

Chitosan-g-poly (acrylonitrile-co-acrylic acid) for wastewater treatment application

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Abstract: Chitosan is a biodegradable natural based polymer obtained from chitin (N-deacetylated derivative), the second most abundant polysaccharide after cellulose and soluble in most organic acids. Graft copolymerization of poly (acrylonitrile-co-acrylic acid) onto chitosan has been successfully carried out using potassium persulfate as an initiator in an aqueous medium. The PAN and PAA homopolymer formed during the reaction were removed from the Chitosan grafted copolymer by Soxhlet extraction using ethanol as the solvent. The prepared graft copolymerization was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) to confirm the formation of the copolymer. The prepared chitosan-g-copolymer at a ratio of 25:75 % of AN-co-AA was tested for wastewater treatment depending on various metal solutions at room temperature containing cadmium ions, times, and pH. The optimal condition was found to be at pH=5, time 120 min, and adsorbent dose 3 mg /L.

The results revealed that the chitosan-g-copolymer prepared was excellent in removing the heavy metals than the copolymer alone. Hence, chitosan-g- poly- AN-co-AA could open the way for wastewater treatment. The thermal stability and the electrical conductivity for all prepared samples before and after grafting were measured. By studying the thermal stability at the different ratio of AN and AA in samples CO_1 , CO_2 , CO_3 , it was found that the most thermal stability sample ratio is CO_3 due to increasing the ratio of AN. While in sample CO_1 with a high ratio of AA, the thermal stability decrease according to the fast decomposition of $-COOH$ of acrylic acid. The conductivity was 3.85×10^{-7} which is more than the copolymer without chitosan, which increases the electron density of the copolymer through the end group effect. As the result of σ has a range $10^{-8} \text{ S/cm}^{-1}$ $10^{-6} \text{ S/cm}^{-1}$ so, all the prepared sample can be used as an electrostatic dissipation application.

Keywords: Chitosan-g-copolymer; poly (acrylonitrile-co-acrylic acid); radical polymerization; metal removal; wastewater treatment.

1. Introduction

Biopolymers were very interested in the removal of heavy metals from aqueous solution as an adsorbent^{1,2}. Chitosan, in particular, is regarded as excellent applicants as it is environmentally friendly, low cost, and a broad source. However, its use as an efficient adsorbent is limited by the disadvantages of lousy chemical resistance and elevated crystallinity³. The number of chemical modifications dedicated to the application of chitosan materials using cross-linking, functional group grafting, and blending polymer or inorganic to remove metals and dyes from wastewater has increased rapidly⁴⁻⁶. Several carboxylated chitosan products have been recorded due to the significant chelating impacts of carboxyl groups. As a modifier

material, polyacrylic acid (PAA) has drawn growing attention as it includes a carboxyl group in each repeated unit and favors metal ion adsorption⁴. In a homogeneous system, biodegradable and ultra-high content grafted chitosan-g-poly (acrylic acid) powder has been effectively synthesized and used as adsorbents to remove Cu (II) in aqueous solution. The peak adsorption capability of the Langmuir model was 210,13 mg / g, showing a remarkable increase in chitosan adsorption ability after polygrafting (acrylic acid)⁷.

For the first time, the methacrylamide (MAM) was grafted on chitosan in the presence of ammonium persulfate (APS) as an initiator by the free radical method. The prepared sample of chitosan and chitosan-

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graft-poly (methacrylamide) were characterized ⁸. Significant factors influencing graft copolymerization

such as reaction time, temperature and concentrations of APS, MAM and chitosan have been investigated to get the greatest grafting parameters. The optimum grafting percentage and graft copolymerization yield values were obtained under the following circumstances: (1 g) chitosan, (4 g) MAM, (0.6 g) APS, (4 h) time and (70°C) temperature.

The characteristics of chitosan-g-PMAM have been improved concerning chitosan, making it can be used as an adsorbent ⁸. A chitosan-g-polyacrylonitrile copolymer was effectively synthesized using the initiator ceric ammonium nitrate through free radical polymerization. Analysis of TGA and DSC disclosed high thermal stability of the graft copolymer. Other research showed that the chitosan-g-polyacrylonitrile is an efficient adsorbent for the removal of Cr (VI) and Cu (II) metal ions from aqueous solutions. Cr (VI) and Cu (II) ion adsorption depend on the original metal ion concentration, adsorbent dose, pH, and contact time. It has been discovered that chitosan-g-polyacrylonitrile is a useful adsorbent ⁹. Cd (II) is one of the toxic metals to which attention has been paid. Because of its severe, dangerous effects on humans, animals, and crops, the removal of cadmium is gaining broad interest from both environmental and economic points of view. This heavy metal has caused severe soil and water contamination. Cadmium has been categorized as a lung, kidney, liver, and reproductive organs that affects human carcinogen and teratogen. A peak guideline concentration of 0.003 mg / L for cadmium in drinking water was set by the World Health Organization (WHO) ¹⁰. To remove copper and cadmium ions from synthetic industrial wastewater, chitosan with nylon 6 membranes was assessed as adsorbents. The percentage of removal of copper increased with an increase in the pH from 3 to 5. In the case of cadmium containing wastewater, the maximum removal of metal occurred at pH 5. The uptake amount of Cu²⁺ ions on chitosan increased rapidly with increasing contact time from 0 to 360 min and then reaches equilibrium after 360 min; the equilibrium constant for copper and cadmium ions is more or less the same for the adsorption reaction ¹¹.

