

Synthesis and Characterization of Some Recycled Polystyrene and Chitosan Based Copolymers for Water Hardness Removal

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Abstract

Two sets of polymeric resins were prepared and used as ion exchange for the estimation of tap water's total hardness. The first set consisted of three different resins based on the sulfonation of the recycled polystyrene cup tea waste, and the other two resins were produced by grafting polymerization of the acrylamide monomer and its extended polyacrylamide polymer. The second set is based on Chitosan and its grafted derivatives of Chitosan-succinyl-poly (ethylene glycol) polymer. All the prepared resins were characterized by FTIR which confirmed the correctness of the sulfonation process and hence the grafting polymerizations on sulfonated polystyrene and Chitosan. The grafting process causes an increasing efficiency of the sulfonated polystyrene resin from 4% to 54% with sulfonated resin-g-acrylamide monomer in removing the tap water hardness. This resulted in an increase in the chain length of the acrylamide monomer grafted onto the resin via free-radical polymerization with potassium persulfate as an initiator. It increases the efficiency of the consumed resin grafted with polyacrylamide to 80.22%. While with the Chitosan grafted set, the efficiency is increased from 19% to 86% with Chitosan-g-N-succinyl-poly (ethylene glycol)

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1. Introduction

Water is one of the important natural resources for the support of all types of life, food security, economic growth, and welfare. It cannot be replaced in many uses and is costly to ship, but to de-pollute is a blessing to the world from Mother Nature [1]. Hard water is water that contains cations with a charge of $+2$, especially Ca^{2+} and Mg^{2+} . These ions do not pose any health threat, but the main problem with hard water is that the formation of mineral deposits by ionic reactions resulting in the formation of an insoluble precipitate of calcium carbonate as an example. These deposits can make hard water unsuitable for many uses, and so a variety of means have been developed to "soften" hard water; i.e., remove the calcium and magnesium ions [2,3]. This precipitate, known as scale, coats the pipes, heaters, boilers, and other units that raise the temperature of the water resulting in large-scale deposits. More serious is the situation in which industrial-sized water boilers become coated with scale: As these deposits build up, however, they reduce the efficiency of heat transfer and the cost in heat-transfer efficiency can have a dramatic effect on the power production [4].

Furthermore, the scale can accumulate on the inside of household appliances, such as dishwashers, and pipes. As scale builds up, water flow is impeded, and hence appliance parts and pipes must be replaced more often than if Ca^{2+} and Mg^{2+} ions were not present in the water. Water hardness is defined as the total calcium and magnesium ion concentration in a water sample, represented as calcium carbonate concentration. Temporary hardness is the portion of total hardness that vanishes when water is added to it. The hardness of the water varies depending on where you go. Surface waters are generally softer than ground waters [5]. The degree of hardness in water is widely used to classify as shown in Table 1.

Table 1: Classification of the type of hardness [5].

Hardness (mg/L)	Degree of hardness
0-75	Soft
75-100	Moderately hard
150-300	Hard
>300	Very hard



With the Eriochrome Black-T indicator, the Ethylenediaminetetraacetic Acid (EDTA) complexation procedure for the water sample is employed in this work to estimate the total hardness of the tap water in Garmat Ali-Basrah Province during February 2021. EDTA is a powerful complicating agent and it forms four to six bonds with Ca^{2+} and Mg^{2+} . Because of its low water solubility, it is employed as a disodium salt that dissolves in water and forms a very stable molecule with no color, a 1:1 combination with calcium and magnesium ions. The resulting complex is very water-soluble [6]. In previous work [7], the strong cationic ion-exchange sulfonated polystyrene resin consumed in the production of electricity was reactivated by grafting polymerization and used in removing the boiler's wastewater hardness. Its efficiency was increased from 54.34% to 55.37%, 56.20%, and 63.22% depending on the type of grafted monomer, and it reached its maximum with polyacrylamide up to 83.68%. Therefore, this study is engaged in recycling polystyrene waste in form of teacups and sulfonation the chopped pieces to prepare sulfonated polystyrene. This will be the base resin to prepare other resins by grafting acrylamide monomer and extending it to polyacrylamide by free-radical grafting polymerization, from one side and another side, we will use chitosan extracted from shrimp shells to prepare another set of resins. All these resins will be used to remove tap water hardness.

