



Polymerization of Acrylic Acid on Chitosan by Gamma Radiation and its Application for the Removal of Metal Ions from Aqueous Solutions

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Abstract

Synthesis of green adsorbent materials for the removal of pollutants is a research priority for sustainable environment. A green hydrogel adsorbent based on graft polymerization of acrylic acid on chitosan was performed using different doses of gamma radiation (5, 10, 15, 20, 30 kGy). The formed hydro-gels were characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Gelation percentage, swelling in different pH solutions, scanning electron microscopy (SEM). The results indicated the formation of a complex between chitosan and Polyacrylic acid. This hydrogel exhibits a higher gelation percentage with increasing irradiation dose, and a much higher swelling ability at alkaline medium. The thermal stability of the hydrogel was found to slightly decrease at 30 kGy. The hydrogel was applied for the removal of Cu^{2+} , Co^{2+} ions from simulated water solutions, and showed potential results. The electron spin resonance (ESR) measurements to the absorbed Cu^{2+} indicated that the polymer active groups were regarded as a strong field ligand on Cu^{2+} .

Keywords: Chitosan; Acrylic acid; Grafting; Gamma radiation; sorption; metal chelation

1. Introduction

There is an increasing interest from both academia and industry in modifying natural materials for various applications. This trend ensures many benefits, including efficiency, sustainability, and cost effectiveness. Chitosan is a polysaccharide prepared by partial deacetylation of chitin, which is the second most abundant natural biopolymer after cellulose. Chitosan is gaining more and more attention due to its nature of being biocompatible and biodegradable. It has been widely studied for the application in biomedicine, waste water treatment, food industry and agriculture [1–8]. Water pollution has become a serious global problem due to the rapid development in different industries. In particular, heavy metal contaminants have hazardous effects on aquatic life, plants, animals and human beings. Heavy metal contaminants results from man activities in different fields such as industry, agriculture, medicine, mining and technological applications [9–11]. The conventional treatment methods for heavy metal

contamination in water, including chemical precipitation, electrochemical treatment and membrane systems [12–15], are expensive and not eco-friendly. Besides, those methods may result in a secondary pollution in effluents. In recent years, growing attention has been drawn to adsorption for its high efficiency in the removal of low concentration contaminants and relatively simple process [8,16,17]. Graft polymerization of acrylic acid to natural polymers has been reported to enhance the water absorptivity; this would increase the metal ion chelation affinity of chitosan [4,18]. Chitosan with its amino group complex with the carboxylic groups of the acrylic monomer, when the acrylic monomer polymerizes, the formed polyacrylic acid chains form interpenetrating network with chitosan chains forming a hydrogel. Ionizing radiations have been proved to be simple and efficient tools for the formation of polymer blends, co-polymers and nanocomposites [4,8,19–22]. In particular, grafting of functional monomers to synthetic polymers and

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natural polymers has gained a great attention [4,8,23,24]. In this work, a green adsorbent hydrogel based on graft polymerization of acrylic acid on chitosan was prepared by gamma radiation induced polymerization. The gel % and swelling character at different pH were determined. The structural and thermal analysis of the hydrogel was performed. The hydrogel was applied for the removal of Co^{2+} and Cu^{2+} ions. In addition, the interaction between the metal ion and the active groups in the polymer was studied using ESR.

Experimental

Materials

Low molecular weight Chitosan (Cs) was obtained from sigma Aldrich, degree of acetylation is 75-85%, soluble viscosity 20-200 Cp (1% solution in 1% acetic acid, Brookfield). Acrylic acid monomer (MW=72.06 g/mol) was purchased from Merck (Germany). Copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and Cobalt (II) sulfate heptahydrate ($\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$) were purchased from Merck (Germany).

Preparation of chitosan/poly(acrylic acid) hydrogel by using gamma irradiation

An aqueous solution of Cs (1 %) in 1 % acetic acid was prepared. Acrylic acid was added to the Cs solution (1:2 v/v) and the solution was stirred for 2 h to ensure homogenous distribution. The solutions were then irradiated with a dose rate of 4.8 kGy /h in sealed tubes in the Co-60 gamma cell facility located at the National Center for Radiation Research and Technology, Cairo, Egypt.