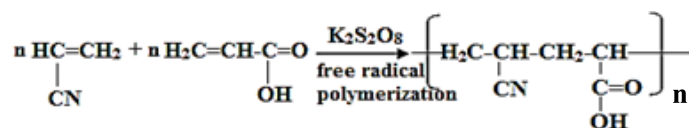
Thus, in our present study, the copolymerization of acrylonitrile (AN) with acrylic acid (AA) comonomer was prepared through free radical polymerization to form poly (AN-co-AA). Since the development of the polymer properties becomes a crucial challenge of the research field for use in various industrial applications. Also, we report on the Graft copolymerization of poly (acrylonitrile-co-acrylic acid) onto chitosan at a specific ratio. Adsorption behavior and performance of the CS-g-poly (AN-co-AA) were determined by various effecting parameters like contact time, initial concentration, and pH value in the removal of Cd (II) from aqueous solution.

2. Materials and methods

As reported ¹², Chitosan was prepared from shrimp shells with 110 kDa of molecular weight and 85 % of the degree of deacetylation in our lab. Acrylic acid (AA) was purchased from Koch-Light Laboratories; potassium persulfate (K₂S₂O₈) and acrylonitrile (AN) were obtained from Sigma-Aldrich and used after get rid of the inhibitor by using NaOH. All solution was prepared using double distilled water. Dimethylformamide DMF obtained from Piochem, ethanol as a solvent from El Nasr Pharmaceutical Chemicals Co., and other reagents using as it is.

2.1. Preparation Poly (acrylonitrile co-acrylic acid) preparation

Potassium persulfate (K₂S₂O₈) was dissolved as an initiator in DMF: water mixture at the beginning with stirring at volume ratio 50:50. The mixture was then added to monomers (AN, AA) and stirred in a three-necked flask for 30min, and the temperature of the bath was set at 60°C ± 2°C. The poly (AN-co-AA) was synthesized by free radical polymerization with code co₁, co₂ and co₃ respectively with different ratio of 25:75 percent, 50:50 percent and 75:25 percent. To remove the AA and AN monomers, the product was completely extracted by washing with ethanol and 3 times with distilled water. The copolymers were then poured for 48 hours in a Petri platter in a vacuum oven at 60°C and then filmed ¹³ as shown in Scheme 2.



Scheme 1. Poly (acrylonitrile co-acrylic acid)

2.2. Chitosan grafted poly (acrylonitrile-co-acrylic acid) Preparation

Based on previous research ⁷, the CS-g-poly (AN-AA) was prepared. 0.1 mg of Cs was dissolved in 25 ml of

5% acetic acid, then take 0.1 of K₂S₂O₈ in the solution of CS for 10 min with magnetic stirring in the reflux. After that, the monomers of AN and AA were added, with ratio 25:75 (co₁) % heated to 60°C and kept stirring for

4hr. Removing the AA and AN monomer need to completely extract the product by washing with ethanol and 3 times with distilled water. The resulting mixture was then cooled to room temperature, and the product was poured into the petri dish and left to evaporate to give code co_4 to the film.

2.3. Characterization of prepared compounds

The chemical structures of the copolymers prepared with different ratio and chitosan -g- poly (AN-co-AA acid) were confirmed by Fourier transforms infrared spectroscopy by Perkin- Elmer 1650 in the range of $4000-500\text{ cm}^{-1}$ where the KBr technique was used. Thermogravimetric analysis TGA was performed for all prepared samples by using a Shimadzu TGA-50H instrument. The rate of heating was $10^\circ\text{C}/\text{min}$ up to 800°C under a nitrogen atmosphere. The evaluations of electrical conductivity DC were measured using a four-probe technique and analyze using Keithley 6517A. It has to be that the sample cut $1\text{ mm} \times 1\text{ mm} \times 1\text{ mm}$ was kept in the middle of two copper electrodes, where two Keithley electrometer terminals were associated accordingly.