2. Experimental

2.1. Materials

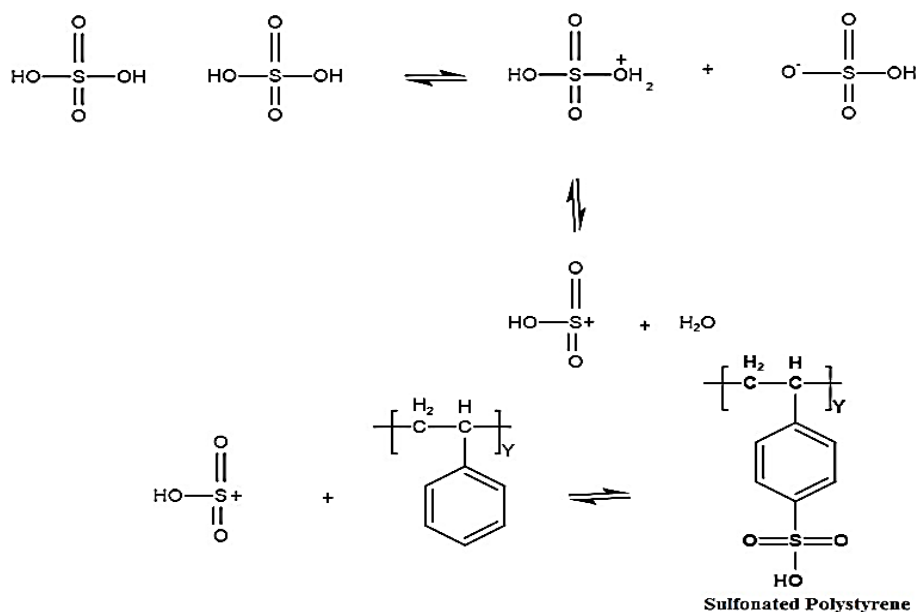
The trash from polystyrene teacups was collected and washed several times with tap and distilled water before drying at room temperature. The dried teacups were chopped into small pieces before sulfonation reaction. Chitosan (DD=85%), acrylamide monomer, succinic acid, polyethylene glycol (M.Wt. 10000 g/mole), ethylenediaminetetraacetic acid (EDTA), and ammonia persulfate were purchased from Sigma Aldrich, and Eriochrome Black T from BDH.

2.2. Preparation of Sulfonated Polystyrene (SPS)

Twenty grams of chopped polystyrene waste teacups were placed in a 250 mL round bottom flask, then 50 mL of 96% sulfuric acid was added at room temperature with continuous stirring [8]. After that, the mixture was refluxed for around 4 hours at 60-65 °C. Scheme 1 depicts the sulfonation chemical route. The process was ceased by adding cold distilled water



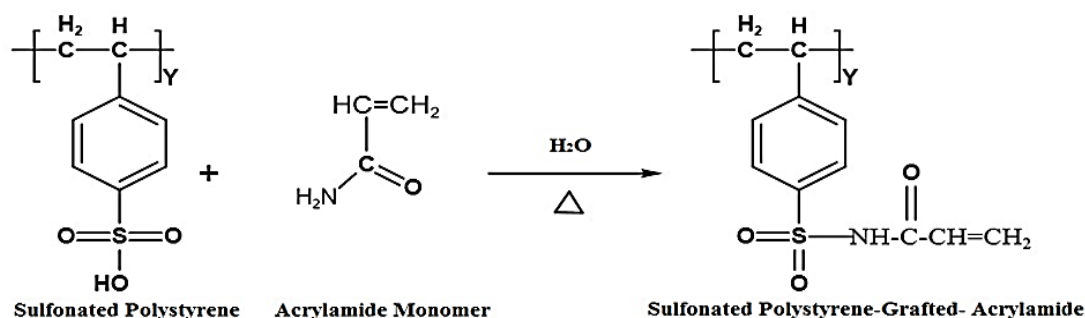
and the SPS was obtained through separation and filtration, and it was then rinsed with distilled water until the pH was neutral, then it was dried at 60 °C.



Scheme 1: Sulfonation route of polystyrene waste (SPS).

2.3. Synthesis of SPS-Grafted-Acrylamide

Weighing 5 g of sulfonated polystyrene resin and placing it in a 100 mL 2-neck round bottom flask filled with 50 mL distilled water and equipped with a magnetic stirrer, then adding 5 g of acrylamide (AAM) monomer. The mixture was left churning at 40°C for 3 hours to complete the grafting procedure. After that, the resin was rinsed several times with distilled water to remove any ungrafted monomer [9,10]. The grafting equation can be represented in the scheme 2.

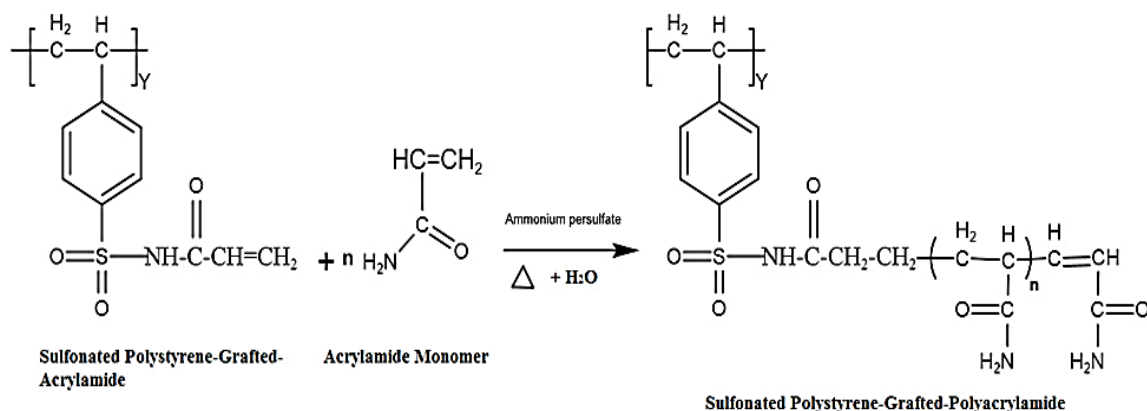


Scheme 2: Chemical equation of grafting acrylamide onto SPS resin.



