

RADIATION SYNTHESIS OF POLY(CHITOSAN/ACRYLAMIDE) HYDROGEL FOR REMOVAL OF NIGROSIN FROM ITS AQUEOUS SOLUTION

ASHRAF MAHER ABDEL-GHAFFAR,* HUSSEIN EL-SHAHAT ALI,** MAYSARA EL-SAYED
ABOULFOTOUH* and NAEEM MOHAMED EL-SAWY*

*Radiation Research of Polymer Chemistry Department, Industrial Irradiation Division, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority, P.O. Box 29, Nasr City, Cairo, Egypt

**Radiation Chemistry Department, Radiation Research Division, National Center for Radiation Research and Technology, Egyptian Atomic Energy Authority, P.O. Box 29, Nasr City, Cairo, Egypt

✉ Corresponding author: A. M. Abdel-Ghaffar, am_abdelghaffar@yahoo.com

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Chitosan hydrogels were prepared by gamma radiation grafting of acrylamide (AAm) onto chitosan (CS). The gelation (%) increased as the AAm content was raised up to the CS/AAm ratio of 1/10 wt%. The grafting yield and the grafting ratios of the Poly(CS/AAm) hydrogel were found to be directly proportional to the increase in AAm contents. The swelling behavior was more pronounced with higher AAm content up to 1/15 wt% in the Poly(CS/AAm), and then decreased with further rise of the AAm content to 1/20 wt%, because of the formation of a highly crosslinked hydrogel, with high hydrogen bonding. The prepared Poly(CS/AAm) hydrogels were characterized by using FTIR, TGA and SEM techniques. The analysis confirmed successful preparation of Poly(CS/AAm) with different compositions. The adsorption capacity of the Poly(CS/AAm) hydrogel with the composition of (1:10 wt%) towards Nigrosin acid dye was found to be higher than that of the other hydrogel formulations. This may be due to the fact that the selected Poly(CS/AAm) hydrogel possesses a highly pronounced swelling behavior and a highly crosslinked structure, compared to the other prepared hydrogels. It has been also noted that the adsorption capacity of the 1:10 wt% Poly(CS/AAm) hydrogel enhanced markedly at pH 2, but decreased at higher pH values, namely, from pH 5 to pH 7.4. This can be explained by the protonation of amide groups of acrylamide and amine groups of chitosan occurring at lower pH. The high adsorption properties of the selected Poly(CS/AAm) hydrogel recommend it as a necessary bioremediation solution to face the high level of acid dye pollutants, such as Nigrosin, in industrial effluents.

Keywords: gamma radiation, grafting yield and ratio, CS/AAm biosorbent hydrogel, Nigrosin acid dye

INTRODUCTION

The rapid increase in the industrial use of dyes has led to the generation of high volumes of contaminated colored effluents from tanneries, fabric dying, rubber and paper manufacturing. Their release into the environment is harmful to biological organisms, threatening entire ecosystems, as they often contain toxic and carcinogenic compounds.¹⁻⁴

Chelating hydrogels have many environmental applications due to their high specificity level, high uptake capacity and durability. In such hydrogels, the chelating functional groups are

located in the side chains or along the polymer backbone.^{5,6}

Many environmental researches have focused on the adsorption of pollutants from wastewater using nanomaterials, activated carbon, ion exchange hydrogels and selective membranes.⁷⁻²² The development of low-cost adsorbents with high adsorption capacity and reusability has become crucial nowadays to face the high level of pollutants in water bodies.^{5,6}

Modified adsorbents, such as hydrogels, have many advantages, compared to activated carbon,

which is generally accepted for its adsorptive properties. They are more economical, easy to prepare, and they offer the possibility for further modifications when compared to activated carbon.^{1,6,23,24} Moreover, modified adsorbent hydrogels have the advantage of reusability, some chemical separation reactions being necessary for their future reuse.¹

Chitosan (CS) is an amino polysaccharide derived from chitin, which is the major component in shrimps and crab shells.²⁵ Chitosan is a biodegradable, pH sensitive, cationic and biocompatible polymer. It can be modified and turned into hydrogels that could be used in wastewater treatment and biomedical applications, owing to its chemically reactive hydroxyl and amine groups.²⁶ However, chitosan has some important limitations, including its solubility, due to its molecular weight, and short storage time (shelf-life), which restrict its applications in many fields.²⁷

