

# ***Graft Copolymerization Of Acrylic Acid Onto Fatty Chitosan: Synthesis, Characterization and Waste Water Treatment***

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## Research Article

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# Abstract

Environment is worsening day by day due to industrial pollution, with hazardous chemicals contributing to the accumulation of heavy metal contaminants in waste water. Waste water polluted by these effluents disrupts the usual use of water for irrigation and marine life. The purity and efficiency of water is a paramount concern of mankind. These effluents must also be treated. Natural biopolymers are industrially desirable because of their ability to remove metal ions found in waste water. Among the many other low-cost absorbents listed, chitosan has the highest sorption potential for several metal ions <sup>(1)</sup>. In specific, we were trying to extract chitosan from shrimp, by N-deacetylation of chitin. The chemical structure of chitosan was characterised by the spectroscopy of Fourier Transform Infrared (FT-IR). The degree of N-deacetylation (DDA) was also calculated from FT-IR data. The use of biosorbent chitosan-fatty acid derivatives makes it possible to extract both heavy metals and organic compounds. In this analysis, the grafting copolymer of fatty chitosan derivatives with acrylic acid polymer was synthesised using ceric ammonium nitrate, the redox nitric acid method under UV irradiation. Synthesized copolymers have been subjected to various analytical techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) to confirm the formation of copolymers and to research their thermal stability. The findings show the formation and strong chemical interaction between fatty chitosan derivatives and acrylic acid. Fatty Chitosan derivatives and prepared grafting copolymers have been treated with copper and chromium-containing metal solutions and the results have shown that fatty chitosan derivatives and prepared copolymers are excellent in the removal of heavy metals such as copper and chromium. Prepared compounds could therefore open the way for industrial waste water treatment.

## 1. Introduction

Much attention has been given in recent years to the removal of toxic and polluting heavy metal ions from industrial effluents, water sources and mine waters. Water quality is a primary concern for humans, as it is directly related to human well-being. <sup>(2)</sup> Water is polluted in many ways, such as effluent of leather and chemical industries, electroplating industries and dye industries <sup>(3)</sup>. The presence of heavy metals in the environment is of significant concern due to their transition from relatively low toxic species into more toxic ones. Some metal ions, such as Hg and Cd, are extremely toxic even at lower concentrations. (0.0010.1mg/ L) <sup>(4, 5)</sup>. Current physicochemical procedures for the removal of heavy metals such as precipitation, reduction, ion exchange, etc are costly and inefficient in the treatment of large amounts. They also produce metal bearing sludges that are difficult to dispose of. More stringent government and media rules and public pressure on effluent discharges have necessitated a search for newer methods of treatment. <sup>(6, 7)</sup>. Biosorption is a viable choice since it is both effective and inexpensive compared to other traditional methods for extracting toxic metals from effluent. Biosorption, which includes active and non-active biomass uptake, is a strong alternative to conventional methods. Biomaterials used for sorption are complex and a variety of mechanisms could occur simultaneously <sup>(6)</sup>. There are some chemical groups in biomass that could theoretically attract and sequester metal ions: acetamido groups in chitin,

amino and phosphate groups in nucleic acids, amino, amido, sulfhydryl and carboxyl groups in proteins and hydroxyl groups in polysaccharides<sup>(8)</sup>. Among the many other low-cost absorbents listed<sup>(9, 10)</sup> chitosan has the highest sorption potential for several metal ions<sup>(7)</sup>. Chitosan (2-acetamido 2-deoxy- $\beta$ -D-glucose(N-acetylglucosamine)) is a partially deacetylated polymer of chitin and is typically prepared from chitin with a strong alkaline solution. The word "chitosan" refers to chitin that has been deacetylated to more than 60 percent. Chitosan has many properties that have created interest in its use such as biodegradability, biocompatibility and non-toxicity<sup>(11)</sup>. The deacetylated component, chitosan, has an amine functional group that is highly reactive to metal ions. This has contributed to research into the use of chitosan in metal absorption. Deacetylation would control the content of glucosamine and thus the fraction of the free amine groups usable for metal binding. These groups are more reactive than the groups of acetamide present on chitin. Their solubility in acidic solutions also varies, with chitosan being soluble. The physicochemical properties of chitosan depend on different parameters, such as degree of deacetylation, polymer weight, etc<sup>(12)</sup>. To enhance the efficiency of chitosan as an adsorbent, crosslinking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon diglycidyl ether and isocyanate have been used<sup>(13)</sup>. Crosslinking agents not only stabilise chitosan in acid solutions in such a way that it becomes insoluble, but also improve its mechanical properties<sup>(14–17)</sup>. The stability can also be achieved by chemical modifications. Chemical modifications leading to the creation of chitosan derivatives, grafting of chitosan and chitosan composites have received a great deal of interest, have been extensively studied and have been widely reported in the literature.

Graft copolymerization of acrylic acid with chitosan is therefore a novel and promising attempt due to the chemical bonding of macromolecules. Studies on the grafting copolymerization of chitosan with various vinyl monomers have been performed with different initiation systems and mechanisms. There are primarily two types of initiation systems i.e. chemical initiation and radiation initiation, to copolymerize various vinyl monomers, such as acrylic acid, vinyl acetate (VA), acrylonitrile (AN), methacrylic acid (MA) and methyl methacrylate (MMA)<sup>(18, 19)</sup>, to chitosan. There are records of grafting of vinyl monomers to polysaccharides using both high energy (e.g.  $\beta$ ,  $\gamma$ , xray) and low energy (e.g. photo, UV light)<sup>(20)</sup>. While graft copolymerization with radiation initiation is an economical and fast process, it is more difficult to handle under technical conditions.<sup>(21)</sup> Graft carboxymethyl chitosan copolymer with methacrylic acid (MA) was prepared using ammonium persulfate as the initiator and its water solubility was greatly improved<sup>(22)</sup>. Chitosan graft copolymer with polyacrylamide has been successfully synthesised in the presence of nitrogen using ceric ammonium nitrate, a redox nitric acid method with UV irradiation<sup>(23)</sup>. The reaction of chitosan graft acrylic acid was performed in a homogeneous acetic aqueous process using ceric ammonium nitrate as an initiator<sup>(24)</sup>. In another study, the graft copolymerization of acrylonitrile (AN and methyl methacrylate (MMA) with chitosan using potassium persulfate as an initiator was studied<sup>(25)</sup>. Similarly, graft copolymerization of acrylonitrile to crosslinked chitosan using ceric ammonium nitrate as an initiator was also tested<sup>(26)</sup>. Ammonium persulfate or potassium persulfate has been used as an initiator alone in most other literature<sup>(22, 25, 27,28)</sup>, and is part of the peroxy-initiator method. But the initiator of ammonium persulfate and sodium thiosulfate can be a redox system, which

can produce two free radicals, thus reducing the decomposition of activation energy at a faster polymerization rate. There are however, few studies of grafting copolymerization for the modification of chitosan using the redox system of ammonium persulfate and sodium thiosulphate as the initiator. The purpose of this study was to perform a kind of chemical modification of the derivatives of chitosan fatty acids by the method of graft polymerization of acrylic acid into the backbone of the derivatives of chitosan fatty acids. In the current work, the products were characterised by FTIR and XRD, which elucidated changes in structure compared to chitosan fatty acid derivatives. The mechanism of the graft reaction has been proposed. In the present research, the efficacy of chitosan grafted acrylic acid in the treatment of waste water was identified and the copolymer was a promising matrix for the adsorption of metal ions.

## **2. Materials And Methods**

Chitosan was extracted from shrimp shells waste. Ceric ammonium nitrate, Acrylic acid ,and all other chemicals used in the experiments were of analytical grade.

### **Preparation of Chitosan**

The preparation of chitosan is divided into three consecutive stages. Demineralisation of shrimp shells. Chitin processing (deproteinization) and chitosan processing (deacetylation). Shrimp shells were dried 2 days in the sun. The shrimp shells were crispy after sun-drying. The shells were then ground into powder. Dry Powder shrimp shells were packed in opaque plastic bottles and kept at room temperature.

### **Demineralization of Shrimp shells**

In this step, the finely powdered shrimp shells are demineralized with HCl. At room temperature, the shrimp shells were demineralized at 5 percent HCl for 24 hours with a solid to 1:6 ratio. After 24 hours, the shells were very squash and rinsed with water to extract acid and calcium chloride and dried in the oven to 60°C. A small amount of treated shell was re-reacted to 10% HCl solution, which showed no generation of bubbles. This test confirms the complete demineralization of the shell.