2.4. Synthesis of SPS-Grafted-Polyacrylamide

The acrylamide monomer grafted sulfonated polystyrene was prolonged by the free radical polymerization mechanism in the 2-neck round bottom flask equipped with a thermometer and condenser. After mixing five grams of acrylamide-g-SPS with 50 mL distilled water, a few crystals of ammonium persulfate were added to act as a free radical initiator. An additional 5 g acrylamide monomer was gradually added to the reaction mixture, which was then refluxed for three hours [7,11]. The liquid was emptied into the water after cooling to room temperature to eliminate any unreacted acrylamide monomer, with the possibility of producing a polyacrylamide homopolymer. After being filtered and washed multiple times with water and acetone separately, the polyacrylamide-g-SPS resin was vacuum dried at 50°C. The Scheme 3 depicts the polyacrylamide-grafted-SPS production process.

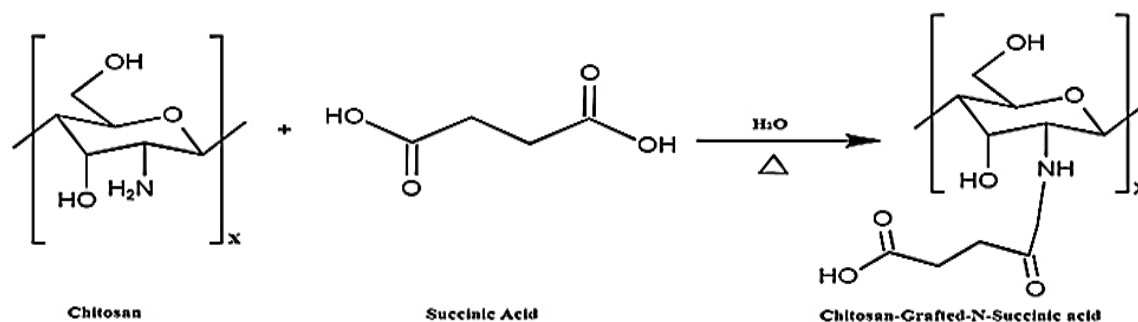


Scheme 3: Formation of polyacrylamide-grafted-SPS.

2.5. Synthesis of Chitosan-Grafted-N-Succinyl-Poly(ethylene glycol)

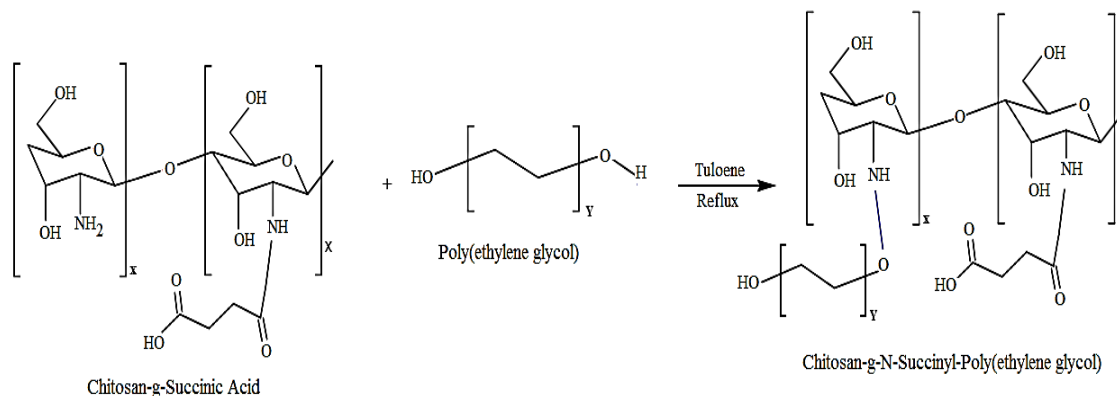
Chitosan-g-succinic acid was made by grafting succinic acid onto Chitosan in a three-neck round bottom flask with a condenser, magnetic stirrer, and thermometer. 5 g Chitosan and 50 mL tetrahydrofuran solvent were combined in the round flask, and then 5 g succinic acid was added. The mixture was magnetically stirred and heated to a refluxed temperature of THF solvent for 2 hours. Then, it was allowed to shake and cool to room temperature [12]. Before being dried in the vacuum desiccator, the Chitosan-g-succinic acid was filtered and washed multiple times with THF and acetone, respectively. The Scheme 4 shows the chemical grafting equations.





Scheme 4: Chemical route of Chitosan-g-succinic acid.

By grafting poly(ethylene glycol), M. Wt. 10000 g/mol, to the obtained Chitosan-grafted-N-succinyl, the following process [154] was used to prolong the Chitosan-grafted-N-succinyl. Five grams of poly(ethylene glycol) were dissolved in 100 mL dry toluene, which was then distilled down to 50 mL. The mixture was then added to 3 g Chitosan-g-succinic acid and refluxed for 3 hours at 110°C with stirring under a dry nitrogen environment [13,14]. After that, it was allowed to cool to room temperature before being filtered and rinsed with diethyl ether multiple times before being dried in a vacuum desiccator. The grafting response is depicted in Scheme 5.



Scheme 5: Synthetic route of grafting poly(ethylene glycol) into Chitosan-g-N-succinyl.

