Egypt. J. Chem. **Vol. 64,** No. 10 pp. 6007 - 6015 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Synthesis and Evaluation of Performance Characteristics Green Composites from Sustainable Fatty Chitosan Graft Copolymer with Acrylic Acid for Wastewater Treatment

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Abstract

Many chitosan adsorbent derivatives for metal ion adsorption have been developed by grafting novel functional groups on the chitosan chain, and these functional groups are combined with chitosan to improve sorption capability. The chemical structure of chitosan was characterized 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 bio sorbent 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 synthesized 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 wastewater treatment.

Keywords: Fatty chitosan, Environmental pollution, Copper ion, Chromium ion, Grafted copolymer.

Introduction

Chitosan is a natural polymer that is antimicrobial, biodegradable, and biocompatible. Chitosan (2-acetamido 2-deoxy—D-glucose(N-acetylglucosamine)) is a partially deacetylated chitin polymer that is typically prepared by treating chitin with a strong alkaline solution. Chitosan was functionalized using a variety of reagents, including alumina [1], alginate [2], cellulose [3], polyvinyl alcohol [4, 5], cyclodextrins [5,6] magnetic nanoparticles [7], ionic liquids [8], etc. Many publications have confirmed the efficacy of functionalizing chitosan with silica particles to treat contaminated waters [9, 10]. There is a lot of interest in developing a perfect green composite for the treatment of contaminated water because of the concern about keeping the environment clean. Chemical industries use a large amount of water during the physical, chemical, and biological processing stages, and they emit a significant amount of wastewater [11]. Many natural adsorbents have been developed to remove a wide range of metal ions from water [12-16]. Heavy metal discharge from industrial operations is more dangerous due to the presence of copper, chromium, zinc, nickel, and cadmium [17]. Copper concentrations in the effluent stream are high enough to cause serious health problems in the brain, kidneys, and anemia. Copper consumption at high doses raises serious toxicological concerns because it can accumulate in the brain, skin, liver, and kidney [18,19]. Furthermore, chromium is a well-known contaminant that is becoming more important due to its highly toxic nature even at low concentrations. Furthermore, water contamination by chromium (Cr) has received increased attention in the current context of global ecology due to this metal's extensive use in textile industries, electroplating, leather processing, metal finishing, and chromium preparation. Chromium exists in three oxidation states: Cr (II), Cr (III), and Cr (VI), with the hexavalent form 500 times more toxic than the trivalent. This Cr (VI) is a carcinogenic agent that can cause serious health problems. [20-23]. There are common conventional methods for removing heavy metals from water, such as ion exchange [24], solvent extraction [25], reverse osmosis [26], chemical precipitation [27], etc.

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Receive Date: 25 April 2021, Revise Date: 26 May 2021, Accept Date: 30 May 2021
DOI: 10.21608/EJCHEM.2021.73857.3656

However, these techniques are either prohibitively expensive or ineffective in terms of achieving high removal efficacy. The adsorption technique is widely used due to its simplicity, rapidity, cost effectiveness, efficiency, and the availability and reusability of adsorbents [28-30]. Chitosan biopolymer is a very appealing material that is regarded as an excellent adsorbent due to its high nitrogen and oxygen content. The presence of reactive amino and hydroxyl groups in its structure allows for some chemical modifications, allowing it to be used in a variety of applications [31–33]. Grafting vinyl monomers onto chitosan is one of the most effective methods for improving chitosan performance without sacrificing its properties, and it is also a challenging field of research with limitless future possibilities. Several studies on the grafting copolymerization of chitosan with various vinyl monomers such as methyl acrylate have been published [34], methyl methacrylate [35], acrylamide [36], acrylic acid [37], and acrylonitrile [38] using redox initiators. 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 characterized 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 fatty chitosan grafted acrylic acid in the treatment of wastewater was identified and the copolymer was a promising matrix for the adsorption of metal ions.