Determination of gelation percentage

Known weights (w_0) of at least three samples of the prepared hydrogel soaked in hot water. The samples were then removed and dried in air for stable drying weight (wd). The gelation percentage (G%) was calculated according to the following equation: $G \% = (W_d/W_0) \times 100$

Swelling characters

Swelling of hydrogels in water, acids and alkalis were carried out by immersing known weight (W_0) samples in distilled water, alkaline solution (0.1N NaOH) or acidic solution (0.1N HCl) for different intervals. The samples were then removed and blotted on filter paper to remove the excess of solution. The swelling percentage was calculated according to the following equation

$$\text{Swelling \%} = [(W_1 - W_0) / W_0] \times 100$$

Where: W_0 is the initial weight of the sample and W_1 is the final weight of the swelled sample.

FTIR spectroscopic analysis

The vibrational spectra were recorded on Fourier Transform Infrared Spectrometer (FTIR), Mattson-Genssis, Unicam, England, over the range 400- 4000 cm^{-1} using KBr disks made by mixing KBr with fine powder of the polymer gel.

Thermogravimetric analysis (TGA)

The thermograms of TGA were recorded on TGA-50, Shimadzu, Kyoto, Japan, at a heating rate of 10°C/min under nitrogen gas from room temperature up to 600°C.

Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Shimadzu DSC (DSC-60) (Kyoto, Japan). The scans were carried out at a heating rate of 10°C/min under nitrogen gas.

Scanning electron microscopy (SEM)

The morphology of the fracture surface of the hydrogel was investigated by SEM. JSM-5400 electron microscope, JEOL, Japan. The samples were coated with gold using a sputter coater before observing the micrographs at 30 kV.

X-ray Diffraction

X-ray diffraction patterns of chitosan/polyacrylic acid samples were measured by using a Philips X-ray diffractometer (PW13900), using Cu-K α radiation.

Sorption of heavy metal ions

The hydrogel samples were used for the removal of Cu^{2+} , Co^{2+} from simulated wastewater. Two solutions of CuSO_4 and CoSO_4 were prepared with a concentration of 500 ppm. Samples of known weight (0.05 gm) of the hydrogel were then immersed in these solutions for different time intervals (from 1h to 24 hours). The metal uptake percentage was determined using the following equation:

$$\text{Metal uptake \%} = [(C_1 - C_0)/C_0] \times 100$$

Where, C_1 and C_0 are the concentrations of the solutions before and after sorption by the hydrogel samples, respectively.

ESR Measurements

ESR measurements were performed using a Bruker spectrometer with a rectangular cavity, at 100 kHz modulation frequencies. The spectrum was recorded as the first derivative curve.

Results and Discussions

Green adsorbent hydrogel of chitosan grafted poly acrylic acid was prepared by making use of the solubility of chitosan in acrylic acid solution. A complex was formed upon solubilization between the carboxylic groups in acrylic acid and amino groups in chitosan structure. Upon gamma irradiation, acrylic acid polymerizes forming an interpenetrating network rich of functional groups, those can be used for the removal of metal ions. The formed hydrogel was characterized and applied for the removal of Co^{2+} and Cu^{2+} ions as shown in the following sections.

Determination of gelation degree

Fig. (1) shows gelation percentages for hydrogels at different doses of gamma irradiation. It is clear from the Figure that the gelation percentage increases with increasing the irradiation dose. Where, it ranges from 70 up to 90 % for radiation doses from 5 to 30 KGy. This is attributed to the increase in the degree of polymerization of acrylic acid with increasing the radiation dose. This results in the formation of a cross-linked interpenetrating network between chitosan and polyacrylic acid complex. It is known that as the degree of crosslinking increases the degree of gelation increases [25].