2.4. Adsorption reactions

Adsorption reactions to removal Cadmium are using the prepared polymers:

All experiments were performed at room temperature using batch technique. Dissolve a suitable amount of CdCl_2 in deionized water and subsequently diluting it to the required concentrations to prepare a stock solution

of (1.0 g/L) $\text{Cd}(\text{II})$ ions. To avoid the formation of metal hydroxide and to come to the metal ion again to the dissolved state, the stock solutions were acidified to required pH with concentrated HCl. The pH values were adjusted from 2 to 9, with 0.1 N NaOH and 0.1 N HCl . Varying the adsorbent dose, the pH of the solution and time of shaking the adsorbent metal solution was used to investigate the cadmium metal removal. The stopper bottles were adjusted at room temperature by stirring at a fixed speed, 200 rpm for 180 min . The samples were taken at definite time intervals at ($5, 10, 20, 30, 60, 90$ and 180 min). After adsorption, the above adsorption systems were centrifuged for 15 min at 3000 r/min , and then 10 ml of each supernatant aliquot was filtered and analyzed for remaining $\text{Cd}(\text{II})$ concentration by an atomic absorption spectrophotometer. Metal solutions that did not contain sorbent served as controls ¹⁰.

3. Results and Discussions

3.1. Chitosan and grafted copolymer characterization

3.1.1. Fourier transforms infrared spectroscopy

FTIR spectra for Cs, (AN-co-AA) copolymer and co_4 are shown in (Figure1). In chitosan, it was appeared strong, and broadband appeared at 3441.71 ; corresponding to the vibration of $-\text{NH}_2$ group and carboxylic acid $-\text{OH}$ stretch, a band related to C-H stretching groups are shown at 2921.5 cm^{-1} , the stretching of the $(\text{C}=\text{O})$ at 1646.61 cm^{-1} and at 1423.32 cm^{-1} according to C-N bond stretching.

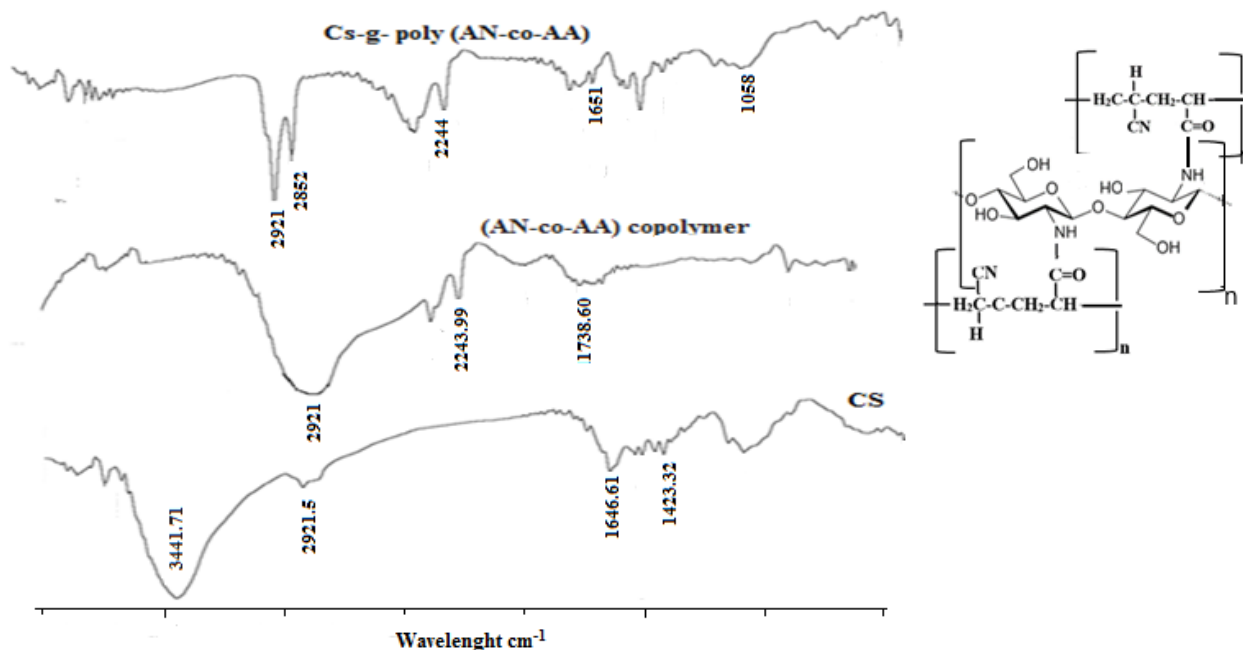


Figure 1. FTIR for Cs, co_2 , and co_4

FTIR spectra for (AN-co-AA) copolymer has an absorption bands at 2243.99 cm^{-1} and 1738.60 cm^{-1} indicates the existing of $\text{C}\equiv\text{N}$ group for AN, $\text{C}=\text{O}$ for AA stretching and peaks in the range between $2500\text{--}3000\text{ cm}^{-1}$ for carboxylic acid $-\text{OH}$ stretch respectively¹⁴. At the same time, the peaks of $\text{C}=\text{C}$ at 1500 cm^{-1} disappeared; this confirms that the copolymerization was occurring.