2.6. Determination of the Total Hardness in Tap Water

The six resins prepared were used in a batch method to estimate the tap water total hardness. Titration of a water sample before and after treatment with each resin made with a standardized solution of ethylenediaminetetraacetic acid (EDTA) using Eriochrome Black T as an indicator is



widely used to determine it. This technique was carried out by first obtaining a 25 mL water sample, then adding 1 mL of ammonia buffer to adjust the pH to 10 ± 0.1 , then adding 1 or 2 drops of Eriochrome Black T indicator solution. The solution turned wine red, suggesting the presence of calcium or magnesium. With vigorous shaking, the mixture was titrated against EDTA until the wine red color turned blue, indicating that the endpoint had been attained. The following equation can be used to calculate the tap water total hardness [7,15]:

$$\text{Total hardness (mg. L}^{-1}\text{)} = V1 \times N \times 100 \times 1000/V$$

Where V (mL) is the volume of the water sample taken and V1 (mL) is the volume of EDTA with N normality. All samples were assessed in triplicate and results were reported as a mean value.

3. Results and Discussion

3.1 Characterization of Prepared Resins by FTIR

Infrared spectroscopy is a technique that may be used to identify unknown substances and count the number of distinct components in a sample. This experiment was conducted to get precise information on the vibrational sources of sulfonated polystyrene teacup debris and their grafted copolymers developed in this study. They were identified as KBr discs using Shimadzu FTIR 8400S spectroscopy because of their availability, which was the best choice given the time and money required for analysis.

3.1.1 Characterization of sulfonated polystyrene (SPS)

The sulfonation procedure allows for the synthesis of functionalized polystyrene, which tolerates for further applications for the polymer derived from teacup waste. This will result in the formation of strong reactive sulphonyl acidic groups, which can be employed as an ion exchange resin or as a center for grafting various chemicals and polymers onto sulfonated polystyrene (SPS) to suit our applications. The FTIR spectrum of sulfonated polystyrene, shown in Figure 1, displayed multiple distinct peaks at various frequencies. The sulfonation reaction was successful since the new sulfonyl functional group was formed. The most important peaks we're looking for are a strong unique peak at 1450 cm^{-1} connected with the (S=O) stretching of the sulfonyl group as a result of the sulfonation process and a wideband at 3417 cm^{-1} indicative



of the vibration of the O–H group of ($-\text{SO}_3\text{H}$). Aromatic (C–H) and aliphatic (C–H) bonds were discovered in the FTIR spectra at $3062\text{--}3028\text{ cm}^{-1}$ and $2920\text{--}2850\text{ cm}^{-1}$, respectively. The aromatic ($-\text{C}=\text{C}$) bond was also responsible for a peak at 1601 cm^{-1} [7,17].

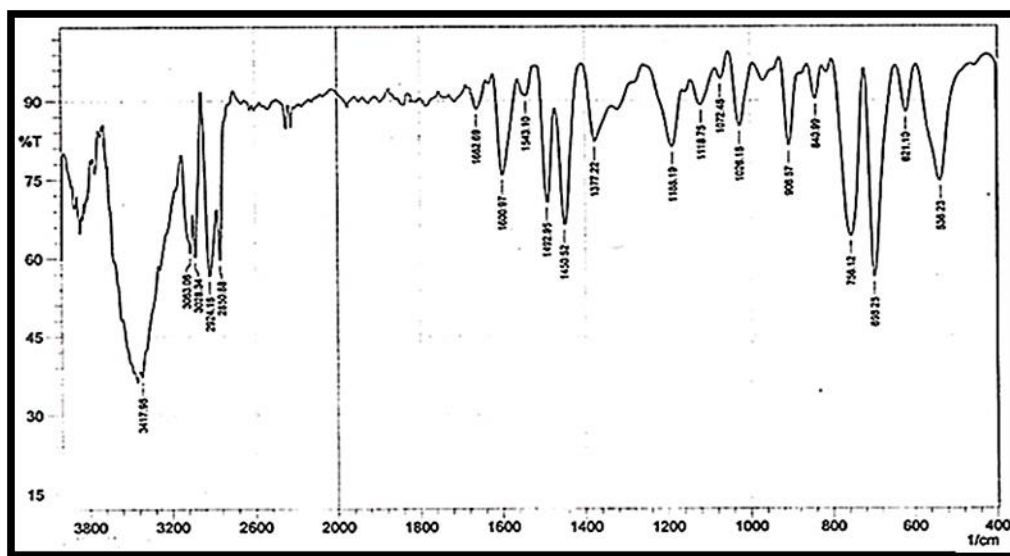


Figure 1: FTIR spectrum of sulfonated polystyrene waste.

3.1.2. Characterization of SPS-grafted-acrylamide

Acrylamide, a vinyl type monomer, was used to graft the amide pendant group onto sulfonated polystyrene (SPS) to increase the functionality of the SPS and therefore the synthesized resin's uses. The FTIR spectrum of the SPS-grafted-acrylamide monomer was as expected, with the characteristic absorption band at $3444\text{--}3425\text{ cm}^{-1}$ attributed to the $-\text{NH}$ group corresponding to the $-\text{OH}$ of the sulfonyl $-\text{SO}_3\text{H}$ group [18,19], Figure (2). Aside from the 1157 cm^{-1} absorption peak attributed to the stretching vibration of the $\text{S}\text{--}\text{N}$ of the sulfonamides $\text{SO}_2\text{--}\text{NH}$ group produced as described in Scheme 2, section (2.3).