Swelling characters

Swelling test provides valuable information about the hydrogel performance. Table (1) shows the swelling % in neutral, acidic, and alkaline solutions for different immersion time intervals at room temperature. Generally, the swelling percentage decreased as the irradiation dose up to 20 kGy. At a higher irradiation dose, the swelling showed a slightly inverted trend for most of the samples. The decreasing trend at irradiation dose up to 20 kGy is attributed to the polymerization of AAc while complexing with chitosan chains resulting in the formation of interpenetrated hydrogel network. This, in turn, would decrease the swelling percentage. On the other hand, at a higher irradiation dose, the degradation in the Cs chains became more pronounced causing the formation of gaps in the network, which could be filled with water explaining the slightly inverted trend [26]. It can be seen that the swelling degree was higher in basic medium

compared to that in acidic medium. A comparison between the swelling percentage in neutral, acidic and alkaline media with time was performed as shown in Table (1). The swelling in alkaline medium (NaOH) shows a higher swelling percentage due to the conversion of carboxylic acid groups into electrolytic groups $\text{COO}^- \text{Na}^+$. Whereas, the swelling percentage in dilute acidic medium is much lower, it may be due to the trapping of chitosan into Poly (acrylic acid), so its ability to abstract H^+ is restricted. percentage

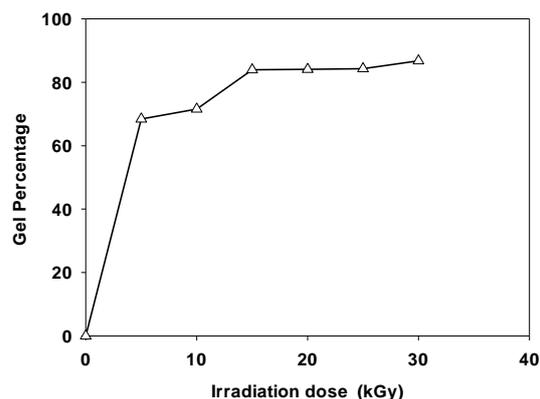


Fig. (1): Gel percentage of the Cs-PAAc hydrogel prepared at different gamma irradiation doses

FTIR Spectroscopy

IR spectra of unirradiated chitosan (Cs) and Poly (acrylic acid) (PAAc)/ chitosan (Cs) hydrogel, after gamma irradiation at various doses are shown in Fig. (2). It can be seen from this Figure that the main characteristic peaks of chitosan are at 3593 cm^{-1} (O-H stretch), 3493 cm^{-1} of (N-H in primary amine), 1637 cm^{-1} , 1549 cm^{-1} of amide 1 and 11, 1031 cm^{-1} (C-N in aliphatic amine) [27]. In the spectrum of Cs/PAAc hydrogel, there is broadening in O-H peak, this broadening increases with the irradiation doses due to the formation of hydrogen bonding between carboxyl groups of PAAc and hydroxyl groups of chitosan. Another hypothesis is that the grafting reaction takes place on the NH_2 group of Cs chains and the OH group of the side carbon [4,28,29] should also contribute to the peak broadening. A new absorption peak appears at 1708 cm^{-1} corresponds to the carboxyl absorption from poly (acrylic acid) [30], and another peak at 2902 cm^{-1} corresponds to NH_2^+ results from electrostatic attraction between amino and carboxylic groups. It is noticeable that at a higher irradiation dose (20 kGy), the O-H band became broader. This is attributed to a higher degree of graft polymerization of AAc to Cs causing the formation

of more hydrogen bonds between them [4]. In addition, at higher irradiation doses more chain scission takes place in the Cs matrix [4,31] resulting in the formation of shorter chains. This would induce the formation of more hydrogen bonds due to the easier conformation of the shorter chitosan chains [4]. In general, by increasing the irradiation dose, the intensities of the characteristic peaks of the hydrogel decreased due to the increased interaction between Cs and PAAc formed by polymerization of AAc.