### **Deproteinization**

Demineralized shells were deproteinized at a solid to solvent ratio of 1:10 (w/v) with 5 percent NaOH solution for 48 hours at 60–70°C. After treatment, the residue was washed with distilled water to extract NaOH. It is then dried for 2 days and the result is called chitin.

### **Chitosan processing (Deacetylation)**

Deacetylation is a method to convert chitin to chitosan by eliminating the acetyl group. After rinsing with distilled water, decalcified chitin was transferred to a 60% sodium hydroxide solution. The solution was heated for 2 hours in a domestic microwave oven for deacetylation. After rinsing with distilled water and drying at 60°C, deacetylated chitin (chitosan) was ready to be used.

## Structural characterization of chitosan

The degree of N-deacetylation (DDA) of chitosan powder was calculated by Fourier transform infrared (FT-IR) spectroscopy using FT-IR JASCO 4100. Samples were screened against a blank KBr pellet at wave number 4000–400 $\text{cm}^{-1}$ . Chitosan DDA was determined on the basis of the following equation. <sup>(29)</sup> :

$$\text{DDA (\%)} = 100 - [(A_{1655} / A_{3450}) \times 115]$$

where;  $A_{1655}$  and  $A_{3450}$  are absorbances at 1655  $\text{cm}^{-1}$  and 3450  $\text{cm}^{-1}$ , respectively.

## Preparation of Fatty Chitosan Derivatives

For the preparation of (Ch-L), (Ch-S), (Ch-OI) and (Ch-Lin) derivatives, 10 mg (lauric acid, stearic acid, oleic acid and linoleic acid) were added individually to the chitosan solution (dissolved in 1% acetic acid) and kept on stirring for 20 h. After that they were poured on glass plates and film drawn and left for air drying for 5 days.

## Preparation of Copolymer

A 2% W/V solution of chitosan and fatty chitosan derivatives were prepared in 2% aqueous acetic acid. A solution of 0.1 M ceric ammonium nitrate (CAN) in 10 ml of 1N nitric acid was added accompanied by a known amount of acrylic acid (Ac) drop by drop with continuous UV stirring. The reaction temperature was held at 70°C for 45 minutes, the substance was precipitated by the use of sodium hydroxide solution with intense stirring. The precipitate washed with distilled water several times to extract the homopolymer formed and filtered.

The grafting efficiency (GE %) and grafting yield (GY %) were calculated as follows:

$$W_g$$

$$\text{Grafting Efficiency (GE\%)} = \frac{W_g}{W_g + W_i} \times 100$$

$$W_g + W_i$$

$$W_g - W_i$$

$$\text{Grafting Yield (GY\%)} = \frac{W_g - W_i}{W_i} \times 100$$

$$W_i$$

Where,  $W_g$  Weight of grafted copolymer;  $W_i$  Weight of homopolymer (acrylic acid).

## Characterization of polymer

Prepared grafted copolymers were analysed in Xray diffraction studies using Xray Powder Diffractometer (XRD – SHIMADZU XD – D1) using Nifiltered Cu K5-007 Xray radiation. Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan composites were performed using a Perkin Elmer simultaneous thermal analyzer (STA 6000) at a temperature range of 50-600-C at a heating rate of 10-C min<sup>-1</sup> under the nitrogen atmosphere.

### **Experimental process of removal of chromium and copper**

Batch experiments were conducted with various concentrations of copper chloride and potassium dichromate to investigate the degree of adsorption. The degree of removal of the two metals was tested separately by changing the time of shaking of the adsorbent metal solution mixture. The pH of each solution has been adjusted. The stoppered bottles were agitated at 30°C by an orbital shaker at fixed speed, 160 rpm at different time intervals. The adsorbates were isolated using Whattman filter paper and the residual metal concentration of the supernatant liquid was measured by the atomic absorption spectrophotometer. Triplicate runs of less than 1% of all experiments were carried out to ensure the reproducibility of the data collected.

## **3. Results And Discussion**

### **3.1. Degree of deacetylation(DDA) of chitosan**

DDA is the percentage of amino groups formed by the deacetylation process. The DDA of chitosan varied in literature, ranging from 40 to 60 percent<sup>[27]</sup>. The majority of commercial samples of chitosan have an average DDA of 70–90 percent<sup>[28]</sup>. For certain special biological applications, higher DDA chitosan (> 95%) was prepared by more deacetylation, which not only increased the cost of preparation but also frequently resulted in partial depolymerization<sup>[31]</sup>. As you can see in Fig. 1, FT-IR analysis of chitosan samples shows that all the characteristic peaks corresponding to the chitosan functional groups have identified. The disappearance of absorption bands at 1540cm<sup>-1</sup> showed a good deproteinization of chitin. Another broad, intense absorption band at approximately 3450cm<sup>-1</sup> was corresponding to the hydroxyl groups (OH) of chitosan and could also be physically adsorbed water molecules. <sup>(32–35)</sup>.

### **3.2 X-ray diffraction (XRD)**

The XRD spectra of chitosan and its grafting copolymer are shown in Fig. 2. Chitosan exhibited two diffraction peaks at 8.65° and 19.9°, which are characteristic of the hydrated crystalline structure of chitosan, while Ch-g-Ac composite displays an X-ray diffraction pattern with no specified peaks, suggesting that the crystallinity of chitosan decreased after modification. It is obvious that the crystallinity of chitosan had vanished when copolymerized. This phenomenon was due to the strong interaction (covalent bond formation) between chitosan and acrylic acid. In other words, copolymerization enhanced the compatibility between chitosan and acrylic acid.

figure 3 shows regular lattice spacing of lauric acid crosslinked chitosan Ch-L and Ch-L-Ac composite. The XRD pattern of chitosan- lauric acid shows sharp diffraction peaks at  $16.2^\circ$ ,  $21.4^\circ$ ,  $23.8^\circ$ ,  $39.4^\circ$  and  $46.3^\circ$ . The peak of d-spacing 4.1 at  $2\theta = 21.4^\circ$  has lower intensity than that appeared in XRD spectra of Ch-L-Ac. Moreover the peak of d-spacing 3.72 at  $2\theta = 23.85^\circ$  has higher intensity than that appeared at  $2\theta = 23.75^\circ$  and a new peak is formed at  $2\theta = 9.7$  in the XRD pattern of crosslinked chitosan lauric acid grafted acrylic acid composite. This is proved the interaction between the component. The XRD pattern of Ch-L-Ac composite shows sharp diffraction peaks at  $6.3^\circ$ ,  $9.7^\circ$ ,  $16.1^\circ$ ,  $20.1^\circ$ ,  $21.4^\circ$ ,  $23.7^\circ$  and  $40.2^\circ$ .

Figure (4) shows XRD pattern for chitosan stearic acid Ch-S and chitosan stearic acid grafted acrylic acid composite Ch-S-Ac. The XRD pattern of chitosan stearic acid shows two sharp diffraction peaks at  $21.3^\circ$  and  $23.6^\circ$  while Ch-S-Ac composite shows sharp peaks at  $7.2^\circ$ ,  $21.7^\circ$  and  $23.9^\circ$ .

Figure (5) shows XRD pattern for chitosan oleic acid and chitosan oleic acid grafted acrylic acid composite. The XRD pattern of chitosan oleic acid shows one broad peak at  $2\theta = 19.6^\circ$  it may be due to the formation of an amorphous material which can be attributed to the intermolecular interaction between chitosan and oleic acid within the films[42]. Ch-Ol-Ac composite shows an X-ray diffraction pattern with no defined peaks, which indicating that the modification is done and the composite is formed.

Figure (6) shows XRD pattern for chitosan linoleic acid and chitosan linoleic acid grafted acrylic acid composite. The XRD pattern of chitosan linoleic acid shows one broad peak at  $2\theta = 18.8^\circ$ . due to the formation of an amorphous material. Ch-Lin-Ac composite shows an X-ray diffraction pattern with no defined peaks.

### 3.3. Thermal Analysis

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) shows the thermal behavior of chitosan grafted acrylic acid (Ch-g-Ac) (Fig. 7), chitosan Lauric acid grafted acrylic acid composite (Ch-L-Ac) (Fig. 8), , chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac) (Fig. 9), , chitosan oleic acid grafted acrylic acid composite (Ch-Ol-Ac) (Fig. 10) and , chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac) (Fig. 11) as a function of % weight loss with temperature. All samples show three different zones. An initial zone of slight loss in weight due to the evaporation of water. Then the break in each thermogram indicates the onset of the decomposition process involving a rapid loss in weight. At the end of this break a slight curvature is formed, which might be due to the formation and evaporation of some volatile compounds. Finally, the decomposition rate decreased gradually to a constant weight representing carbonization<sup>(36)</sup>.