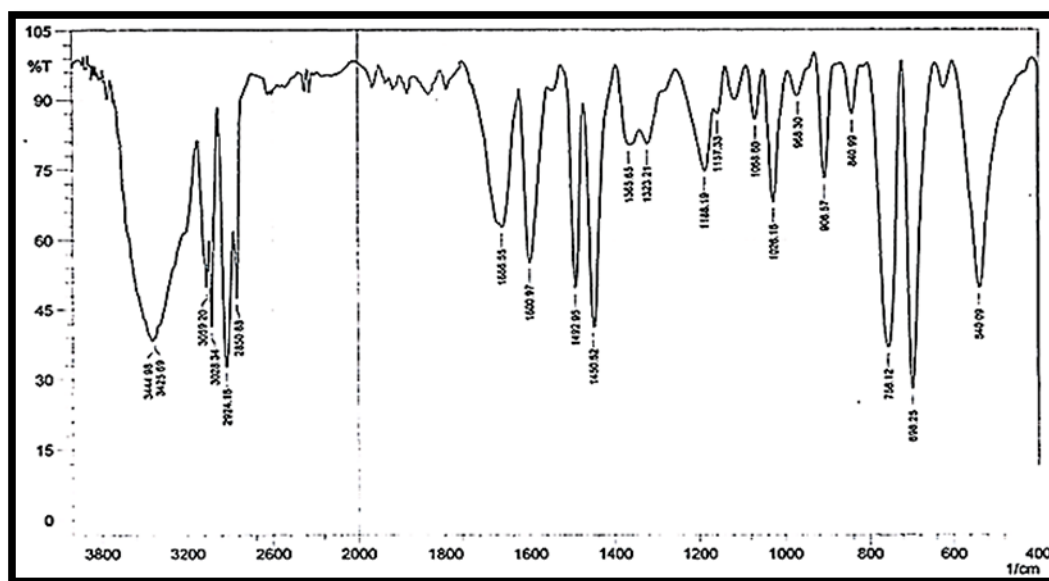


Figure 2: FTIR spectrum of SPS-g-acrylamide.

Figure 2 also demonstrates a band at 1666 cm^{-1} that corresponds to the stretching vibration of the amide carbonyl ($\text{NH}-\text{C}=\text{O}$) group [20]. It overlaps with the vinyl ($\text{C}=\text{C}$) bonds at around 1620 cm^{-1} and widens, indicating that the grafting of acrylamide monomer onto the SPS was done appropriately [14]. The presence of the acrylamide ($\text{C}=\text{C}$) monomers' double bond is confirmed by the presence of the peak at 1026 cm^{-1} attributed to the carbon-hydrogen bending vibrations associated with the ($\text{C}=\text{C}$) double bond [21,22].

3.1.3. Characterization of SPS-grafted-polyacrylamide

As stated in, the SPS was extended by free-radical grafting polymerization of an additional acrylamide monomer in the presence of an ammonium persulfate initiator (section 2.4). The infrared spectra of SPS-grafted-polyacrylamide are shown in Figure 3. The peaks are the same as the SPS-grafted-acrylamide FTIR spectrum shown in Figure 2. The most prominent peak observed at 1666 cm^{-1} , which is attributed to the stretching vibration of the carbonyl amide group ($-\text{CO}-\text{NH}$), is demolished, and this is attributed to the disappearance of the ($-\text{C}=\text{C}-$) double bond of acrylamide, which confirms its free radical polymerization [17,23], as shown schematically in Scheme 3, Section (2.4).

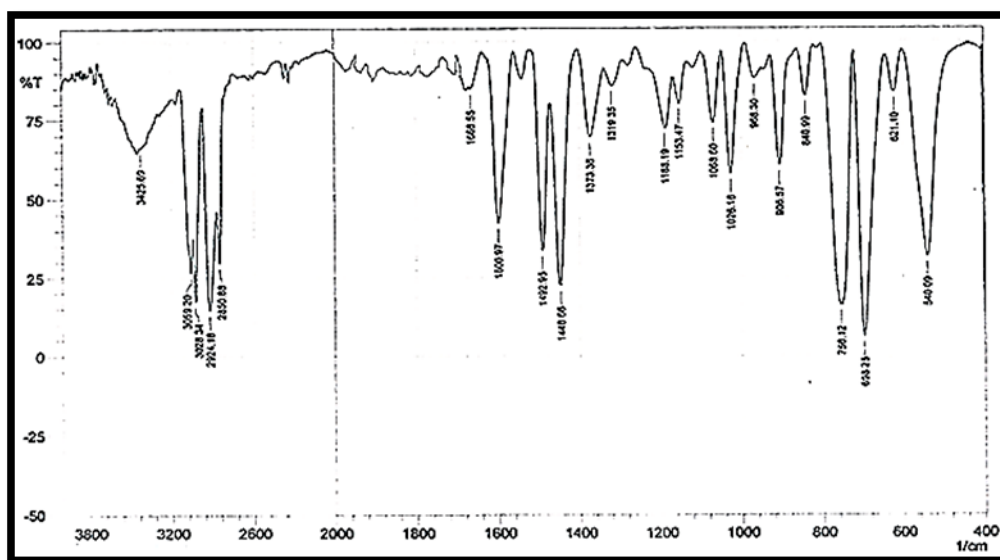


Figure 3: PSS-grafted-polyacrylamide.

3.1.4. Characterization of Chitosan

The commercial Chitosan utilized in this investigation was also characterized using FTIR. The spectrum obtained is shown in Figure 4. It has a broadband peak at 3445 cm^{-1} due to (-OH) and (-NH) stretching, as well as a weak band with a peak at 1647 cm^{-1} for amide I, which is typically leftover from the deacetylation process, which matches well with the provider's degree of deacetylation of 85, (Section 2.1). This is further supported by a strong band at 1415 cm^{-1} due to the (C-N) stretching bond [24,25].