Many research works have reported on modifications of chitosan (CS) by grafting of different chemical functional groups, either individually or by binary graft systems, such as phosphate, sulfonate, carboxyl, amido, amino and hydroxyl groups,⁶ to enhance its physical, chemical, and shelf-life properties.^{1,28} In addition these, further enhancements have been investigated to confer ionic characteristics to chitosan and increase its adsorption capacity, developing CS bioadsorbents.⁶

The main objective of the present study has been the preparation of a non-toxic and inexpensive CS-based hydrogel bioadsorbent. The preparation of the CS hydrogels was performed using a direct gamma radiation grafting process. Gamma radiation is the most suitable technique

for the preparation of Poly(CS/AAm), without using any additives. The characteristics and structures of the original CS and the modified Poly(CS/AAm) hydrogels, with different contents of AAm, were investigated. The adsorption capacity (Q) of the Poly(CS/AAm) hydrogels towards Nigrosin acid dye was studied under different conditions to examine the effect of different pH values and dye solution concentrations on the adsorption performance of the developed hydrogel.

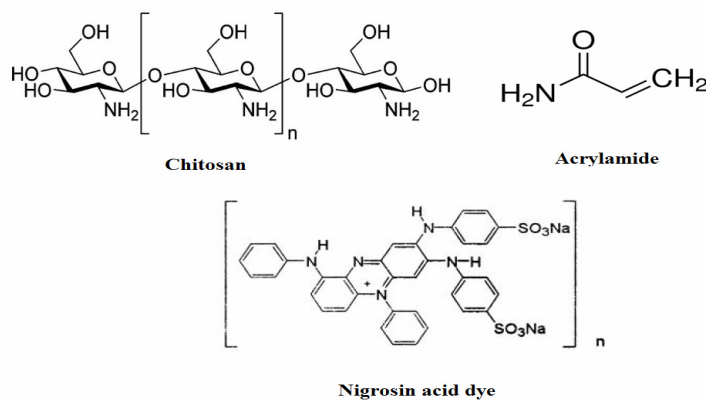
EXPERIMENTAL

Materials

Chitosan, (C₆H₁₁NO₄)_n, with low Mw (Mw = 100,000-300,000), was obtained from Acros, New Gercy, Sigma Aldrich, while acrylamide and citric acid were received from Lobachemie Ltd., Mumbai, India. Glacial acetic acid was purchased from El-Nasr Pharmaceutical Chemicals, Egypt. Disodium hydrogen phosphate was purchased from El-Nasr Company, Egypt. Nigrosin acid dye, (water-soluble, CI number 50420), was provided by Qualikems Fine Chem., Pvt. Ltd., India.

Preparation of Poly(CS/AAm) hydrogels

A concentration of 1% of chitosan was dissolved in 2% acetic acid, in addition to distilled water, in the presence of heat at 80 °C, with stirring until complete dissolution. 10 mL of dissolved chitosan solution was transferred to different glass ampoules, and then AAm was added to the CS solution, according to the CS/AAm ratios of 1:5 wt%, 1:10 wt%, 1:15 wt% and 1:20 wt%. The ampoules were sealed well and exposed to gamma irradiation at a dose of 20 kGy and a dose rate of 0.56 Gy/s. The gamma irradiation facility is located at the Egyptian Atomic Energy Authority (National Center for Radiation Research and Technology), Cairo, Egypt.



Scheme 1: Structures of compounds used

Characterization of prepared hydrogels

Gelation percentage

The prepared hydrogels were cut into regular discs, dried, and weighed. The samples were immersed into hot distilled water at 80 °C for 3 hours, then extracted from the water and dried at 40 °C until constant weight. The gelation percentage (G, %) was calculated using the following equation:

$$\text{Gelation (\%)} = \frac{W_g}{W_o} \times 100 \quad (1)$$

where W_g and W_o are the weight of the dried disc after and before immersion, respectively.