The sample co_4 which prepared by reaction of NH_2 groups of Cs and $-\text{COOH}$ groups of AA of copolymer,

3.1.2. XRD

XRD pattern of Cs, co_1 and co_4 was shown in (Figure 2). The band in chitosan-g-(AN-co-AA) spectrum showed the shifted of 2θ due to the grafting of copolymer onto the chitosan backbone. The XRD patterns of chitosan changed after grafted and shifted to a lower angle ($2\theta = 17.81$). Acharyulu et al. reported that the intensity

it appears as a band at 1651 cm^{-1} which attributed to CONH groups. It is expected that there will be a reaction between NH_2 groups of Cs and $\text{C}=\text{C}$ of copolymer which has disappeared. The peaks at ($2921\text{--}2852.07\text{ cm}^{-1}$ m or s) (C-H stretching) was appearing with increasing the intensity beside to the presence of the peaks of the $\text{C}\equiv\text{N}$ group for copolymer and 2245 cm^{-1} and 1058 cm^{-1} of C-OH group for Cs. The presence of these functional groups plays a vital role in Cd(II) ions adsorption¹⁵.

of the crystalline peak of the grafted polymers decreased or shifted with the extent of grafting¹⁶. Meanwhile, the copolymer shifted to a higher angle at ($2\theta = 27.39$) after grafted. The changes were attributed to the destruction of hydrogen bonds between hydroxyl and amino groups after chemical modification¹⁷.

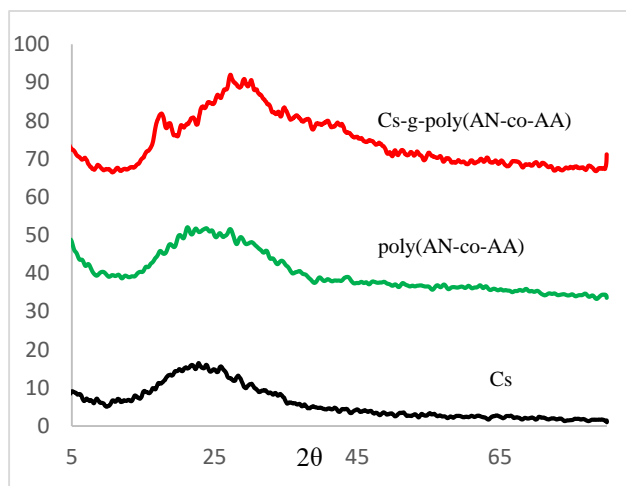


Figure 2. XRD of chitosan and co_4

3.1.3. SEM

As shown in the (Figure 3), it is noteworthy that, owing to a powerful inter- and intra-hydrogen bonding, chitosan introduced a soft and nonporous on the surface. On the contrary, the surface of co_4 has more visible pore structure.

The chemical modification of raw chitosan using by the grafting skeleton affected the surface structure of the copolymer, making the co_4 have high porosity lead to higher adsorption⁸.

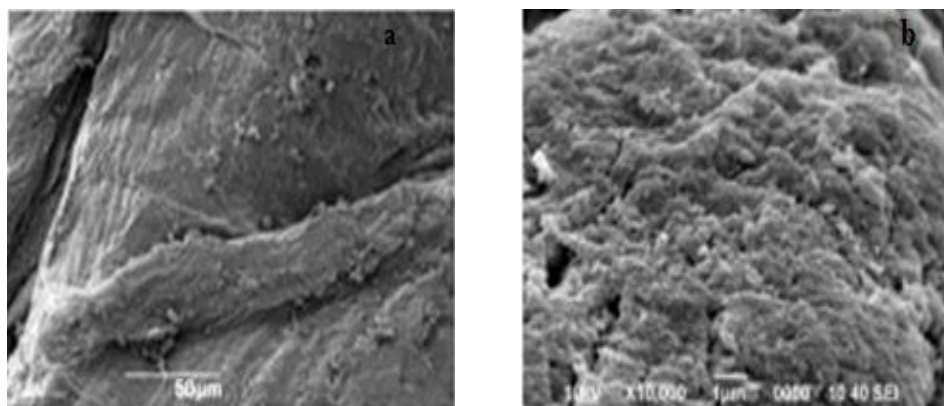


Figure 3. SEM for Cs and co_4

3.2. Factors Influence of Cd (II) ion adsorption

(Figure 4a-c) showed the adsorption effectiveness of the adsorbent depending on the solution's pH, adsorbent dosage and contact time at room temperature) ¹⁸.