Materials and Methods

Chitosan was extracted from shrimp shells waste. Ceric ammonium nitrate, Acrylic acid, lauric acid, stearic acid, oleic acid and linoleic acid were of analytical grade.

Preparation of Chitosan

The preparation of chitosan is divided into three consecutive stages. Demineralization of shrimp shells. Chitin processing (deproteinization) and chitosan processing (deacetylation) [39-41]. 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

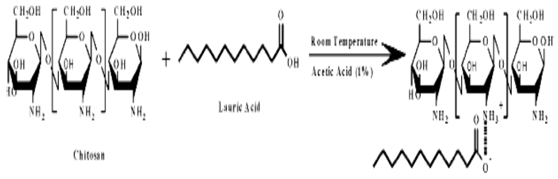
The degree of N-deacetylation (DDA) of chitosan powder was calculated by Fourier transform infrared (FT-IR) spectroscopy using FT-IR JASCO 4100. Samples were screened against a blank KBr pellet at wave number 4000–400cm−1. Chitosan DDA was determined based on the following equation. [42]

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

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

Preparation of Fatty Chitosan Derivatives

For the preparation of (Ch-L), (Ch-S), (Ch-Ol) 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.



Scheme 1: Preparation of fatty chitosan derivatives.

Preparation of Copolymer

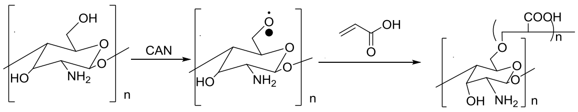
A 2% W/V solution of chitosan [37] and fatty chitosan derivatives were prepared in 2% aqueous acetic acid. A solution of 0.1 M ceric ammonium nitrate (CAN) in 10 ml of 1N nitric acid was added accompanied by a known amount of acrylic acid (Ac) drop by drop with continuous UV stirring. The reaction temperature was held at 70 °C for 45 minutes, the substance was precipitated by the use of sodium hydroxide solution with intense stirringThe 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:

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

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

Where, Wg Weight of grafted copolymer; Wi Weight of homopolymer (acrylic acid).



Scheme 2: Preparation of chitosan-grafted acrylic acid copolymer [43].

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^{-1} 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 [44,45].

Results and Discussions

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 [46]. The majority of commercial samples of chitosan have an average DDA of 70–90 percent [47] . 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 [48]. 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^{-1} showed a good deproteinization of chitin. Another broad, intense absorption band at approximately 3450cm^{-1} was corresponding to the hydroxyl groups (OH) of chitosan and could also be physically adsorbed water molecules [49-52]. I_{1655} and I_{3450} are light intensity of- NH_2 and -OH groups at 1655 and 3450cm$^{-1,}$ respectively.

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

Chitosan sample	DDA (min)	I_{1655}	I_{3450}	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

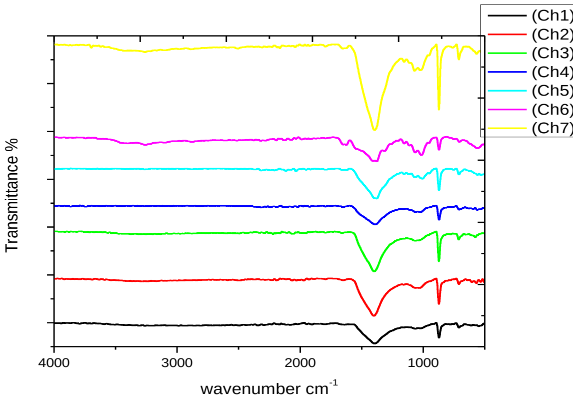


Fig. 1. FT-IR spectra of chitosan.

X-ray diffraction (XRD)

The XRD spectra of chitosan and its grafting copolymer are shown in Figure 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.