The percentage weight loss with temperature are given in Table 2. The initial decomposition temperature (IDT) for chitosan grafted acrylic acid (Ch-g-Ac) started at  $150.6^\circ\text{C}$ , which is lower than the initial decomposition temperature of , chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac) ( $178.6^\circ\text{C}$ ). On the other hand the initial decomposition temperature of , chitosan lauric acid grafted acrylic acid composite (Ch-L-Ac), , chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac) and ,

chitosan oleic acid grafted acrylic acid composite (Ch-OI-Ac) started at (128.6°C), (145.2°C) and (135.8°C) respectively .

Table 1  
*Degree of deacetylation (DDA) values obtained from FT-IR data.*

Chitosan sample	DDA (min)	I <sub>1655</sub>	I <sub>3450</sub>	DDA (%) FTIR
Ch1	10	93.99	88.73	40.38
Ch 2	20	84.34	68.80	47.62
Ch 3	30	90.14	76.06	56.37
Ch 4	40	97.61	93.70	57.24
Ch 5	50	95.78	88.36	59.93
Ch 6	60	94.12	70.1	80.38
Ch 7	90	97.24	80.09	85.5
I <sub>1655</sub> and I <sub>3450</sub> are light intensity of- NH <sub>2</sub> and -OH groups at 1655 and 3450cm <sup>-1</sup> , respectively.				

Table 2

Thermal stability of chitosan composites in nitrogen atmosphere at a heating rate of 10°C. min<sup>-1</sup>

Sample code	IDT <sup>a</sup> (°C)	ADT <sup>b</sup> (°C)	wt. loss (%)									
			°C									
			100	200	300	400	500	600	700	800	900	
Ch-g-Ac	150.6	165.2	4.7	50.1	70.0	82.5	91.8	96.2	99.3			
Ch-L-Ac	128.6	230.4	0.48	35.0	62.6	67.5	73.4	77.2	81.4	83.4	85.2	
Ch-S-Ac	145.2	146.0	0.11	25.5	62.7	69.4	72.4	80.2	82.1	84.1	85.3	
Ch-OI-Ac	135.8	224.9	1.3	25.8	52.4	62.0	72.4	76.0	79.5	81.7	84.9	
Ch-Lin-Ac	178.6	228.9	1.9	16.0	49.2	72.2	94.5	99.5				
<sup>a</sup> IDT : the initial decomposition temperature.												
<sup>b</sup> ADT : the active decomposition temperature.												

The DTA curves show the active decomposition temperature (ADT) for ), chitosan lauric acid grafted acrylic acid composite ( Ch-L-Ac) which is 230.4°C and goes on decreasing for chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac),chitosan oleic acid grafted acrylic acid composite (Ch-OI-Ac), chitosan grafted acrylic acid (Ch-g-Ac) and chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac) to (228.9°C), (224.9°C), (165.2°C) and (146.0°C) respectively.



## Effect of contact time

It is clear from Figs. 12 ,13 indicated that the percentage removal of copper increased with the increase in contact time before equilibrium was reached. Other parameters such as dose of adsorbent and pH solutions were kept constant. It is illustrated that the percentage removal of copper were 97%, 95.4%, 66.6 % and 33.3% for chitosan lauric acid (Ch-L), chitosan stearic acid(Ch-S), chitosan oleic acid (Ch-Ol) and chitosan linoleic acid (Ch-Lin) respectively. On the other hand were 40% ,30% ,35% ,27.7% and 33.3% for chitosan grafted acrylic acid (Ch-g-Ac), chitosan lauric acid grafted acrylic acid composite( Ch-L-Ac), chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac), chitosan oleic acid grafted acrylic acid composite (Ch-Ol-Ac) and chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac ). (Fig. 14 ,15) showing that % removal of chromium were 74.6%, 56.5%, 27.3 % and 16.6% for chitosan stearic acid(Ch-S), chitosan lauric acid (Ch-L), chitosan linoleic acid (Ch-Lin ) and chitosan oleic acid (Ch-Ol)respectively. While were 43.3% ,33.3% ,22% ,10% and 13.3% for chitosan grafted acrylic acid (Ch-g-Ac), chitosan lauric acid grafted acrylic acid composite ( Ch-L-Ac), chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac), chitosan oleic acid grafted acrylic acid composite (Ch-Ol-Ac) and chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac ).

The initial rapid adsorption then gives way to a very slow approach to balance, saturation is reached in 1 hr for chromium and 4 hr for copper. The rapid initial removal rate may be due to the availability of sufficient vacant adsorbing sites in the presence of higher metal ion concentration gradients. Subsequently, the percentage of metal ion removal rates decreased dramatically due to the reduced number of empty adsorption sites. Further increase in contact time did not increase the uptake due to deposition of metal ions at the available adsorption sites on adsorbent materials. 240 min is therefore set as the minimum contact time for the maximum removal percent of copper ion and 60 min for chromium ion.

## Conclusion

Prepared fatty chitosan derivatives and their grafted acrylic acid copolymers have been developed in the presence of CAN as redox initiator and have been confirmed by FTIR, XRD, TGA and DTA. It has been shown that these compounds have high thermal stability and these adsorbents are found to be favourable for the removal of metal ions from waste water. Significant results have been identified for the industrial application. As a consequence, fatty chitosan grafted acrylic acid can be used for waste water treatment.

## Declarations

### Conflict of Interest

Potential conflict of interest exists:

We wish to draw the attention of the Editor to the following facts, which may be considered as potential conflicts of interest, and to significant financial contributions to this work:

The nature of potential conflict of interest is described below:

**No conflict of interest exists.**

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

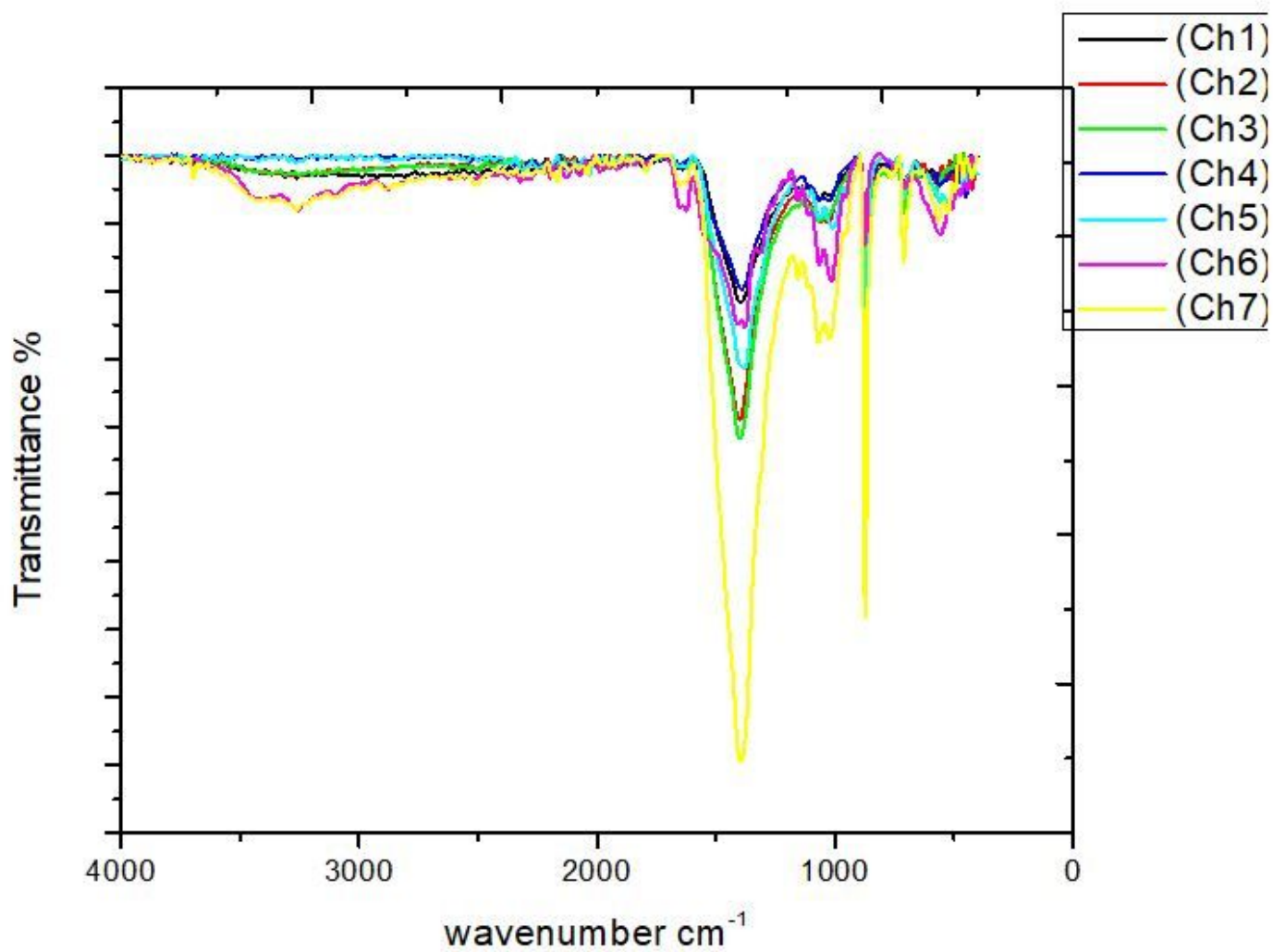
## References

1. Deshpande MV(1986) "Enzymatic degradation of chitin and its biological applications", Journal of Scientific and Industrial Research, 45: 277-281.
2. Jadhav HV, (1992) "Element of Environmental Chemistry", Himalaya Publishing Home. India,38.
3. Sudha PN, (2010) "Chitin, Chitosan, Oligosaccharides and Their Derivatives", Ed.SeKwon Kim, CRC Press ,561-585 .
4. Alkorta I, HernandezAllica J, Becerril JM, Amezagua I, Albizu I, and Garbisu C, (2004) "Recent findings on the phytoremediation of soils contaminated with environmentally toxic heavy metals and metalloids such as zinc, cadmium, lead, and arsenic", Reviews in Environmental Science and BioTechnology, 3(1):71-90.
5. Wang JL, (2002)"Microbial Immobilization Techniques and Water Pollution Control", Science Press, Beijing 261-271.
6. Volesky B, (2001)"Detoxification of metalbearing effluents: biosorption for the next century", Hydrometallurgy, 59: 203-216.
7. Udaybhaskar P, Iyengar L and Prabhakar Rao AVS, (1990)"Hexavalent chromium interaction with chitosan", Journal of Applied Polymer Science, 39: 739-747.
8. Volesky B, and Holan ZR, (1995)"Biosorption of heavy metals"Biotechnology Progress, 11: 235-250.
9. Olin TJ, Rosado JM, Bailey SE, and Bricka RM,(1996) "Low cost Sorbents screening and engineering analysis of zeolite for treatment of metals Contaminated water and soil extracts – final report", Report SERDP.
10. Bailey SE, Olin TJ, and Bricka RM, (1997) "Lowcost sorbents: literature summary", Technical Report SERDP971, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.
11. Varma AJ, Deshpande SV, and Kennedy JF, (2004)"Metal complexation by chitosan and its derivatives: a review", Carbohydrate Polymer, 55: 77-93.

12. Guibal E, (2004) "Interactions of metal ions with chitosanbased sorbents: a review", *Separation and Purification Technology*, 38:43-74.
13. Chiou MS, Ho PY, and Li HY, (2004) "Adsorption of anionic dyes in acid solutions using chemically crosslinked chitosan beads", *Dyes and Pigments*, 60:69-84.
14. Crini G, and Badot PM, (2008) "Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solution by adsorption process using batch studies: A review of recent literature", *Progress in Polymer Science*, 33: 399-447
15. Mariza M, Dimitra A, Dimitrios NB and George K, (2020) " Chitosan Grafted with Biobased 5-Hydroxymethyl-Furfural as Adsorbent for Copper and Cadmium Ions Removal Polymers", 12, 1173; doi:10.3390/polym12051173.
16. Mirza N A, Arif H, Muhammad N A, Tajamal H, Adnan M, Muhammad H K, Toheed A, (2020) Synthesis and characterization of a novel chitosan-grafted polyorthoethylaniline biocomposite and utilization for dye removal from water *Open Chemistry*; 18: 843–849.
17. Wenqian W, Qiuyu M, Qi L , Jinbao L, Mo Z, Zheng J and Kai Z, (2020) Chitosan Derivatives and Their Application in Biomedicine . *Int. J. Mol. Sci.*, 21, 487; doi:10.3390/ijms21020487.
18. Shantha KL, Udaya B, and Panduranga RK (1995) "Tailormad Chitosans for drugdelivery", *European Polymer Journal*, 31(4):377-382.
19. Ren L, Miura Y, Nishi N, and Tokura S (1993) "Modification of chitin by ceric Salt initiated graft polymerization – preparation of poly(methylmethacrylate) grafted chitin derivatives that swell in organic solvents", *Carbohydrate Polymer*, 21(1): 23–27.
20. Singh V, Tripathi DN, Tiwari A, and Sanghi R (2005) "Microwave promoted synthesis of chitosan graft poly( acrylonitrile)", *Journal of Applied Polymer Science*, 95: 820-825.
21. Beck RHF, Fitton MG and Kricheldorf HR, (1992) "Handbook of Polymer Synthesis: Part B", (Ed. Kricheldorf H.R.), Marcel Dekker, New York (Chapter 25).
22. Sun T, Xu P, Liu Q, Xue J, and Xie W, (2003) "Graft copolymerization of methacrylic acid onto carboxymethyl chitosan", *European Polymer Journal*, 39(1): 189-192.
23. Ansar AZ, Venkatesan J, Kim SK., and Sudha, PN (2011) "Beneficial effect of chitosan graft polyacrylamide copolymer in removal of heavy metals from industrial dye effluents", *International Journal of Environmental Sciences*, 1(5):820-833.
24. Prashanth KVH, and Tharanathan RN (2003) "Studies on graft copolymerization of chitosan with synthetic monomers", *Carbohydrate Polymer* 54(3):343-351.
25. Pourjavadi A, Mahdavinia GR, Zohuriaan MMJ, and Omidian H (2003) "Modified chitosan. I. Optimized cerium ammonium nitrate induced synthesis of chitosan graft polyacrylonitrile", *Journal of*

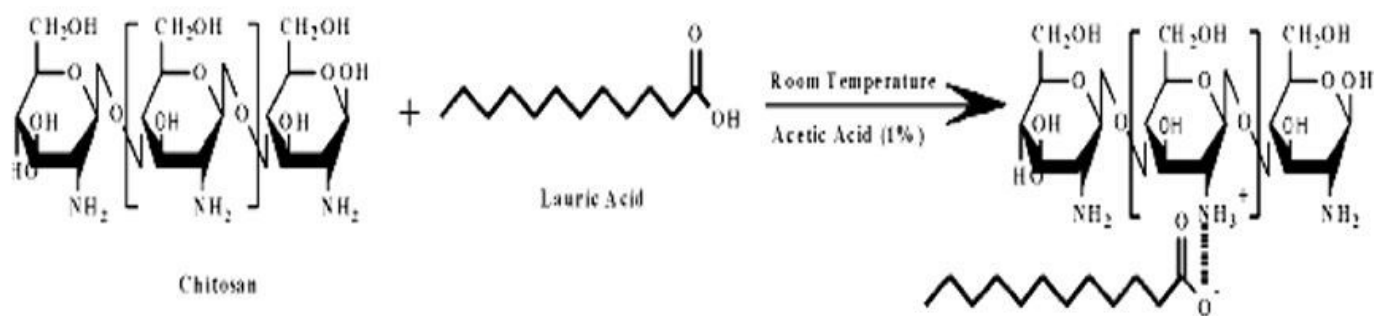
26. Ramya R, Sankar P, Anbalagan S, and Sudha PN (2011) "Adsorption of Cu(II) and Ni(II) ions from metal solution using crosslinked chitosanacrylonitrile copolymer", *International Journal of Environmental Sciences*, 1(6):1323-1338.
27. Retuert J and Yazdani PM (1993) "Cocatalyst effect in potassiumpersulfate initiated grafting onto chitosan", *Polymer Bulletin*, 31(5):559-562.
28. Hsu SC, Don TM, and Chiu WY(2002) "Free radical degradation of chitosan with potassium persulfate", *Polymer Degradation and Stability*, 75(1):73-83.
29. Baxter A, Dillion M, Taylor K, Roberts G (1992) Improved method for I.R. determination of the degree of acetylation of chitosan, *Int. J. Biol. Macromol.* 14:166–169.
30. Abdulganiyu, U., Saminu, M. M. and Aminu, M. Graft Copolymerization and Characterization of Styrene with Chitosan via Radical Polymerization *ChemSearch Journal* 8(1): 56 – 63, June, 2017
31. Tolaimate. A., Desbrieres .J., Rhazi .M., Alagui. A., Contribution to the preparation of chitins and chitosans with controlled physico-chemical properties, *Polymer (Guildf)* 44 (26) (2003) 7939–7952.
32. Hafsa J, Charfeddine B, Smach MA, Limem K, Majdoub H, Sonia R (2014) Synthesis, characterization, antioxidant and antibacterial proprieties of chitosan ascorbate, *Int. J. Pharm. Chem. Biol. Sci.* 4 (4):1072–1081.
33. Wanule D, Balkhande JV, Ratnakar PU, Kulkarni AN, Bhowate CS(2014) Extraction and FTIR analysis of chitosan from american cockroach, *Periplaneta americana*, *Int. J. Eng. Sci. Innov. Technol.* 3 (3):299–304.
34. Kaya M, Baran T, Asan-Ozusaglam M, Cakmak YS, Tozak KO, Mol A, Menten A, Sezen G (2014) Extraction and characterization of chitin and chitosan with antimicrobial and antioxidant activities from cosmopolitan Orthoptera species(Insecta), *Biotechnol. Bioprocess Eng.* 20 (1):168–179.
35. Taher FA, Amin RM, Abd El-Aziz A, Abou Senna FM, Abou El-Nou MF, El-Mehdawy AA (2017) Characterization and antibacterial effect of chitosan nanoparticles prepared by ball-milling from shell of shrimp, *Penaeus semisulcatus* (Crustacea: Penaeidae), *Al Azhar Bulletin Sci. Conf.* 43–52
36. Tosh B, (2011) Thermal Analysis of Cellulose Ester Prepared From Different Molecular Weight Fractions of Cellulose Pulp, *Indian J. Chem. Technol.*, 18,451.