3.2.1. Effect of pH

The aqueous solution's pH value is a significant control parameter in the method of adsorption. These pH values influence the adsorbent surface charge, the degree of ionization and adsorbate speciation during adsorption. The studies were performed at separate initial pH varying from 2 to 9 in order to assess the influence of this parameter on the adsorption. Also, the zero-point charge (pH_{ZPC}) for the co_4 was determined around $pH = 4.9$. co_4 performed the experiment with an initial

20 mg L^{-1} cadmium ion concentration containing 3g of adsorbent /L at room temperature with a 2h contact time.

The concentration of H^+ ions was high in acidic media. This led to the growth of positive charge on co_4 's active sites, as well as a contest between Cd (II) ions and H^+ in the bulk of the solution to be attached to the copolymer's active binding sites. Therefore, reducing the positive surface charge results in lowering the electrostatic repulsion between surface ions and metal ions. In the meantime, Cd (II) adsorption is declining in the alkaline medium, owing to the creation of soluble hydroxyl complexes. The outcome in (Figure 4a) shows that at an equilibrium pH of 5, the highest removal of Cd (II) was achieved ¹⁹.

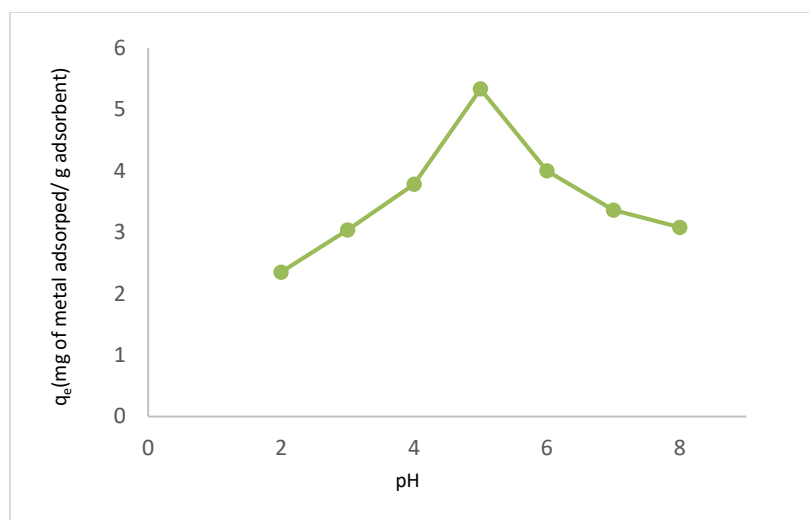


Figure 4a. The effect of pH on the desorption capacity of co_4 (the Cd(II) initial concentration, contact time, and amount of adsorbent was 20 mg/L , 2h, and 3 g/l, respectively).

3.2.2. Effect of Contact Time

The tests on adsorption were conducted at different times of contact. (Figure 4b) demonstrates the impact of

contact time on Cd ion adsorption at an original concentration of 20 mg L^{-1} , adsorbent dose (3 g/L), at room temperature, $pH = 5$ at contact time up to 180 min.

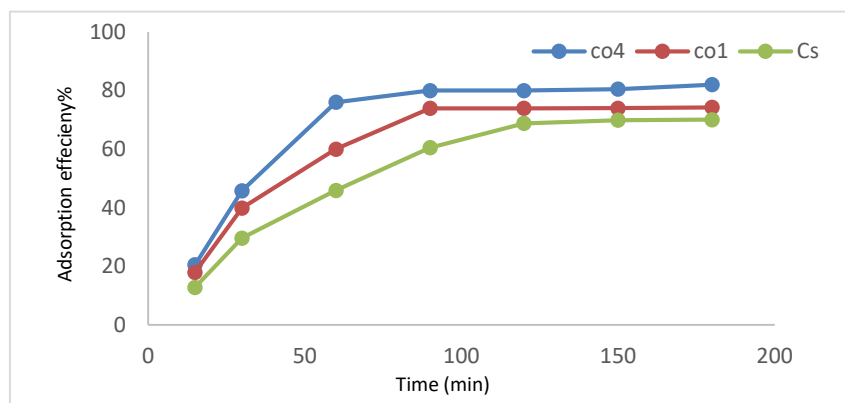


Figure 4b. The effect of time on the adsorption efficiency of Cs, co_1 and co_4 (the initial concentration, pH and amount of adsorbent were 20 mg/L , 5, and 3 g/L, respectively)

The adsorption capacity of co_4 was quite larger than that of co_1 or Cs within 180 min, confirming that the introduction of copolymer (AN-co-AA) increasing the porosity of co_4 as seen in (Figure.3) which are favorable for improving adsorption capacity. For the first 60 min, the Cd adsorption rate is high, and after about 120 min, equilibrium is finally created. The abundance of active sites on the adsorbent surface could be attributed to the rapid adsorption of Cd ions at the initial stages of contact time.