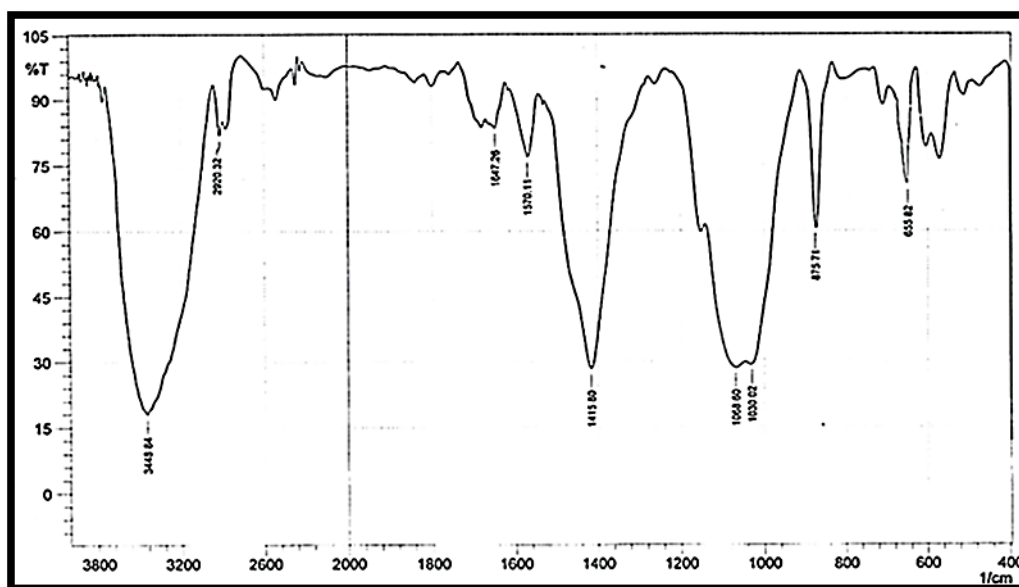


Figure 4: FTIR spectrum of Chitosan.

3.1.5. Characterization of Chitosan-N-succinyl and its extended poly(ethylene glycol) derivative

Due to the versatility of chemical changes of Chitosan [26], researchers are always exploring new applications and specialized uses for Chitosan derivatives. Chitosan is a unique cationic polysaccharide with exceptional complex properties and a high affinity for numerous surfaces, even when unchanged. Grafting copolymerization is an important and feasible method for modifying Chitosan [27]. A distinguishing chemical structure of Chitosan is the presence of key reactive basic amino groups that can be used as grafting centers onto the Chitosan backbone to match our purpose of the work and their applications. Graft copolymerization of succinic acid onto Chitosan can provide desirable properties and expand the range of applications for Chitosan. The spectrum of chitosan-grafted-succinic acid is also studied using FTIR, as illustrated in Figure 5. The most distinguishable peak is of carbonyl group which belongs to the free carboxyl groups ones appears at 1717 cm^{-1} implying that real grafting has occurred on the Chitosan [92],

Apart from what has been stated about chitosan itself, grafting succinic acid onto it is thought to provide the most impressive peaks. To begin, one of the two acid carbonyl groups is grafted to Chitosan via reaction with the amino groups, converting them to amide, which appears



as a strong band at 1647 cm^{-1} , while the other acid group is presumably free and unattached, and their carbonyl can be found in the acid region at 1716 cm^{-1} due to $\text{C}=\text{O}$ stretching vibrations [14,27]. Figure 5 also shows a strong absorption peak in the $3444\text{--}3338\text{ cm}^{-1}$ range, which corresponds to the overlapping stretching vibrations of the functional groups $-\text{OH}$ and $-\text{NH}$. The C-H group's stretching vibrations have absorption maxima of 2877 cm^{-1} and 2924 cm^{-1} .

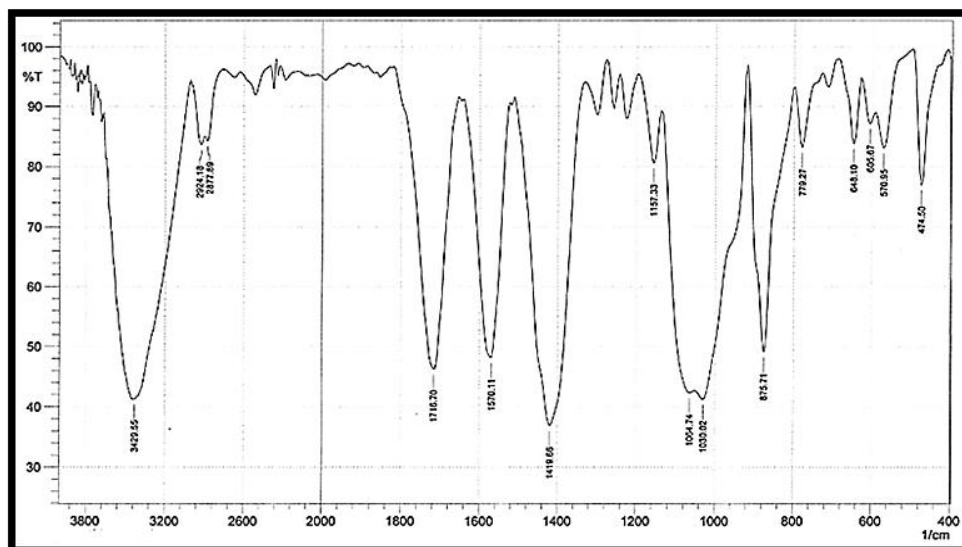


Figure 5: FTIR spectrum of Chitosan-g-succinic acid.