## Figures



**Figure 1**

FT-IR spectra of chitosan.



**Figure 2**

Preparation of fatty chitosan derivatives.

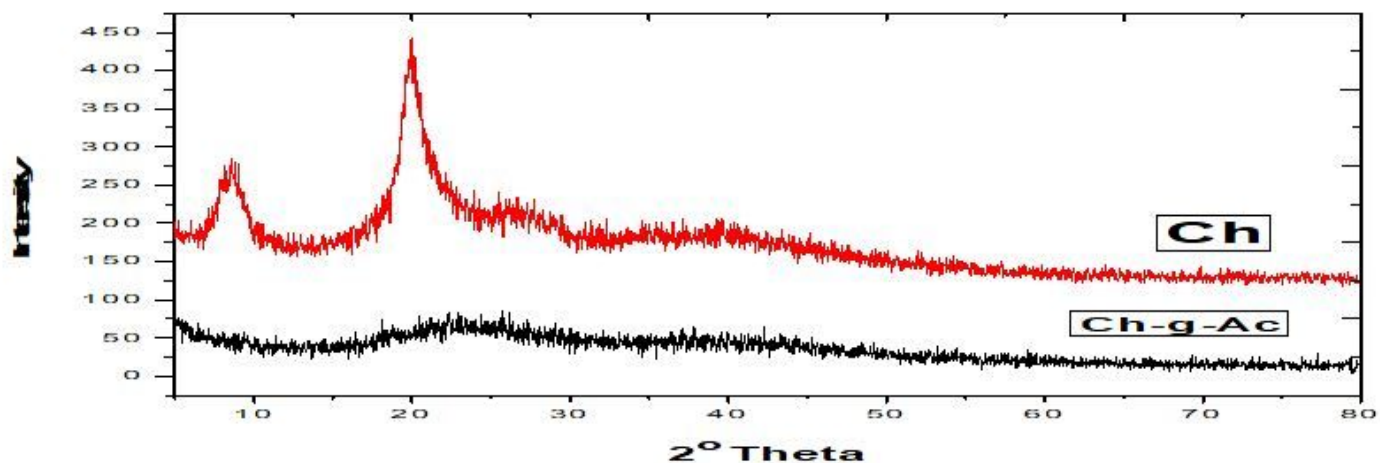


Figure 3

XRD analysis of chitosan (Ch) and chitosan-g-acrylic acid(Ch-g-Ac).

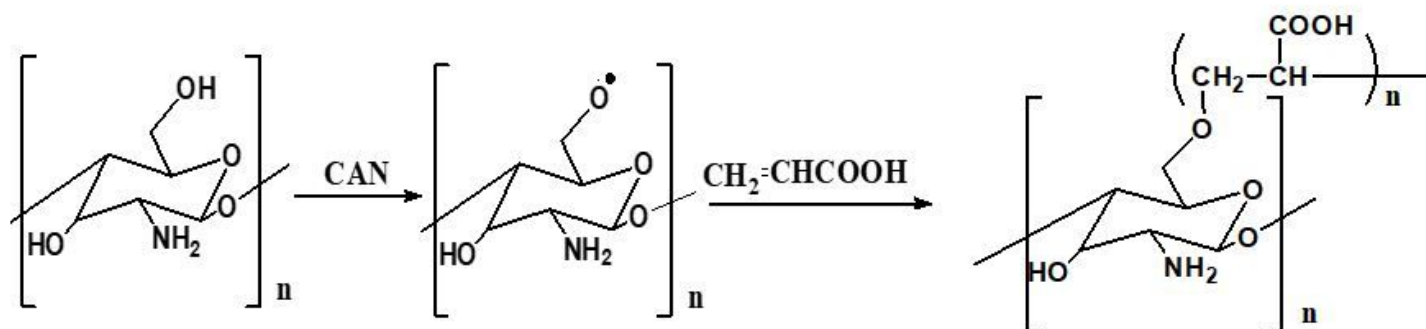
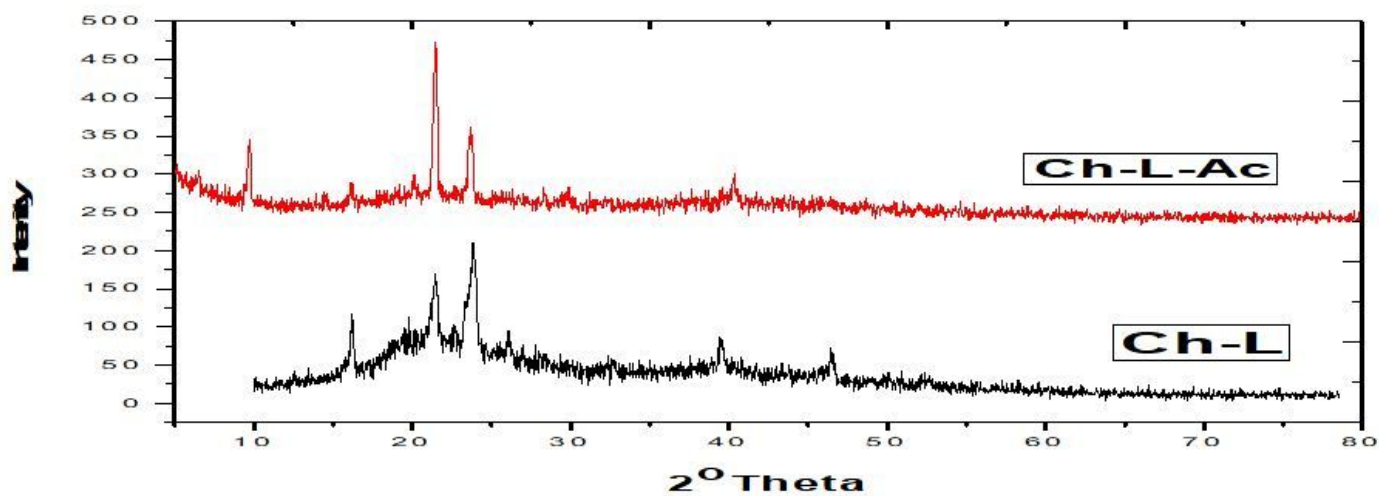


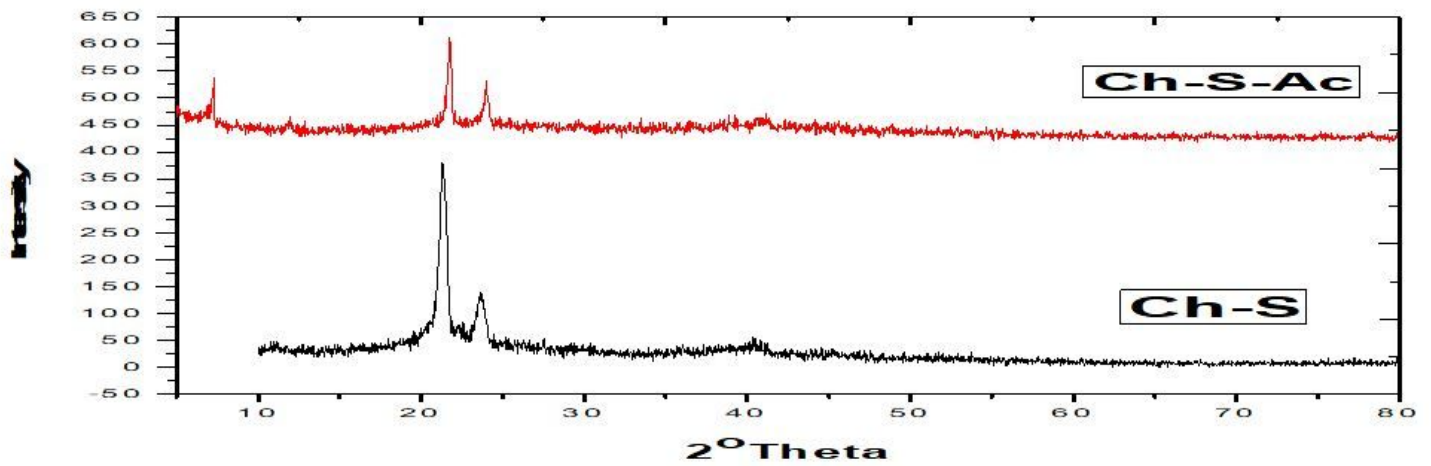
Figure 4

Preparation of chitosan-grafted acrylic acid copolymer (30).