The adsorption subsequently became less effective with the gradual occupancy of these sites. A further rise in contact time did not improve adsorption, so for further studies, the optimum contact time for the adsorbent was chosen as 120 min. The results stated that 70.25, 74.05 and 82.00 percent respectively, are found to be the removal effectiveness of Cs, co_1 and co_4 . co_4 's removal effectiveness is higher than the other polymers.

3.2.3. Effect of Adsorbent Dose

One of the significant parameters of adsorption is the dose of adsorbents. It can be seen that the amount of adsorbents increases with the adsorption. This can be explained by increased accessibility at a large quantity of the adsorbent of the active sites or surface area. The proportion of adsorption rises from the copolymer doses of 1.0-5.0 g / L. (Figure 4c) showed the adsorbent dose effect on Cd ions adsorption. When adsorbent was reached in equilibrium, there was no significant change in the addition of the adsorbent dose. Thus, for the maximum removal percentage Cd (II), the optimum adsorbent dose was 3 mg / L. When adsorbent was reached equilibrium, further addition of adsorbent dose did not cause any significant change. Thus the optimum dose of the adsorbent for the maximal removal percent Cd (II) was 3 mg/L.

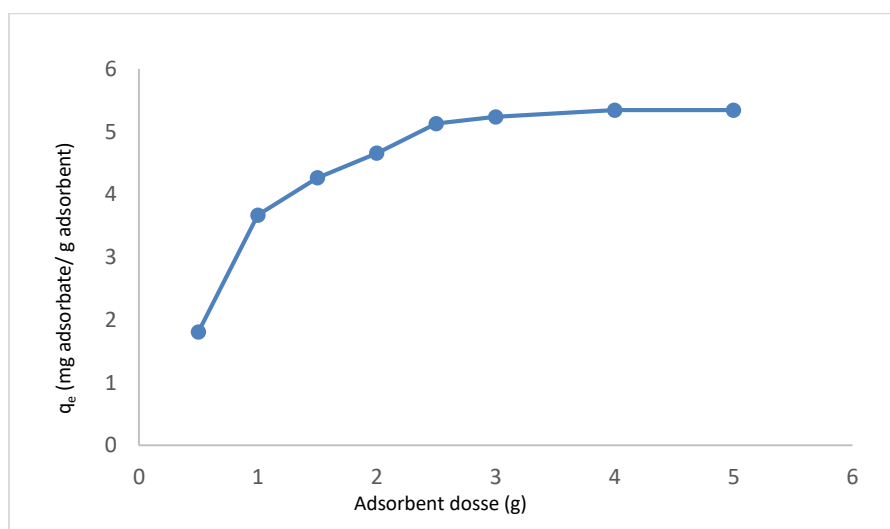
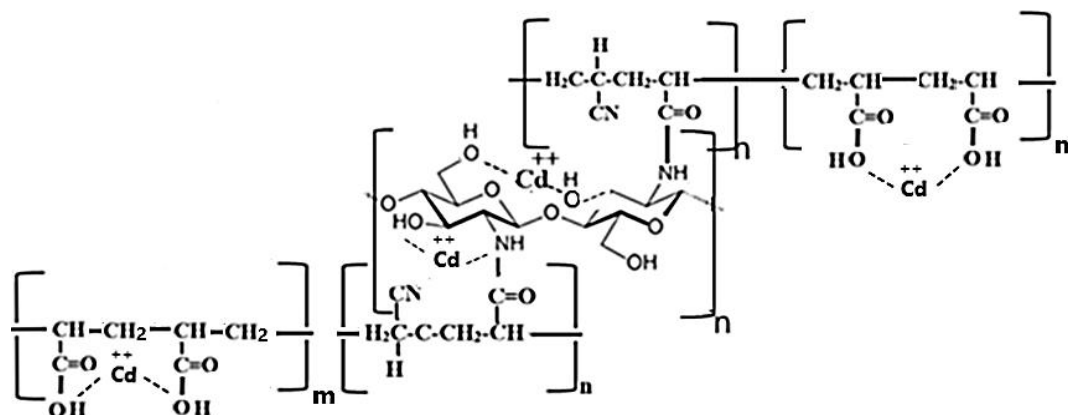