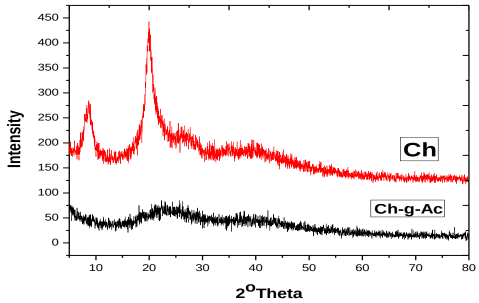


Fig. 2. XRD analysis of chitosan (Ch) and chitosan-g-acrylic acid (Ch-g-Ac).

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 °, 21.4 ° , 23.8 ° , 39.4 ° and 46.3°. The peak of d-spacing 4.1 at 2θ = 21.4 ° has lower intensity than that appeared in XRD spectra of Ch-L-Ac .More over the peak of d-spacing 3.72 at 2θ =23.85 ° has higher intensity than that appeared at 2θ = 23.75° and a new peak is formed at 2θ = 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 ° , 9.7 ° , 16.1 °, 20.1 ° , 21.4 ° , 23.7 ° and 40.2°.

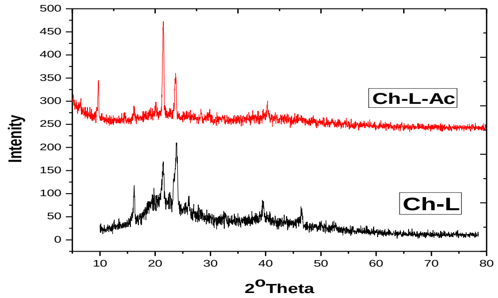


Fig. 3. XRD analysis of chitosan lauric acid (Ch-L) and chitosan lauric acid-g-acrylic acid composite (Ch-L-Ac).

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° and 23.6 ° while Ch-S-Ac composite shows sharp peaks at 7.2 °, 21.7 ° and 23.9 ° .

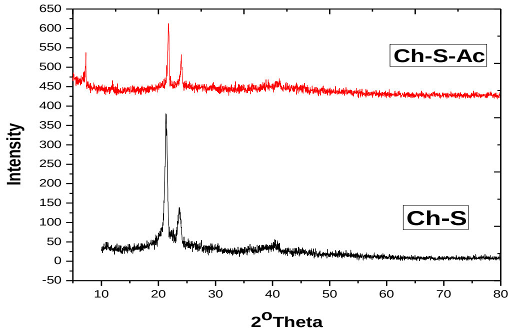


Fig. 4. XRD analysis of chitosan stearic acid (Ch-S) and chitosan stearic acid-g-acrylic acid composite (Ch-S-Ac).

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□= 19.6° 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 [53]. 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.

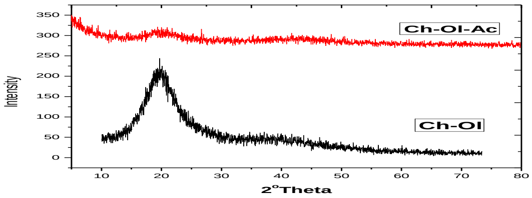


Fig. 5. XRD analysis of chitosan oleic acid (Ch-Ol) and chitosan oleic acid-g-acrylic acid composite (Ch-Ol-Ac)

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□= 18.8°. due to the formation of an amorphous material. Ch-Lin-Ac composite shows an X-ray diffraction pattern with no defined peaks.

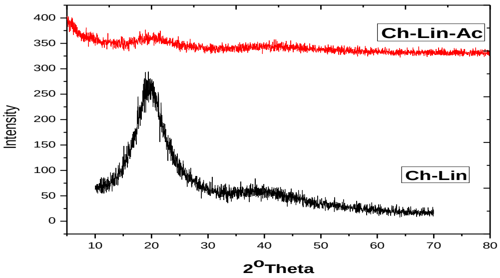
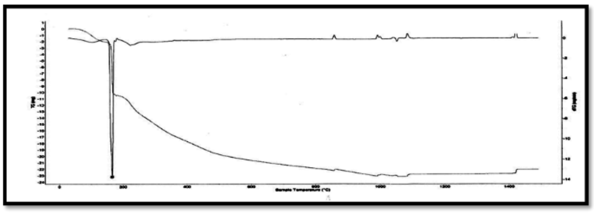


