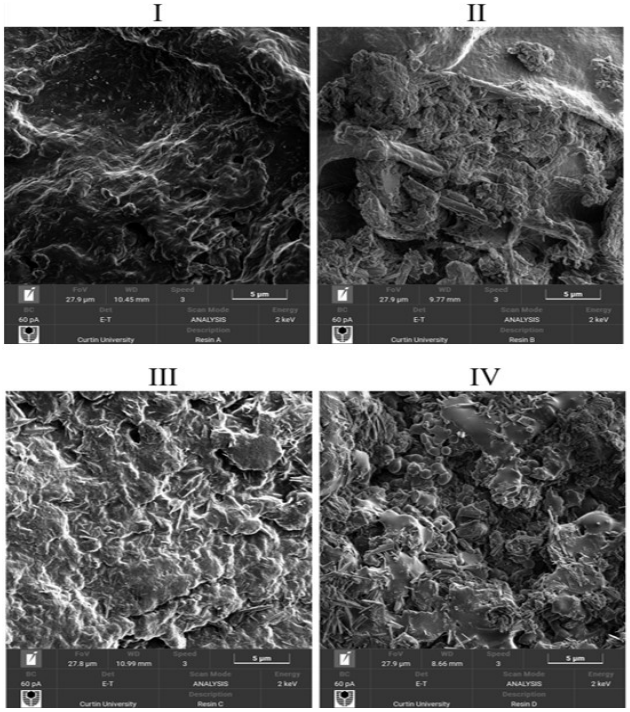

Fig -3: SEM analysis (11 500x magnification) of chitosan resin beds after each type of modification I- unmodified; II – DM; III – FM; IV – SM

Based on the SEM images of samples I–IV taken at both low (Fig-2) and high (Fig -3) magnifications, significant morphological differences were observed, reflecting the impact of the applied modification methods on the chitosan resin beds surface.

In the case of the unmodified resins (I), the surface of the samples shows a relatively smooth and homogeneous morphology. At lower magnification, the spherical shape of the resin beads is well preserved, with a compact and slightly porous surface. High-magnification images reveal a mildly undulating texture with few irregularities, indicating limited surface area and relatively low accessibility of active sorption sites.

The first modification method, based on the dry resin modification process (II) induced a noticeable increase in surface roughness. At low magnification, surface deformation and the appearance of cracks can be observed. At higher magnification, the structure appears fragmented and partially fibrous, suggesting increased porosity and potentially enhanced adsorption capabilities due to greater surface development.

The second modification method, by using the fresh, wet chitosan resin (III), results in a clearly altered surface topography. While the spherical structure of the particles was retained, numerous folds and surface indentations were visible. At higher magnification, the resin exhibits a significantly wrinkled and textured surface, indicative of a higher specific surface area. This morphological development is definitely favourable for the improvement of the sorption properties.

Last but not least, pre-polymerized modification (IV) led to the clearest structural transformation of the chitosan resin beds. Low-magnification images show irregularly shaped and severely deformed particles with clearly damaged surfaces. At higher magnification, a deeply porous and sponge-like structure is evident, characterized by numerous cavities and open channels. Such a morphology is expected to considerably enhance the accessibility of active sites, thereby probably improving sorption performance.

3. CONCLUSIONS

The presented study demonstrated the successful immobilization of hydroxydibenzo-14-crown-4 ether onto chitosan resins using three different modification methods. The highest immobilization efficiency was achieved by using a pre-polymerization (SM) method although it is likely that a substantial portion of the crown ether was trapped within the internal matrix of the resin rather than be adsorbed at the surface. As a result, this may impact its potential effectiveness in future ion-exchange or extraction applications.

The fresh resin modification method (FM) showed a clearly higher surface immobilization ratio, compared to the DM method, highlighting the significance of the resin hydration state on the modification outcome. The reduced porosity and volume shrinkage in the dry resin likely limited the accessibility and diffusion of the crown ether into the polymer network.

SEM analysis revealed distinct morphological changes induced by each modification approach. While the unmodified chitosan resin displayed a compact and relatively smooth surface, the DM and FM samples exhibited increased roughness and surface texture, potentially enhancing their adsorption performance. Last, the SM modification methods result in the most advanced surface transformation, characterized by extensive porosity and structural deformation.

To sum up, observed experimental results confirm that the method of crown ether immobilization significantly influences both the physicochemical properties and microstructural characteristics of obtained chitosan resins. Further studies are recommended to evaluate the functional performance of modified chitosan resins in the field of selective lithium recovery from water, wastewater and other highly salinized solutions.

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