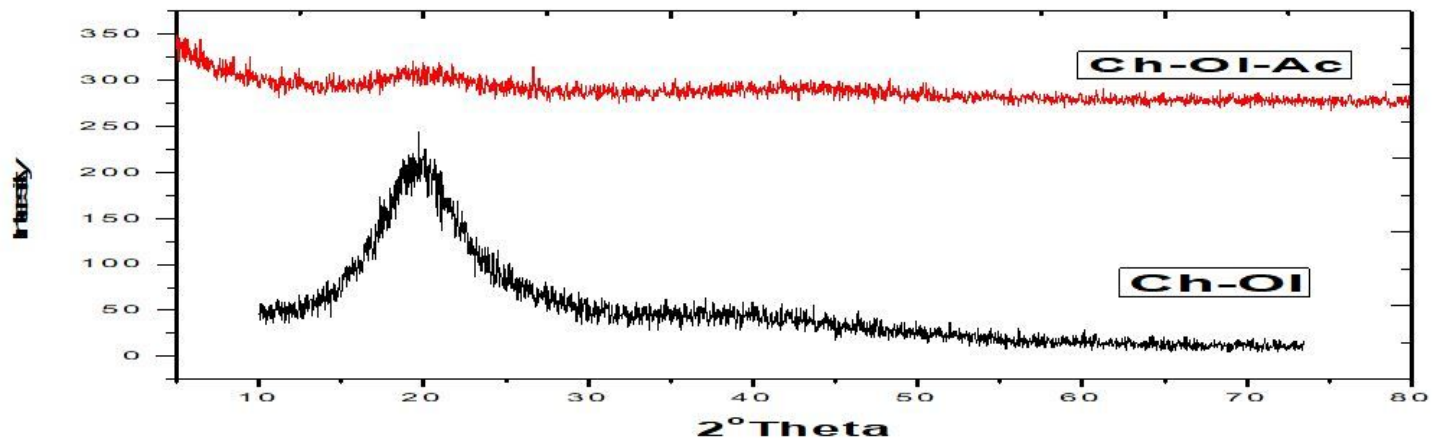
**Figure 5**

XRD analysis of chitosan lauric acid (Ch-L) and chitosan lauric acid-g-acrylic acid composite (Ch-L-Ac).



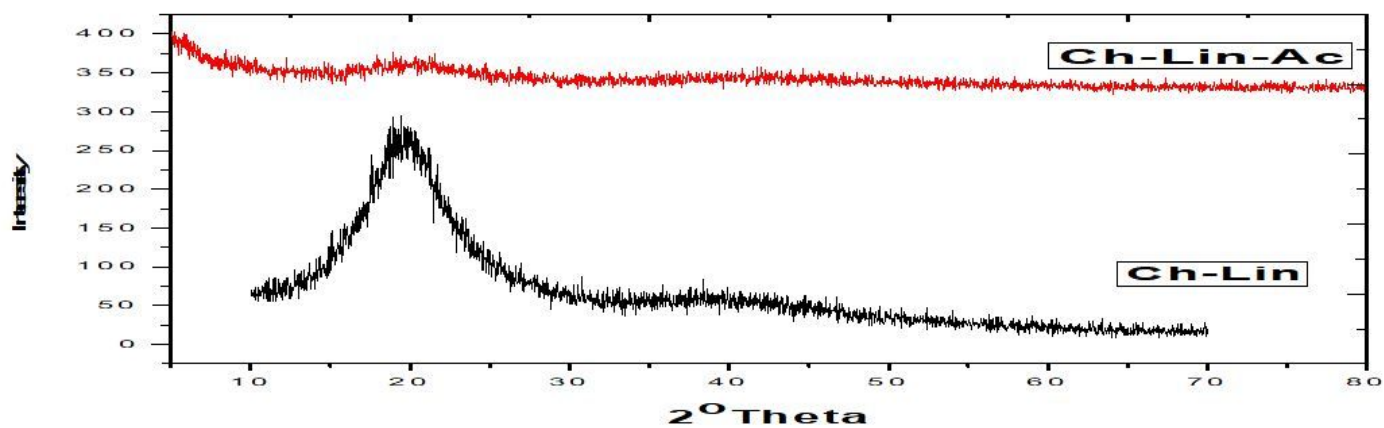
**Figure 6**

XRD analysis of chitosan stearic acid (Ch-S) and chitosan stearic acid-g-acrylic acid composite(Ch-S-Ac) .



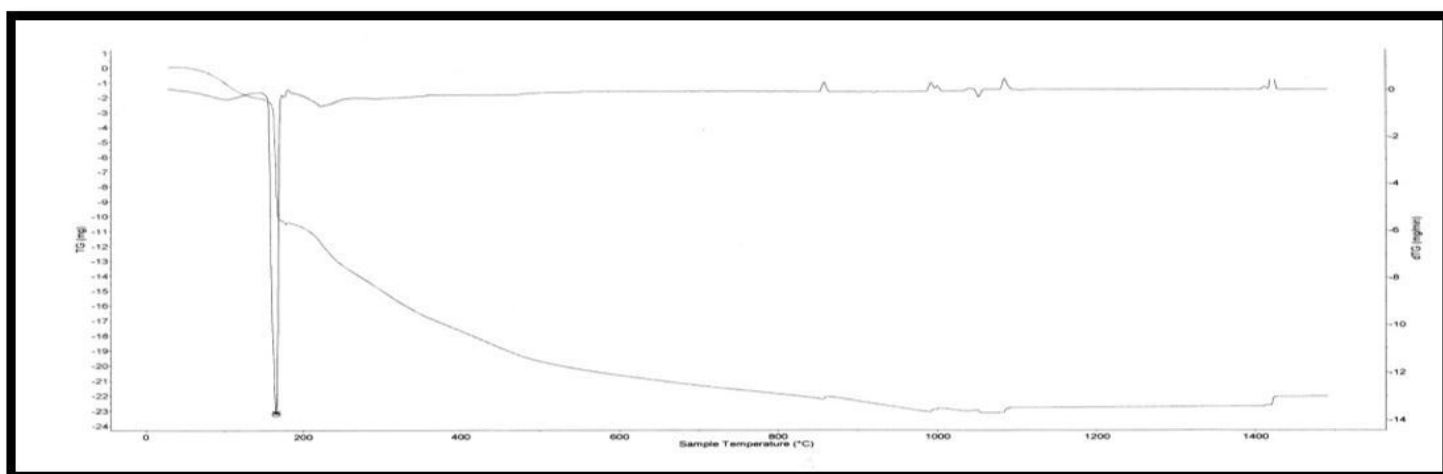
**Figure 7**

XRD analysis of chitosan oleic acid (Ch-OI) and chitosan oleic acid-g-acrylic acid composite(Ch-OI-Ac)