Figure 4c. The effect of adsorbent dose on the removal efficiency of Cd(II) (at pH 5, the initial concentration of Cd was 20 mg/L and contact time, 2h)



Scheme 2. Mechanism of Cadmium adsorption by Chitosan grafted poly (acrylonitrile-co-acrylic acid)

3.2.4. Mechanism of Cadmium adsorption

In the adsorption of Cd(II) ions, the presence of functional groups (OH, NH and COO) as mentioned in FTIR plays an important role. The coordinate bond with metallic ions is initiated by the amine group. The bond is formed between the free electron of the nitrogen in the amine group and the void orbitals of the metal. Nevertheless, the introduction of new functional groups ($-\text{COO}-$) on the chitosan surface by grafting on copolymer AN-co-AA leads to an increase in sites available. E. Guibal¹⁵ stated that by introducing new functional groups, the density of sorption sites on the chitosan surface increased. On the other hand, the hydroxyl (OH) and amino (NH) groups may form several complexes with metal cations, as shown in Scheme 2.

3.2.5. TGA

Thermogravimetric analysis (TGA) was used to determine the weight loss percentage at the rate of

heating was 10°C/min up to 800°C under a nitrogen atmosphere. (Figure 5) shows the thermal analyses curve for co₁, co₂, co₃, co₄ and Cs. The first stage for all samples is at a temperature between 40-120°C due to evaporating the moisture while in the case of co₄ and Cs the temperature increases in this stage to reach to 180 and 220°C due to loss of moisture adsorbed by the polysaccharide and any organic solvents. It appeared that Cs and co₄ decomposed faster than poly (AN-co-AA) between 220 and 450°C. It indicates the thermal stability of chitosan is increased after the grafting of poly (AN-co-AA) due to the strong hydrogen bond (NH₂, OH) of chitosan with copolymer¹⁷. On the other hand, by studying the thermal stability at the different ratio of AN and AA in samples co₁, co₂, co₃, it was found that the most thermal stability sample ratio is co₃ due to increasing the ratio of AN as shown in Table 1. While in sample co₁ with a high ratio of AA, the thermal stability decrease according to the fast decomposition of $-\text{COOH}$ of acrylic acid.

Table 1. Thermal parameters of the prepared samples as a function of 10% & 50% weight loss, and char residue at 700°C.

Sample code	Temp at 10% Weight loss	Temp at 50% Weight loss	Char residue at 750°C
co ₁	233	290	5.63
co ₂	188	348	21.70
co ₃	209	433	33.88
co ₄	218	273	6.08
Cs	197	343	2.07

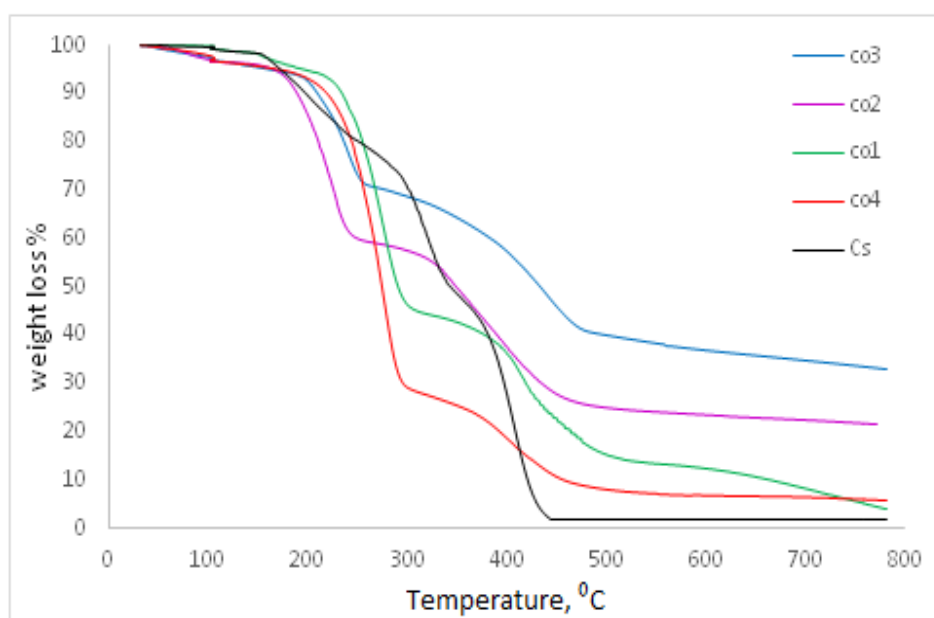


Figure 5. TGA for co₁, co₂, co₃, co₄ and Cs

3.3. Electrical conductivity

Here, the electrical conductivity of different ratio of copolymers co_1 , co_2 , co_3 and co_4 were studied. From the study of the relationship between the current (I) and the volt (V), the prepared samples give a straight line passing the starting point, so it is Ohmic relation as in (Figure 6a).