Table (1): Swelling percentages in neutral, acidic and alkaline media of PAAc/Cs hydrogels prepared at different gamma irradiation doses

Irradiation dose (kGy)	Neutral medium			Acidic medium	Alkaline medium			
	24 h	48 h	72 h	2h	1 h	2 h	24 h	72 h
5	58	59.01	58.80	88.6	284	454	1823	3736
10	57	57.00	54.42	70.04	244	387	2028	2623
15	49	49.41	47.52	75.86	382	598	2115	4946
20	45	44.49	40.81	85.40	255	401	2167	3425
25	52	54.25	53.91	74.80	308	453	1748	2653
30	54	56.45	56.59	83.20	192	352	1568	1337

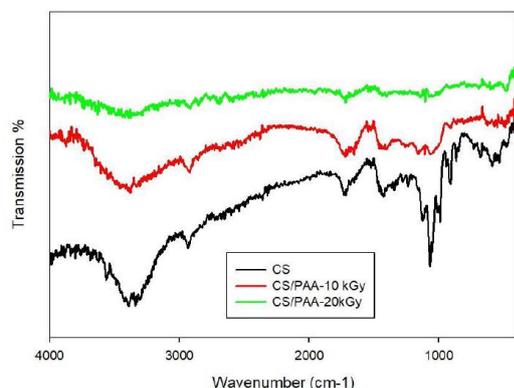


Fig. (2): FTIR of PAAc/Cs hydrogels prepared at different doses of gamma irradiation

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of the hydrogel prepared at various doses by plotting the weight remaining percentage with temperature. Fig. (3) Shows the TGA thermograms and the rate of decomposition reaction curves of Cs/PAAc hydrogels. In addition, Table (2) displays the weight loss percentages at different decomposition temperatures, for the same materials, abstracted from the corresponding TGA thermograms.

Theoretically, the strength of the covalent bonds formed between atoms in a polymer molecule determines the thermal stability of the polymer. The average dissociation energies of Cs and of PAAc depend on their covalent bonds values; it is 378.6 kJ/mol for Cs and 344.7 kJ/mol for PAAc. This leads to the conclusion that the thermal stability of Cs is

higher than that of PAAc, and it was expected that the presence of PAAc with Cs would decrease the thermal stability. However, the formation of hydrogen bonds between Cs and PAAc would be restrict the chain mobility and consequently increases their thermal stability.

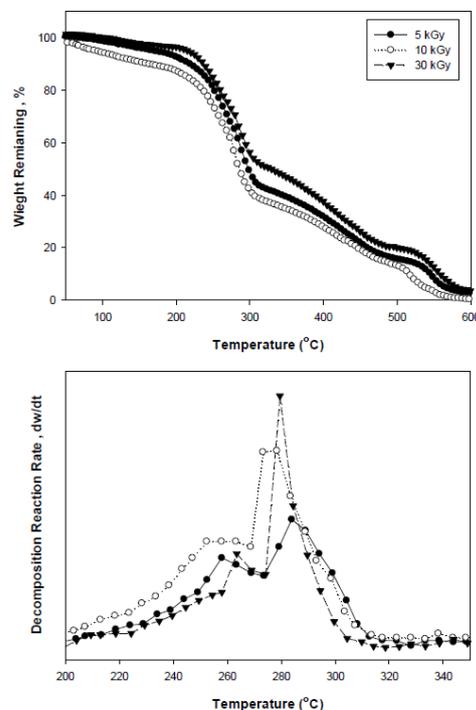


Fig. (3): TGA thermograms and decomposition reaction rate, dw/dt , for PAAc/Cs hydrogels prepared at various doses of gamma irradiation

Based on the TGA study, some points can be concluded:

- 1- TGA of gel samples showed a weight loss between 50 and 200 °C. This corresponds to the loss of bound and adsorbed water [4].
- 2- The weight loss from 210 °C to 360 °C was about 44% of the weight, due to the degradation of most side chains [4].
- 3- the peaks around 250 and 280 °C are assigned to the decarboxylation of PAA and de-acetylation of chitosan respectively [4,32].
- 4- The TGA of the hydrogels prepared at various irradiation doses had the same trend regardless to irradiation dose.
- 5- At higher irradiation doses chitosan undergoes partial chain scission due to the breakage of glycosidic bonds [4,33]. This may contribute to the lowering of thermal stability for samples irradiated at 30 kGy.

As shown in Table (2), it summarizes the effect of increasing irradiation dose on the thermal stability. It is obvious that the weight loss (%) increased slightly with increasing irradiation dose. The rate of decomposition reaction curves displayed similar trends, in which all the hydrogels go through one maximum indicating a good interaction between Cs and PAAc in their hydrogels. The values of T_{max} was found to slightly decrease with increasing the irradiation dose. This indicates that the thermal stability of hydrogels decreased with the increase in irradiation doses.