**Figure 8**

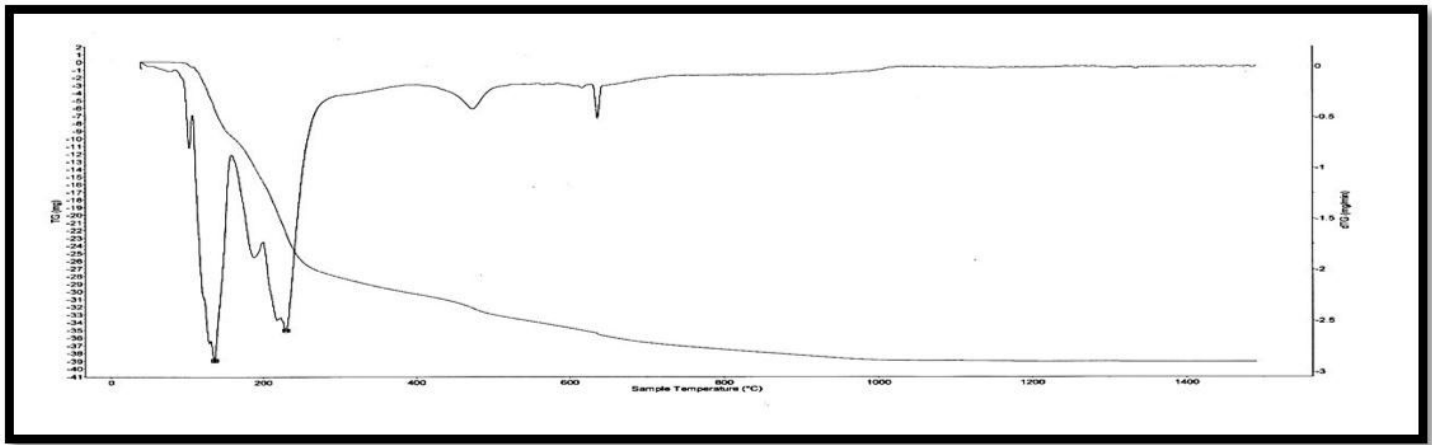
XRD analysis of chitosan linoleic acid (Ch-Lin) and chitosan linoleic acid-g-acrylic acid composite(Ch-Lin-Ac) .



**Figure 9**

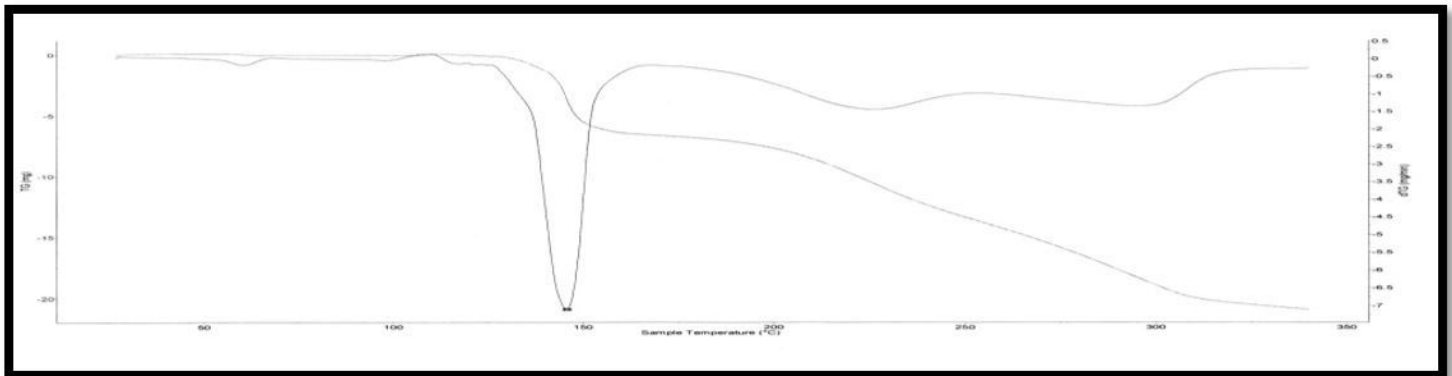
Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan grafted acrylic acid (Ch-g-Ac).





**Figure 10**

Thermo gravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan lauric acid grafted acrylic acid composite( Ch-L-Ac).



**Figure 11**

Thermo gravimetric analysis (TGA) and differential thermogravimetric analysis (DTA)of chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac).

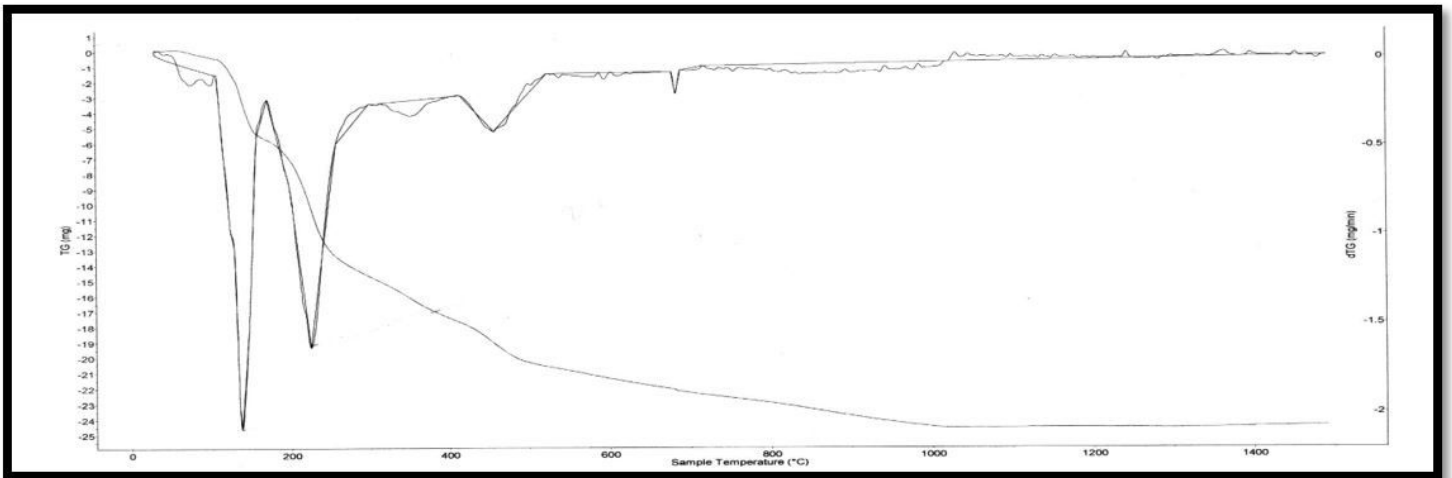


Figure 12

Thermo gravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan oleic acid grafted acrylic acid composite (Ch-OI-Ac).

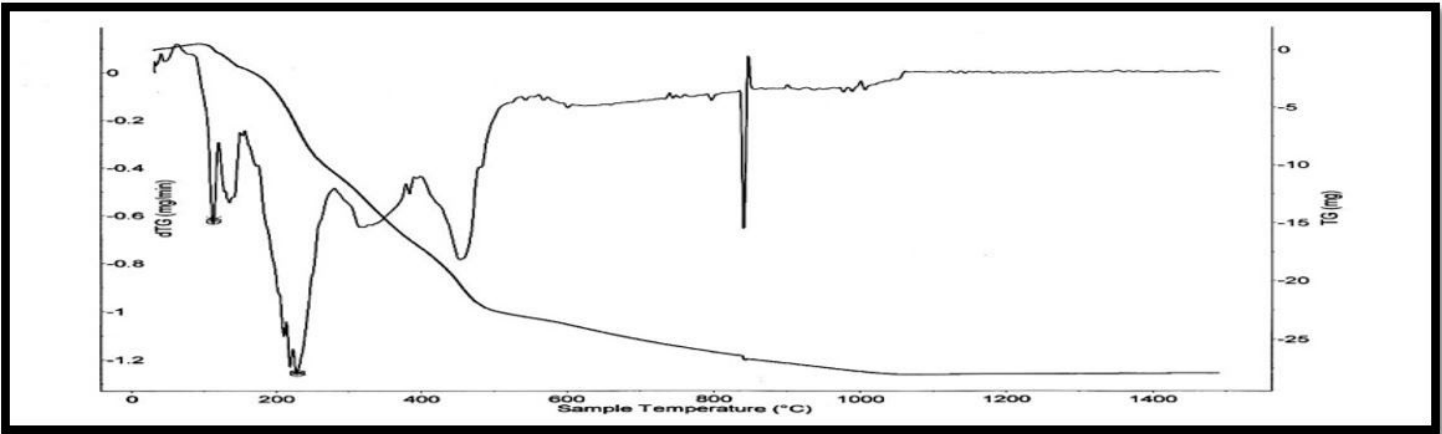


Figure 13

Thermo gravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac).