With poly(ethylene glycol) chain length (10000 g/mol), the Chitosan-succinic acid grafting process was extended. Figure 6 shows the FTIR spectrum acquired. The FTIR spectrum of Chitosan-N-succinyl-grafted-poly(ethylene glycol) reveals absorption at 3452 cm^{-1} for (O-H) and (N-H), as well as two peaks at 2742 cm^{-1} and 2885 cm^{-1} for methylene group ($-\text{CH}_2-$) vibration. The $-\text{C}=\text{O}$ stretching vibrations of the ester carbonyl group were represented by the typical peak at 1732 cm^{-1} , and the band 1597 cm^{-1} was ascribed to ($\text{C}=\text{O}$, NH_2). The characteristic of C-O-C stretching vibrations of repeated $-\text{OCH}_2\text{CH}_2$ units of PEG block and the $-\text{COO}-$ band stretching vibrations were ascribed to the strong peaks at 1145 and 1111 cm^{-1} , respectively, as illustrated in Figure 6.

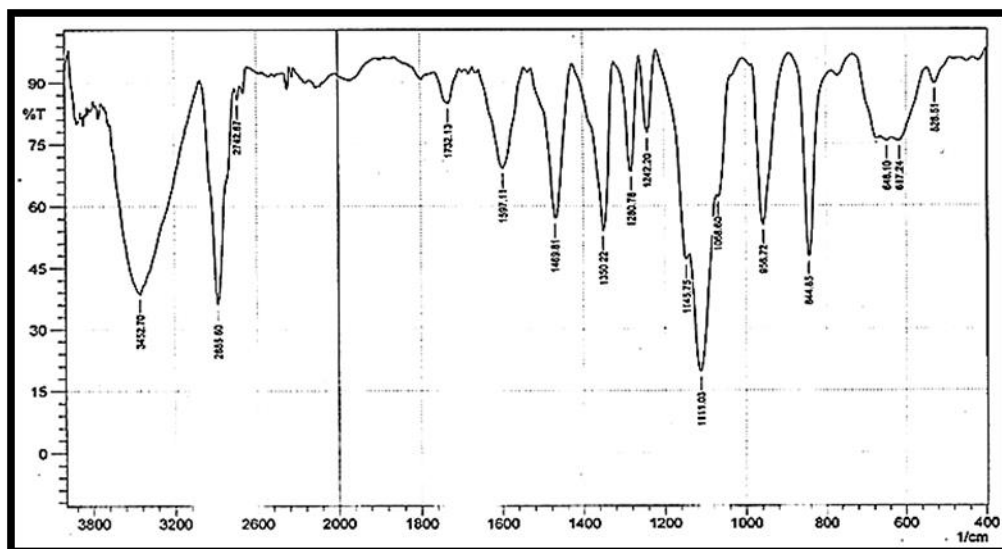


Figure 6: FTIR spectrum of Chitosan- N-succinyl-g-poly(ethylene glycol).

3.2 Total hardness Measurements of Tap Water

Water Hardness levels can range from 0 to hundreds of milligrams per liter. The EDTA titration method is used to calculate hardness in water because it may be determined by adding a little quantity of Eriochrome Black T indicator to an aqueous solution containing calcium and magnesium ions at a pH of 10 ± 0.1 , resulting in a wine red colored complexes [22,23]. Calcium and magnesium ions have a greater affinity for EDTA. As a result, when EDTA is introduced, the former complexes (Ca-EBT and Mg-EBT) are disrupted and new blue-colored complexes (Ca-EDTA and Mg-EDTA) are created. When all of the ions have been complexed, the solution becomes blue, signaling the conclusion of the titration. This procedure was carried out first to determine the tap water's total hardness without using any of the prepared resins. The conditions utilized and the results obtained are listed in Table 2. It appears from Table (2) that the overall hardness of the raw tap water was 455 ppm before treatment with any of the produced resins. This number will be used to compare the efficiency of the prepared resins in this study.

In this procedure, the produced sulfonated polystyrene resin and its grafted derivatives, specifically SPS-g-acrylamide and SPs-g-polyacrylamide, are employed. Table 3 shows how effective they are at removing total hardness from tap water samples. The SPS resin's



performance in reducing water hardness appears to be relatively low, with only 4.40 percent measured.

Table 2: Measured total hardness of tap water before treatment.

Date	28/02/2021
Time	10 am
pH	8.18
Total Volume	1L
Titrated Volume	10mL
Average EDTA Volume	4.25mL
Total Hardness	455ppm

Grafting the synthesized SPS resin with acrylamide monomer improved its effectiveness slightly, with a 54.94 percent efficiency, which is regarded as a favorable change. To improve this efficiency, the grafting conditions had to be optimized. In the presence of ammonium persulfate as an initiator, free-radical grafting polymerization was used to expand the grafted acrylamide monomer by polymerizing additional monomer (section 2.4). This was a fantastic move that allowed the % efficiency to rise. As shown in Table 3, the SPS-g-polyacrylamide resin rolled 80.22 percent of the metal ions causing the tap water hardness under examination. This could be attributed to the acrylamide monomer repeating unit's chain length increasing, resulting in the grafted resin's improvement and % efficiency increasing. It also gives an impression of the success of the grafting polymerization process, which allows for greater room to use the prepared SPS resin from polystyrene waste, and it may be considered a positive step in chemical recycling that delivers both economic and environmental benefits.