Table (2): Weight loss (%) at different temperatures of Cs/PAAc hydrogels prepared at different doses of gamma irradiation

Dose (kGy)	Weight Loss (%)					T_{Max} (°C)
	100°C	200°C	300°C	400°C	500°C	
5	1.42	7.67	53.24	68.82	84.49	286
10	5.85	13.02	59.30	72.72	87.14	278
30	2.81	10.07	58.28	73.29	86.37	279

The decrease in thermal stability associated with the increase in the irradiation dose can be attributed to the induced chain scission of chitosan chains as the irradiation dose increases [4].

Differential scanning calorimetry measurements

DSC was used to investigate the glass and melting transitions of Cs/PAAc hydrogel. Fig. (4) shows the DSC thermograms for Cs/PAAc hydrogel prepared at various doses of gamma irradiation. The different kinetic parameters abstracted from these thermograms are summarized in Table (3). It is well known from the literature that chitosan exhibits an endothermic peak around 123 °C. This peak is assigned for the rearrangement and mobility of water molecules absorbed through hydrogen bond with Cs hydroxyl groups. In Fig. (4), the DSC thermograms of the prepared hydrogels, exhibit an endothermic peak at around 170 °C for the hydrogels irradiated at 10, 20, 30 KGy. This may be attributed to the entrapment of water molecules in the cross-linked interpenetrated network, formed between Cs and PAAc, by radiation induced polymerization of acrylic acid. Another endothermic peak appears for the hydrogels, in the range from 260 to 280 °C, which is associated with the decarboxylation of PAAc. This peak is known to appear at about 263 °C [32]. The elevation in the temperature of this transition is explained by the involvement of the carboxylic

groups of PAAc in hydrogen bonding with amine groups of chitosan.

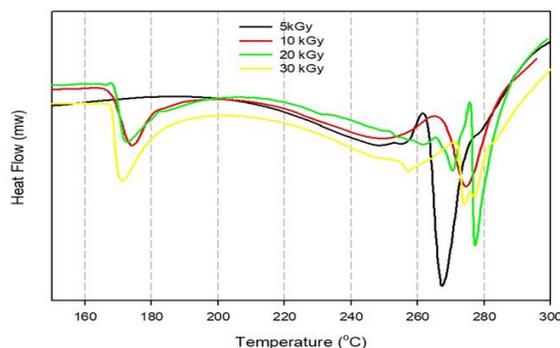


Fig (4): DSC thermograms of PAAc/Cs hydrogels prepared at various doses

Table (3): DSC parameters of PAAc/Cs hydrogels prepared at different doses of gamma irradiation

Dose (kGy)	T_g (°C)	T_m (°C)
5	139	267
10	173	272
20	172	276
30	170	272

This peak appears at 170 °C in the gel prepared at 10 KGy and shifted to low temperatures with increasing the irradiation dose. An additional endothermic peak in the DSC thermograms at 247 °C was recorded for the hydrogel prepared at 5KGy, and increases to higher temperatures for the prepared gels at higher doses. This can be attributed to the cleavage of the electrostatic interactions between carboxylic and amine groups. Table (3) reveals that the T_g values are strongly influenced by increasing the irradiation doses.

Scanning electron microscopy (SEM)

Fig. (5) shows the SEM micrographs of the fracture surfaces of PAAc/Cs hydrogels prepared at different doses of gamma irradiation. The images reveal that the surface was smoother as the irradiation dose increased from 5 to 20 kGy. This can be attributed to the increased interaction between COO-groups in PAAc and NH_2^+ groups in Cs, which indicates a more coherent structure of Cs/PAAc complex. It is noticeable that at higher irradiation doses (20 and 30 kGy) some cracks were developed in the fracture surface. These cracks are attributed to radiation induced chain scission due to the breakage of glycosidic bonds [4,33]. This result is consistent with the results obtained from the thermal analysis