Determination of grafting yield and ratio

Grafting yield and grafting ratio were determined gravimetrically, using the following equations:²⁹⁻³³

$$\text{Grafting yield} = \frac{W_g - W_o}{W_o} \times 100 \quad (2)$$

where W_g is the weight of the prepared hydrogel after extraction, and W_o is the weight of original CS;

$$\text{Grafting ratio} = \frac{W_g}{W_o} \times 100 \quad (3)$$

where W_g is the weight of the prepared hydrogel after extraction, and W_o is the weight of original CS.

FTIR spectroscopy analysis

The infrared spectroscopic analysis of the grafted bio-blend film was accomplished in the range of 400-4000 cm^{-1} , using a FTIR-Vertex 70 Spectrophotometer, Bruker, Germany.

Swelling studies

Equilibrium swelling

The prepared hydrogel samples were immersed into distilled water at ambient temperature. Swollen discs (gels) were extracted from the water, dried, and weighed many times until the weight of the discs remained stable and it was measured for each disc (after 72 h). The swelling ratios at equilibrium (Q) were calculated using the following equation:

$$Q = \text{Equilibrium swelling} = \frac{W_s - W_d}{W_s} \times 100 \quad (4)$$

where W_d is the weight of dried hydrogels, W_s is the weight of the swollen gels at equilibrium.

Swelling behavior at different pH values

The grafted hydrogel discs were immersed into a buffer solution composed of disodium hydrogen phosphate and citric acid, at different pH values (2, 5 and 7.4) for 96 hours, at 25 °C. The swelling percentage was calculated from Equation (4).

UV-Vis spectroscopy

The removal of Nigrosin acid dye by the prepared hydrogel Poly(CS/AAM) was determined using a ThermoScientific UV-Vis spectrophotometer (Germany), within the scan range of 190-1100 nm. The absorbance of Nigrosin acid dye solution was

determined at $\lambda_{\text{max}} = 570$ nm, for different concentrations of the Nigrosin acid dye solution to construct the calibration curve.

Adsorption capacity

The adsorption capacity of the prepared Poly(CS/AAM) hydrogels towards Nigrosin acid dye was investigated. Solutions with different Nigrosin concentrations, namely, of 10, 20, 30, 40, 50 and 100 mg/L, were prepared. Then, the Poly(CS/AAM) hydrogel, with a weight of 0.1 g, was added to 10 mL of Nigrosin acid dye solution at ambient temperature. The adsorption capacity (Q) of the hydrogel towards Nigrosin acid dye was determined according to Equation (5):

$$Q = (C_i - C_f) V / W_b \quad (5)$$

where C_i is the initial concentration and C_f is the final concentration of Nigrosin acid dye (mg/mL), W_b is the weight of the Poly(CS/AAM) hydrogel (g) and V is the volume of the solution (mL). The uptake of the Nigrosin acid dye was determined by using the standard calibration curve. The values of adsorption capacity of the Poly(CS/AAM) hydrogel towards Nigrosin acid dye, calculated by Equation (5), were converted from mg/g to g/g, and presented in Figure 5 (a, b).³²

RESULTS AND DISCUSSION

Effect of monomer concentration on gelation (%)

The effect of varying the AAM content on gelation (%) is presented in Figure 1. It is noted that the gelation percent increases along with the increase in the AAM content up to 1/10 wt% in the Poly(CS/AAM) hydrogel, then slightly decreased. This is perhaps explained by the fact that the amount of free radicals increases as a consequence of intensified crosslinking of the hydrogel structures during the irradiation graft copolymerization operation up to the CS/AAM of 1/10 wt%. This may be due to the formation of hydrogen bonding interactions between the amide group of AAM and the hydroxyl groups of CS chains within the polymeric network, therefore the gelation (%) increases. However, further increasing the content of AAM beyond 10 wt% leads to a decrease in gelation (%), as at higher AAM content, the solution viscosity rises and the solution becomes more heterogeneous, which leads to less motility of the molecules, thus limiting AAM grafting onto CS and increasing the AAM homopolymer formation. As a result, gelation (%) decreases.³⁴

Grafting yield and grafting ratio

From Table 1, it can be noticed that the grafting yield and the grafting ratio increase with rising AAm content. This may be explained by the fact that, with higher AAm content, the free radicals formed by gamma radiation are more available. Therefore, higher grafting ratio and grafting yield were acquired.