Fig. 6. XRD analysis of chitosan linoleic acid (Ch-Lin)

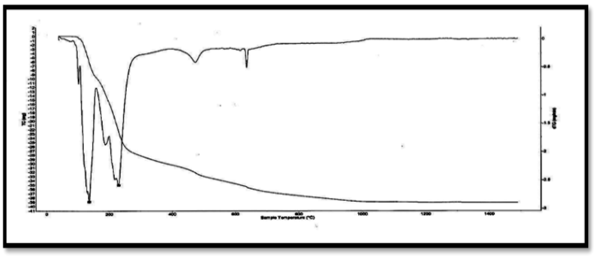
and chitosan linoleic acid-g-acrylic acid composite (Ch-Lin-Ac).

Thermal Analysis

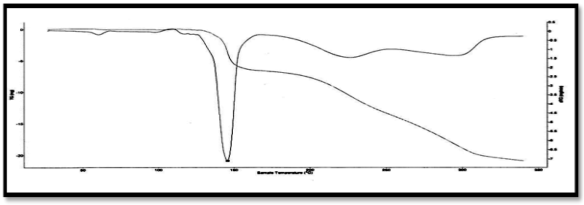
Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) shows the thermal behavior of chitosan grafted acrylic acid (Ch-g-Ac) (Fig. 7), chitosan Lauric acid grafted acrylic acid composite(Ch-L-Ac) (Fig. 8),), chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac) (Fig. 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 [54].



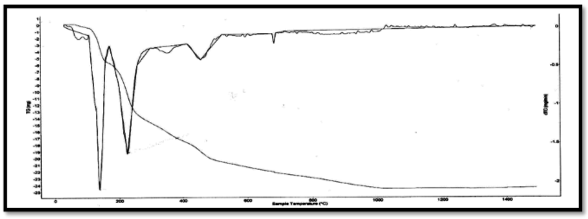
(Fig 7) Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan grafted acrylic acid (Ch-g-Ac).



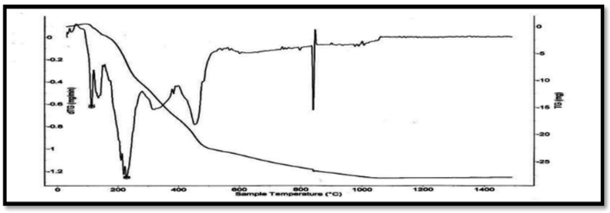
(Fig 8) Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan lauric acid grafted acrylic acid composite (Ch-L-Ac).



(Fig 9) Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA)of chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac).



(Fig 10) Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan oleic acid grafted acrylic acid composite (Ch-Ol-Ac).



(Fig 11) Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac).

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°C, which is lower than the initial decomposition temperature of), chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac) (178.6°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-Ol-Ac) started at (128.6°C), (145.2°C) and (135.8°C) respectively .

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-Ol-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.

Application of prepared compound in wastewater treatment

Effect of contact time

It is clear from Figures 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). (Figure 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.

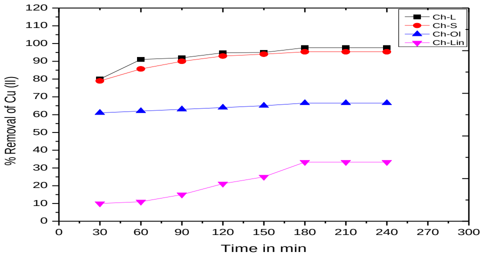


Fig 12: Percentage removal of Cu (II) of chitosan lauric acid (Ch-L), chitosan stearic acid (Ch-S), chitosan oleic acid (Ch-Ol) and chitosan linoleic acid (Ch-Lin) at different time interval.