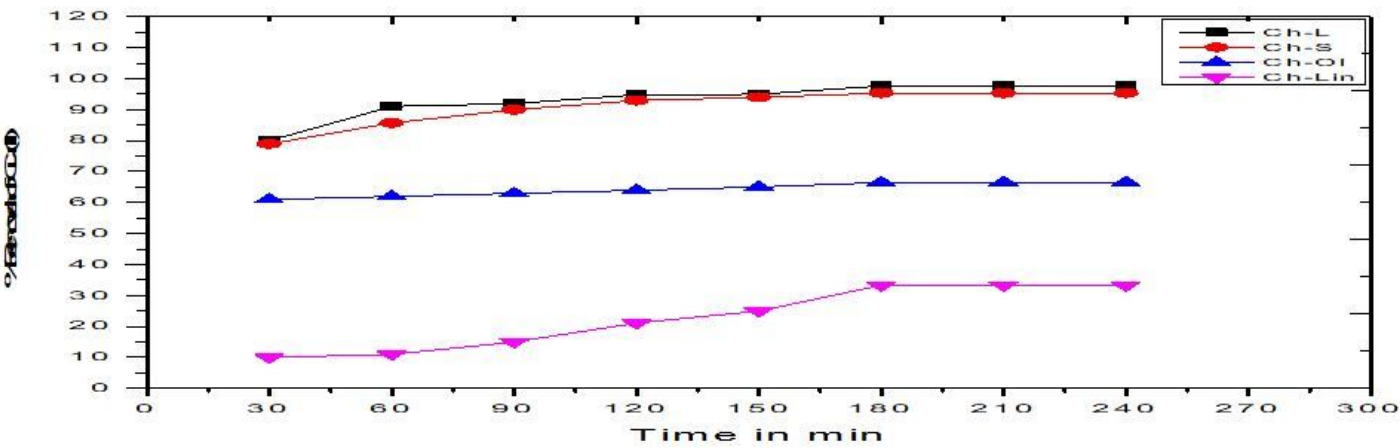
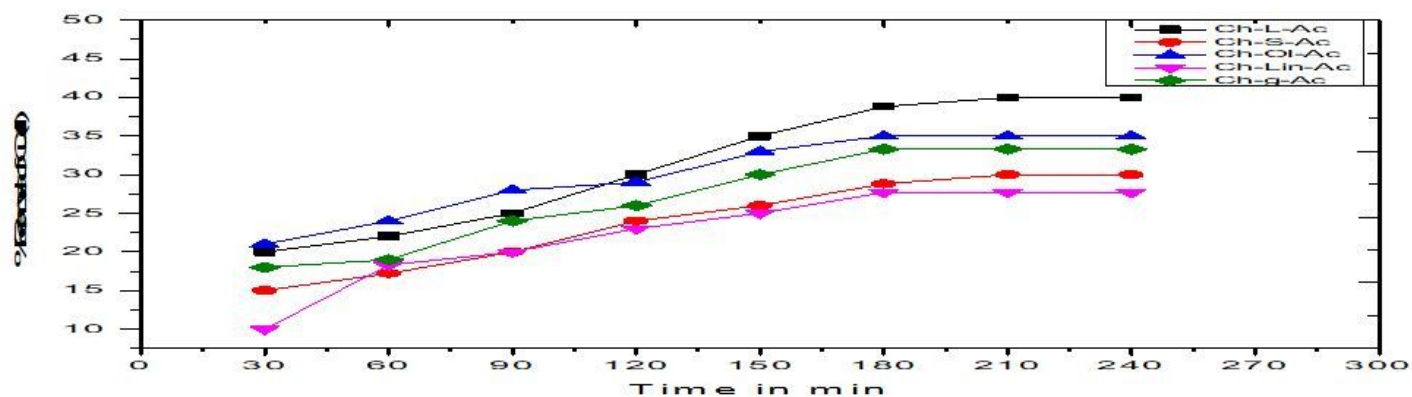


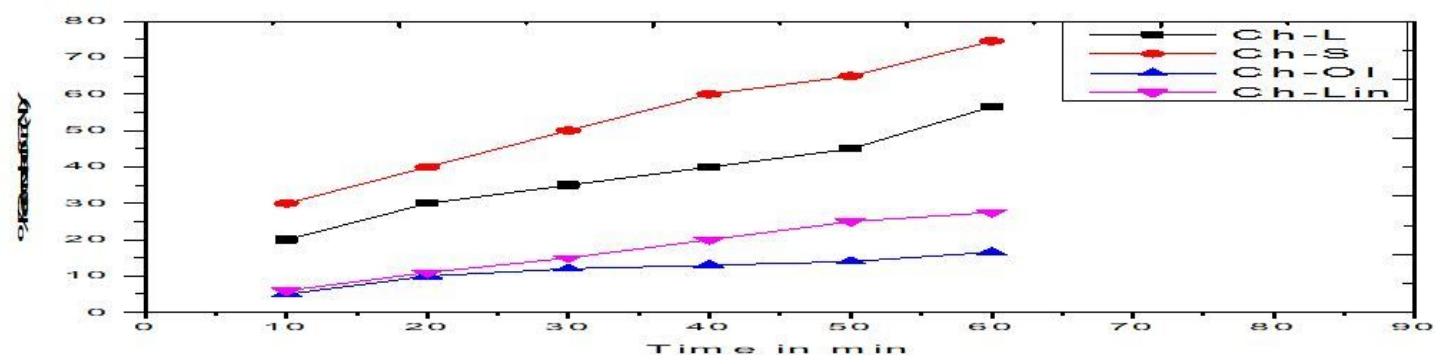
Figure 14

Percentage removal of Cu (II) of chitosan lauric acid (Ch-L), chitosan stearic acid(Ch-S), chitosan oleic acid (Ch-OI) and chitosan linoleic acid (Ch-Lin) at different time interval.



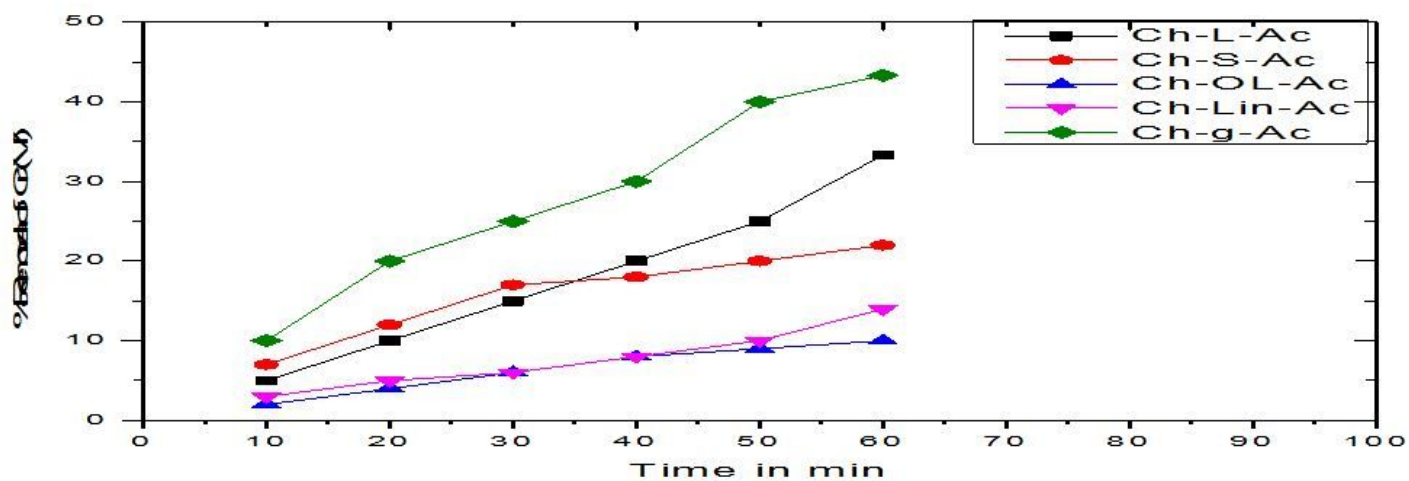
**Figure 15**

Percentage removal of Cu (II) of chitosan grafted acrylic acid (Ch-g-Ac), chitosan lauric acid grafted acrylic acid composite (Ch-L-Ac), chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac), chitosan oleic acid grafted acrylic acid composite (Ch-Ol-Ac) and chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac) at different time interval.



**Figure 16**

Percentage removal of Cr (VI) of chitosan lauric acid (Ch-L), chitosan stearic acid(Ch-S), chitosan oleic acid (Ch-Ol) and chitosan linoleic acid (Ch-Lin) at different time interval.



**Figure 17**

Percentage removal of Cr (VI) of chitosan grafted acrylic acid (Ch-g-Ac), chitosan lauric acid grafted acrylic acid composite ( Ch-L-Ac), chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac), chitosan oleic acid grafted acrylic acid composite (Ch-OL-Ac) and chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac ) at different time interval.