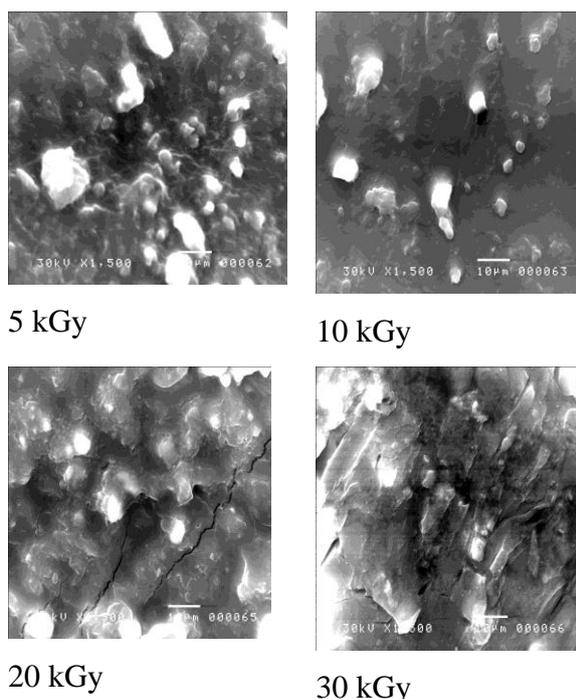


Fig. (5): SEM micrographs of PAAc/Cs hydrogels prepared at various doses of gamma irradiation

Sorption of heavy metal ions

The hydrogel prepared at 20 kGy was investigated for the removal of Cu^{2+} and Co^{2+} from simulated solutions of concentration of 500 ppm. The efficiency of the hydrogel was investigated by considering the maximum metal ion uptake. Fig. (6) shows the relationship between metal uptake and treatment time for Co^{2+} and Cu^{2+} ions. It can be seen that the metal uptake (expressed in ppm) increases with time till it reaches a maximum metal uptake capacity. Results show that the hydrogel has a higher tendency towards Co^{2+} ions than Cu^{2+} ions. These results can be explained by taking into consideration the size of metal ions, their diffusion through the pores of the hydrogel and the stability of their chelation to the polymer hydrogel. The affinity of PAAc/Cs hydrogels towards such metal ions may be attributed also to the presence of free hydroxyl groups along its macromolecular structure which enhances the hydrophilic character and absorption capacity.

Electron spin resonance (ESR) measurements

ESR spectrum of the polymer-metal compounds reflects the interaction between the spin of central metal ion and the active groups in the polymer. The adsorption pattern and spectroscopic splitting factor (g -value) are related to the interaction between the

ion and the polymer. ESR spectrum of Cu^{2+} adsorbed on PAAc/Cs is shown in Fig. (7). The ESR spectrum of solid state metal ion-polymer measured at room temperature showed anisotropic with resolved hyperfine structure.