FTIR analysis

The FTIR spectrum of CS in Figure 2(a) shows some characteristic and significant peaks. Thus, the broad absorption band around 3289 cm^{-1} is due to the overlap between hydroxyl (O-H) and (N-H) of the amine groups. The band at 2883 cm^{-1} is a stretching vibration assigned to aliphatic CH. The bands at 1573 and 1375 cm^{-1} are assigned to N-H of NH_2 , $-\text{CH}_2$ bending. The bands at 1148 and 1025 cm^{-1} represent the anti-symmetric stretching of the C-O-C bridge, and skeletal C-O-C in anhydroglucose units, respectively.²⁶ The band at 1640 cm^{-1} corresponds to the hydroxyl (O-H) of the polysaccharide. The bands appearing

at 894 and 607 cm^{-1} correspond to the bending vibration of C-H groups.

The spectrum of Poly(AAm) shown in Figure 2(b) reveals the bands at 3326 cm^{-1} and 3180 cm^{-1} , which are assigned to N-H of amide groups. The band appearing at 2931 cm^{-1} is attributed to the stretching vibration of aliphatic CH. The bands at 1647 cm^{-1} and 1600 cm^{-1} are characteristic of the carbonyl (C=O) of the amide groups. The band located at 1444 cm^{-1} corresponds to the bending vibration of C-H groups.

For the prepared Poly(CS/AAm) hydrogel, the characteristic groups are shown in Figure 2 (c-f) for different AAm content formulations. The combined overlapped peak between hydroxyl (O-H) and (N-H) of the amide groups was shifted, appearing at 3329 cm^{-1} , and the peak assigned to the N-H of amide groups was shifted to 3183 cm^{-1} . Another band shifted to 2979 cm^{-1} is attributed to the stretching vibration of the aliphatic CH. The two peaks corresponding to the stretching vibration of an amide carbonyl group shifted to appear at 1648 cm^{-1} and 1602 cm^{-1} .

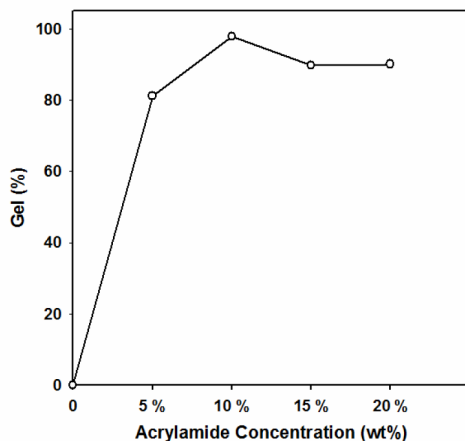


Figure 1: Effect of varying AAm content on gelation (%) of the Poly(CS/AAm) hydrogel at the irradiation dose of 20 kGy

Table 1

Effect of varying AAm content on grafting yield and ratio of the Poly(CS/AAm) hydrogel

CS/AAm (wt%)	Grafting yield	Grafting ratio
1/5	524.16	624.17
1/10	1240.78	1340.78
1/15	1722.67	1822.67
1/20	2374.11	2474.11