The electrical conductivity (σ) of AN-co-AA with different ratio co_1 , co_2 , co_3 and co_4 was investigated at room temperature using a four-probe method and analyzed with Keithley 6517A shown in (Figure 6b). The PAN is no conducting polymer, and its electrical conductivity at room temperature lies between 10^{-8} to 10^{-11} S cm^{-1} related to the previous study²⁰. In this work, the data showed that σ of the copolymer depends on the

ratio of AN and AA. By measuring σ for the different ratio of copolymer, it was found that the conductivity increased by increasing the ratio of AA due to increasing the number of mobile ions. The electrical conductivity was 2.12×10^{-7} , 6.89×10^{-8} and 2.02×10^{-8} for co_1 , co_2 and co_3 respectively. While is mentioned from previous studies, pure chitosan films exhibited an average conductivity of 1.91×10^{-7} S/ cm^{-1} ²¹. From the results, we choose the best ratio, which gave the highest σ and prepared to graft chitosan in situ with co_4 . The conductivity was 3.85×10^{-7} which is more than the copolymer without chitosan, which increases the electron density of the copolymer through the end group effect. As the result of σ has a range 10^{-8} S/ cm^{-1} to 10^{-6} S/ cm^{-1} so, all the prepared sample can be used as an electrostatic dissipation application²².

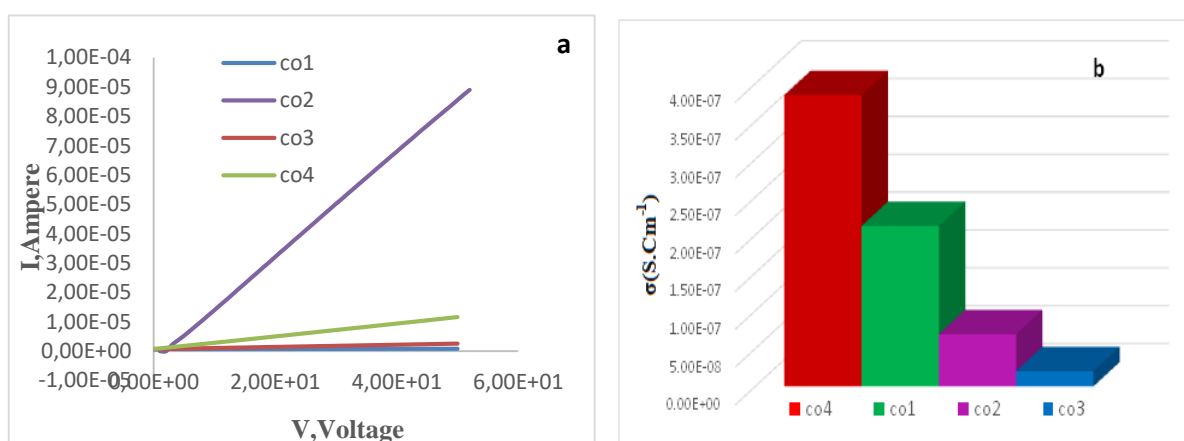


Figure 6. Electrical conductivity for co_1 , co_2 , co_3 and co_4

4. Conclusion

In our search, we prepared poly (acrylonitrile-co-acrylic acid) at different ratios of 25:75%, 50:50% and 75:25% respectively by free radical polymerization with code co_1 , co_2 and co_3 . Graft copolymerization of the 25:75 percent ratio of poly (acrylonitrile-co-acrylic acid) on chitosan was successfully performed using $K_2S_2O_8$ as an initiator in aqueous media. All samples were characterized by FTIR, XRD, and SEM. CS-g-poly (AN-AA) sample was used to remove the Cd^{++} ion from wastewater. Adsorption effectiveness of adsorbent depended on pH of the solution, contact time and adsorbent dosage at room temperature. The optimum condition was pH= 5, 120 min time, and 3 mg/L adsorbent dose. It was found from the analysis of thermal stability (TGA) for all samples that due to increasing the ratio of AN, the most thermal stability sample ratio is co_3 .

On the contrary, the thermal stability decreases in sample co_1 with high AA ratio as a result of the rapid decomposition of $-COOH$ of acrylic acid. The conductivity increased by increasing the AA ratio due to increasing the number of mobile ions, according to the

results of the electrical conductivity. The prepared samples can be used as an application for electrostatic dissipation between 10^{-8} S / cm^{-1} - 10^{-6} S / cm^{-1} .

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6. Conflicts of interest

The authors declare no competing financial interest.

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