Table 3: % Efficacy of the prepared different resins in removing tap water hardness.

Resin	pH	Weight (g)	Volume sol. (mL)	Sample volume (mL)	Average EDTA volume T_{ave} (mL)	Total Hardness (ppm)	% Efficacy
No resin	8	-	25	10	4.25	455	-
SPS	8	0.1	25	10	2.05	435	4.40
SPS-g-Acrylamide	8	0.1	25	10	4.35	205	54.94
SPS-g-polyacrylamide	8	0.1	25	10	0.9	90	80.22
Chitosan	8	0.1	25	10	3.65	365	19.78
Chitosan-g-N-succinyl-PEG	8	0.1	25	10	0.45	45	90.11

The other natural polymer used as an ion exchange resin for removal of tap water hardness was Chitosan readymade purchased from sigma Aldrich Company, but it's originally extracted from shrimp shells waste as mentioned in section (2.1) and its prepared grafted derivative Chitosan-g-N-succinyl-poly (ethylene glycol) polymer as mentioned in section (2.5). Tap water hardness removal was comparable for the two resins at the same conditions used for the determination of total tap water hardness before and after treating with the first set of resins prepared, SPS, SPS-g-acrylamide, and SPS-g-polyacrylamide, as shown in Table 2.

The effectiveness of chitosan resin in removing tap water hardness was recorded at 19.78% efficacy (Table 3), which is considered low, but it seems better than the prepared SPS resin. It appears that despite the presence of the amine and hydroxyl groups, (CS) may not owing to a non-cross-linking structure that improves the polymeric network and the effectiveness of these groups, as well as the resin in general. Grafting with succinic acid and extending this with the poly(ethylene glycol) polymer chains strongly enhances the chitosan efficiency, and this was true as the efficiency percent increased from 19.78 to 90.11% respectively as exhibited in Table



3. This implies that Chitosan-based derivative impart a range of different analytical applications and these agreed well with results reported in the literature [12,28].

5. Conclusions

A recycled polystyrene waste was successfully sulfonated and grafted with acrylamide monomer in this study, and the latter was converted to a polyacrylamide polymer using ammonium persulfate as a free radical initiator. Chitosan was also grafted with succinic acid and extended with a poly(ethylene glycol) polymer chain. All six resins have been characterized by FTIR, confirming the correctness of the sulfonation reaction of the polystyrene waste polymer and grafting process. In terms of removing tap water hardness caused by metal ions Ca^{2+} and Mg^{2+} in ordinary tap water, the highest removal results were obtained with Chitosan-g-N-succinyl-poly(ethylene glycol) resin, with an efficiency percent of 90.11, and the second was SPS-g-polyacrylamide, with an efficiency percent of 80.22%. Results imply that chitosan and its derivatives have better environmental and economic benefits than conventional SPS and its derivatives in tap water treatment. To show the effectiveness of our optimal %efficiency results as the future work, we ought to apply them to other tap water and raw water.



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تحضير وتشخيص بعض البوليمرات المشتركة من البولي ستايرين والكيوسان المعاد تدويرهم

لإزالة عسرة المياه

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المستخلص

تم تحضير مجموعتان من الراتنجات البوليمرية واستخدامها كمبادلات أيونية لتقدير عسرة مياه الصنبور الكلية. تألفت المجموعة الأولى من ثلاثة راتنجات مختلفة المعتمدة على سلفنة مخلفات البولي ستايرين المعاد تدويرها لأكواب الشاي، وتم إنتاج الراتنجات الأخرى عن طريق عملية البلمرة التطعيمية مع مونومر الأكريلاميد ومن ثم بوليمر البولي أكريلاميد، وتستخدم المجموعة الثانية على الكيوسان المستخلص من مخلفات قشور الروبيان الجاهز ومشتقة المطعم بحامض السكسينيك وبولي (أكلايكول الإيثيلين) [كيوسان-N-سكسينيل- بولي (كلايكول الإيثيلين)]. شحصت جميع الراتنجات المحضرة بمطيافية الأشعة تحت الحمراء التي أكدت صحة عملية السلفنة وبالتالي البلمرة التطعيمية على البولي ستايرين المسلفن والكيوسان. انتجت عملية التطعيم كفاءة متزايدة في إزالة العسرة الكلية لماء الصنبور لراتنج البوليسترين المسلفن من 4% إلى 54% مع مونومر الراتنج المطعم بمونومير الأكريلاميد ومن ثم إلى 80.22% عند بلمرة المونومير إلى البولي أكريلاميد. بسبب زيادة في طول سلسلة من مونومر الأكريلاميد المطعمة على الراتنج عن طريق بلمرة الجذور الحرة. بينما مع مجموعة الكيوسان والكيوسان المطعم بحامض السكسينيك وحامض السكسينيك-بولي (كلايكول الإيثيلين) لوحظ زيادة في نسبة الكفاءة من 19.78% المقاسة للكيوسان إلى 78.02% كيوسان-حامض السكسينيك إلى 86.81% للكيوسان المطعم بحامض السكسينيك-بولي (كلايكول الإيثيلين).