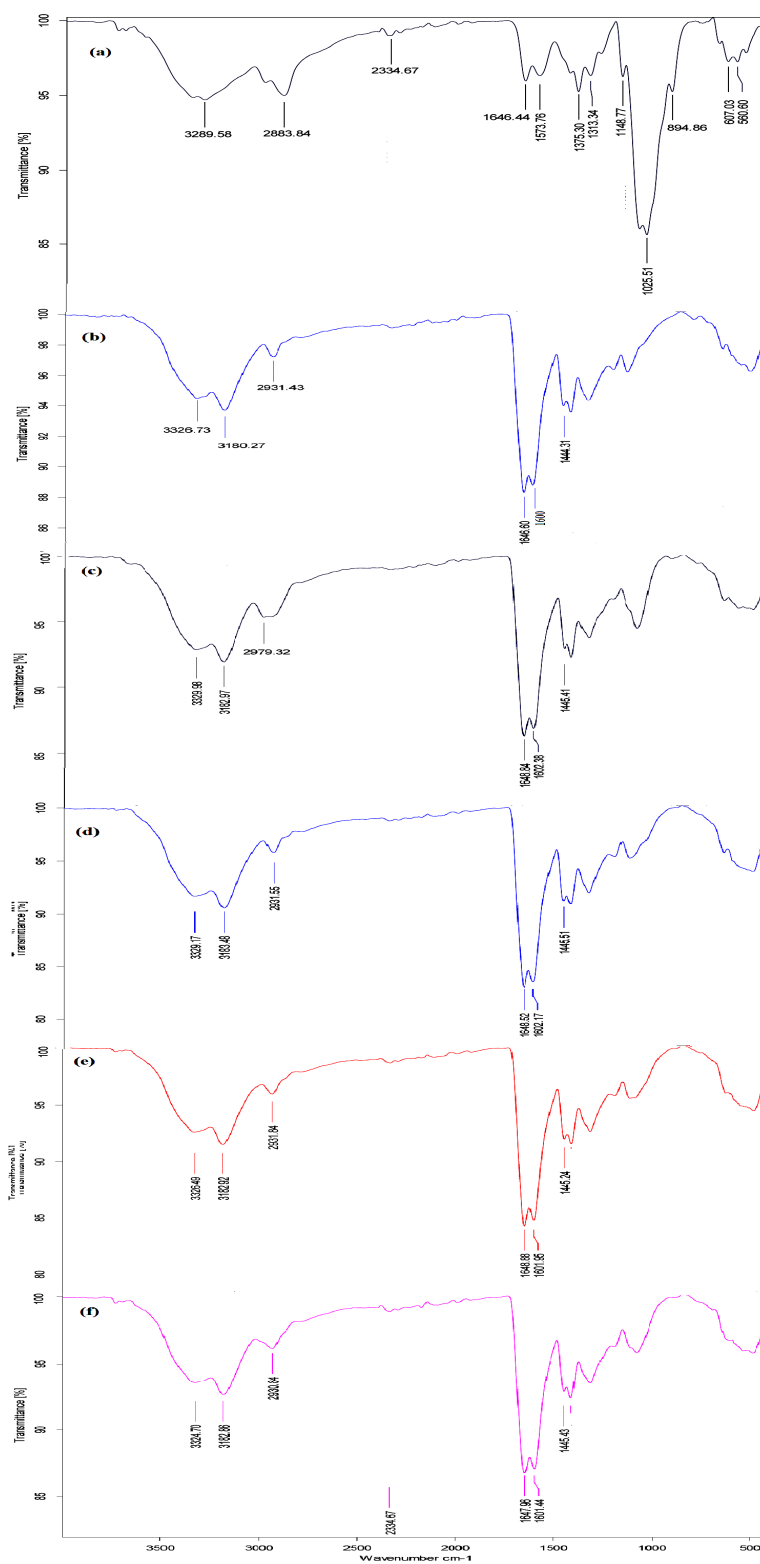


Figure 2: FTIR spectra of (a) original CS, (b) Poly(AAm), different Poly(CS/AAm) hydrogels: (c) Poly(CS/AAm) (1/5 wt%), (d) Poly(CS/AAm) (1/10 wt%), (e) Poly(CS/AAm) (1/15 wt%), and (f) Poly(CS/AAm) prepared at 20 kGy

The band located at 1444 cm^{-1} , corresponding to the bending vibration of C-H groups, was shifted to 1441 cm^{-1} . The intensities of the characteristic peaks increased with increasing the AAm contents in the hydrogel. The presence of the above-mentioned peaks confirms the successful grafting of CS by AAm to form the Poly(CS/AAm) hydrogel with different AAm content.

Swelling behavior

Equilibrium swelling

Figure 3 shows the impact of varying AAm content on the swelling behavior of the prepared Poly(CS/AAm) hydrogels. It can be observed that swelling (%) is directly related to the changes in the AAm content: as the AAm concentration increases, the swelling (%) increases as well up to 1/15 wt% in the Poly(CS/AAm), beyond which it decreases (1/20 wt%). Considering the hydrophilic nature of AAm, the rising content of AAm up to the ratio of 1/15 wt% in the Poly(CS/AAm) led to an increase in crosslinking between the hydrogel chains. Beyond this value (at 1/20 wt%), the intense crosslinking led to the formation of a more dense and tight structure, and as a consequence, the pore size was minimized, restricting the free spaces available for water retention, which directly affected the osmotic force needed for directing water into the Poly(CS/AAm) hydrogel network.^{31-33,35}