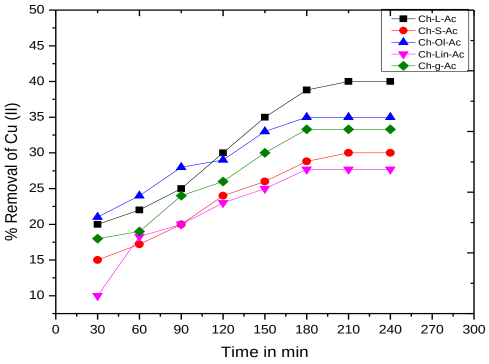


Fig 13: Percentage removal of Cu (II) of chitosan grafted acrylic acid (Ch-g-Ac), chitosan lauric acid grafted acrylic acid composite (Ch-L-Ac), chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac), chitosan oleic acid grafted acrylic acid composite (Ch-Ol-Ac) and chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac) at different time interval.

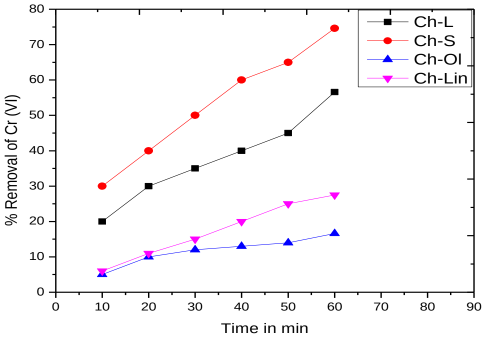


Fig 14: Percentage removal of Cr (VI) of chitosan lauric acid (Ch-L), chitosan stearic acid (Ch-S), chitosan oleic acid (Ch-Ol) and chitosan linoleic acid (Ch-Lin) at different time interval.

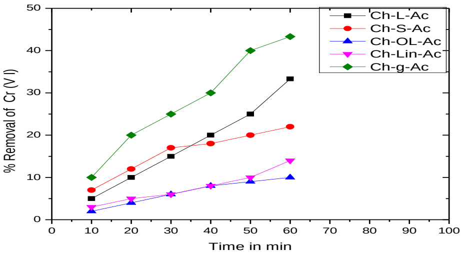


Fig 15: Percentage removal of Cr (VI) of chitosan grafted acrylic acid (Ch-g-Ac), chitosan lauric acid grafted acrylic acid composite (Ch-L-Ac), chitosan stearic acid grafted acrylic acid composite (Ch-S-Ac), chitosan oleic acid grafted acrylic acid composite (Ch-Ol-Ac) and chitosan linoleic acid grafted acrylic acid composite (Ch-Lin-Ac) at different time interval.

Table 2. Thermal stability of chitosan composites in nitrogen atmosphere at a heating rate of 10°C. min^{-1}

Sample code	IDT[a] (°C)	ADT[b] (°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-Ol-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	_	_	_

[a]IDT : the initial decomposition temperature.

[b]ADT : the active decomposition temperature

Conclusion

The bioactive low-cost natural polymer chitosan (CS) is obtained in this paper by treating it with a strong alkaline medium. Deacetylation with a high degree of deacetylation (DDA) is obtained (85.5 percent). We were able to create a new functionalized chitosan adsorbent (fatty chitosan) by introducing fatty acids into its chain via the amino group. 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 XRD, TGA and DTA. It has been shown that these compounds have high thermal stability. The obtained adsorbents were efficiently used for removing copper (II) ions and chromium ions from aqueous solutions, and the results confirmed what we expected when designing this work, revealing that the adsorbents achieved a maximum adsorption capacity greater than that reported by many chitosan-based adsorbents in previous works. As a result, fatty chitosan and fatty chitosan grafted acrylic acid can be used to create a green composite for wastewater treatment.

Conflicts of interest

"There are no conflicts to declare".

Funding sources

"There are no funding sources to be listed".

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