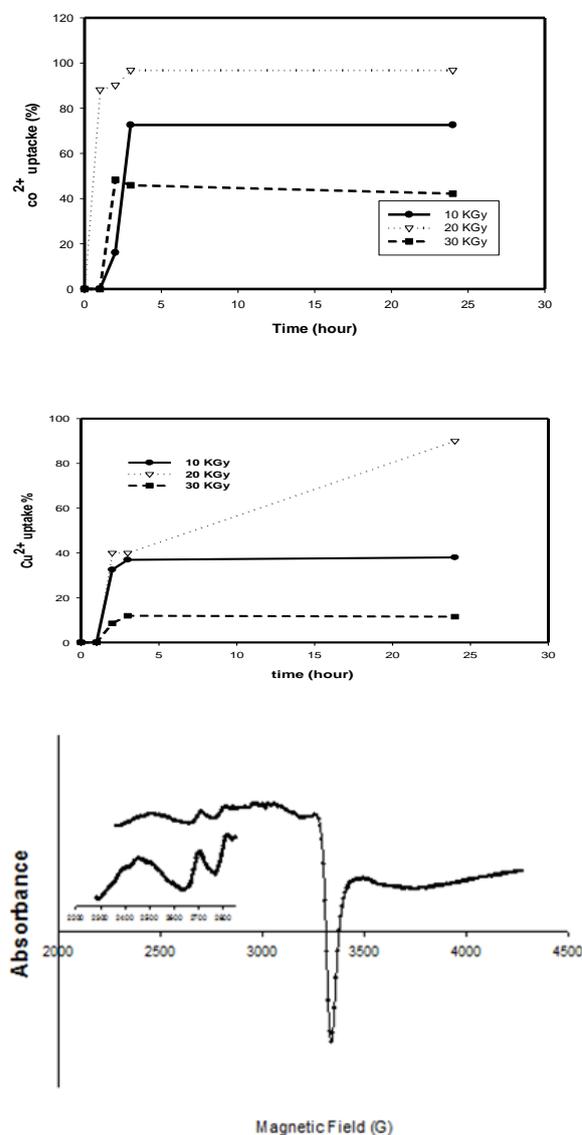


Fig. (7): ESR spectrum of solid stat Cu^{2+} -polymer measured at room temperature.

The g -tensor having the values ($g_{\perp} = 2.08024$ and $g_{\parallel} = 2.1102$) i.e. $g_{\parallel} > g_{\perp} > 2.0023$ indicates the probability of square planer stereochemistry. The spectrum indicates that no there is binuclear interaction between Cu^{2+} ion and the polymer where no adsorption band at 1500 G. The g_{\parallel} tensor is the parameter that reflects the covalent character of metal ion –polymer bonds, for ionic bonding environments the g_{\parallel} value is normally ≥ 2.3 and for covalent

environment g_{\parallel} is less than 2.3 [34]. According to the recorded data, the bonds between the polymeric ligand and the copper ions are more covalent than ionic in character. The values of g -tensors can be used to calculate the G -value indicating whether the polymer functional group acts as a strong field ligand or a weak field ligand. The following equation is used to calculate the G -value

$$G = (g_{\parallel} - 2.002) / (g_{\perp} - 2.002)$$

If the G -value is higher than 4.0, the polymer function group is regarded as a weak field ligand whereas, less than 4.0, the polymer function group is regarded as a strong field ligand. According to the proposed g_{\parallel} and g_{\perp} values for Cu^{+2} -polymer, the G -value = 1.3819 indicates a strong field action of the polymer function groups on Cu^{+2} .

Then the sample was heated at 80 °C for 24 hr. the ESR spectrum pattern is **slightly** changed indicating the coexistence of two species (Fig. 8). This probably a superimposed pattern, due to the existence of some Cu^{+2} as CuSO_4 not coordinated with the polymer.

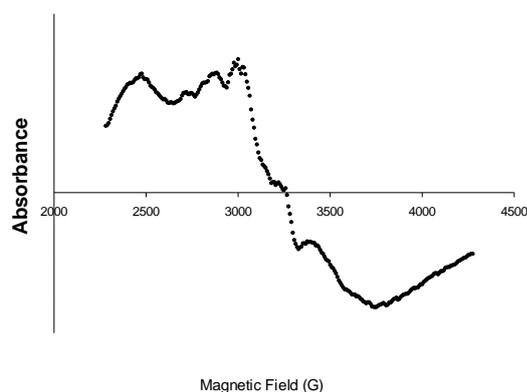


Fig. (8): ESR spectrum of solid state Cu^{2+} polymer after heating at 80 °C for 24hr and measured at room temperature

Conclusions

Hydrogels formed by template polymerization of AAC monomer on Cs were formed by dissolving Cs in AAC solution and irradiating it to different doses (5, 10, 15, 20, 30 KGy). A polymer complex was formed between PAAc and Cs as shown in FTIR spectrum. TGA analysis showed that all prepared hydrogels have thermal stability and they are stable with increasing irradiation doses from 5 up to 20 KGy. The crystalline part was found to increase in the range of radiation doses from 5 to 30 kGy, due to radiation induced chain scission in the amorphous

part. The **hydrogels** are effective towards the uptake of Cu^{2+} and Co^{2+} , especially for 20 Kgy irradiated hydrogel. The polymer active groups were regarded as strong field ligand on Cu^{2+} . the hydrogels based on chitosan are potential adsorbent for the removal of metal ion contaminants in an efficient and cost effective way.

Conflicts of interest

The authors declare no conflict of interest

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