Swelling at different pH values

The radiation graft copolymerization of AAm onto CS resulted in the formation of a polymeric hydrogel network with amide groups (CONH_2) and amine groups of CS. From Figure 4, it is noted that the swelling percentage enhanced significantly at pH 2, but decreased at higher pH values – from pH 5 to pH 7.4. This is due to an enhancement in protonation of the amide groups of AAm and the amine groups of CS at lower pH (pH 2), leading to electrostatic repulsion, where the chains will extend out, so more free zones inside the polymer networks will be formed, thus, it can uptake and hold a large amount of water. The water molecules will be diffused in the inner structure of the hydrogel network, through the large pores, which leads to an increase in swelling %. Meanwhile, as the pH rose to 5 and 7, the degree of protonation of the amide groups of AAm and the amine groups of CS decreased, and the degree of hydrogen bond formation between the amide groups of AAm and the amine groups of CS led to a decline of the swelling behavior.³⁶ Therefore, the Poly(CS/AAm) hydrogel is considered a pH-sensitive hydrogel and the pH 2 has been selected as the optimal pH value for the maximum adsorption capacity. Moreover, it was noticed that the swelling % decreased as the AAm content in the Poly(CS/AAm) hydrogels increased, which may be caused by the crosslinked network of the formed hydrogel and by increased hydrogen bond formation within the hydrogel.

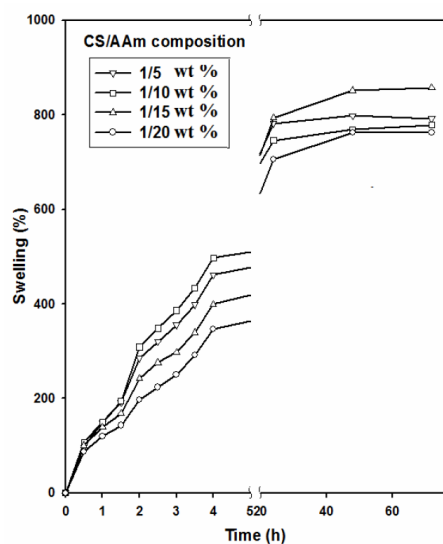


Figure 3: Effect of time (h) on swelling (%) for different Poly(CS/AAm) hydrogel compositions, prepared at the irradiation dose of 20 kGy

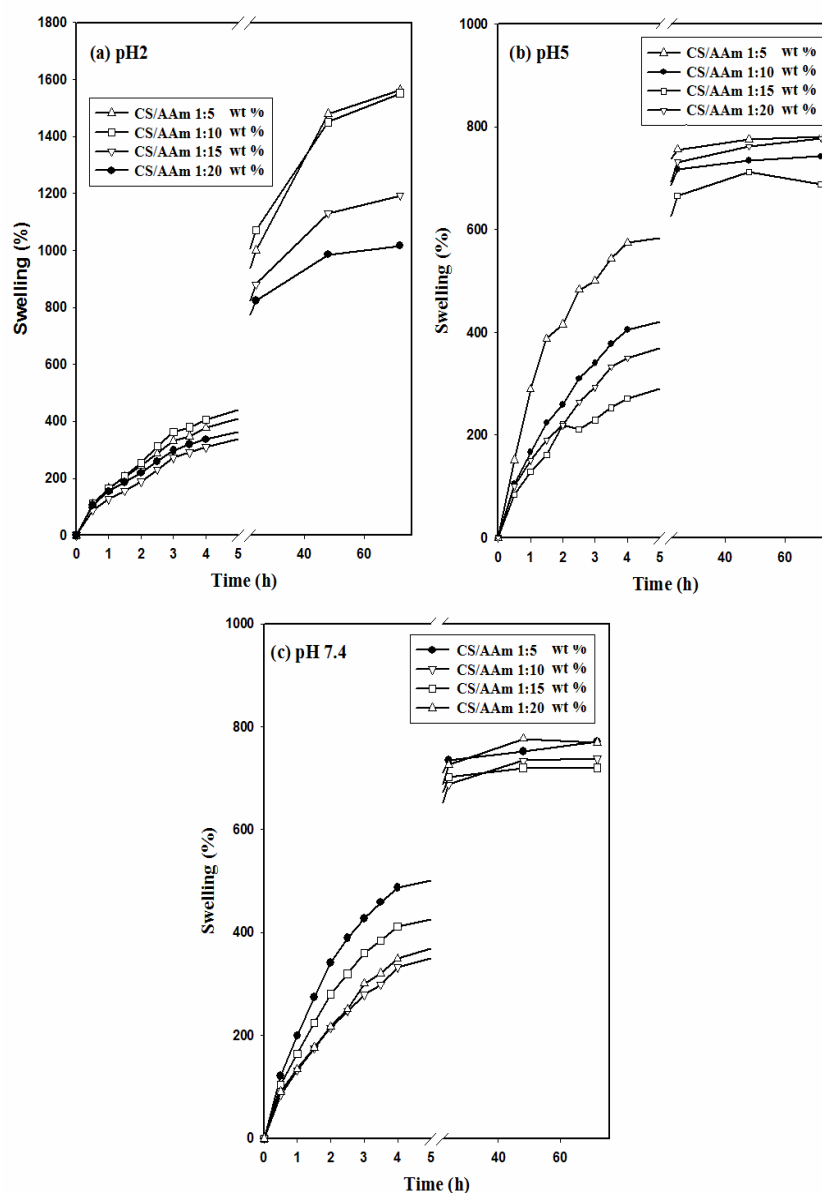


Figure 4: Effect of different pH values ((a) pH 2, (b) pH 5 and (c) pH 7) on swelling (%) for different Poly(CS/AAm) hydrogel compositions, prepared at the irradiation dose of 20 kGy

Removal of Nigrosin acid dye

From an industrial perspective, the adsorption of acid dyes is a very practical technique, due to its low cost, easy operation and efficiency. The 1/10 wt% Poly(CS/AAm) hydrogel was selected for examining its efficiency in the removal of Nigrosin acid dye from solutions, due its higher hydrophilic properties at pH 2.

Figure 5 (a and b) presents the effects of different pH values and dye concentrations on the adsorption capacity of the selected 1/10 wt% Poly(CS/AAm) hydrogel, respectively, towards

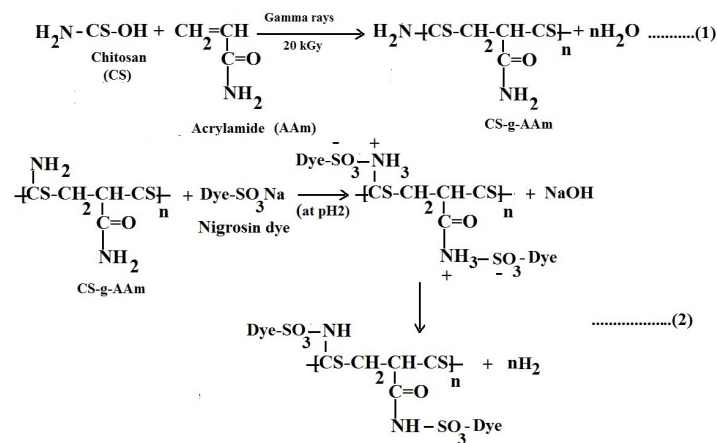
Nigrosin acid dye, which was calculated by Equation (5).^{31-33,35}

From Figure 5 (a), it is noticed that the adsorption capacity of the 1/10 wt% Poly(CS/AAm) hydrogel increases over time. In addition, its adsorption capacity is enhanced markedly at pH 2, and decreased at higher pH values from pH 5 to pH 7.4. As has been explained above, this can be due to an enhancement in protonation of the amide groups of AAm and the amine groups of CS at lower pH 2, resulting in electrostatic repulsion, which

causes the chains to extend, allowing for the formation of more available spaces inside the polymer chain network. This enables the hydrogel to uptake and hold a larger amount of water containing the acid dye. The acid dye diffused into the inner structure of the hydrogel network through the large pores, resulting in a higher adsorption capacity. However, as the pH increased, from pH 5 to 7, the degree of protonation of the amide groups of AAm and the amine groups of CS decreased and the formation of the hydrogen bonding occurred, which led to a decrease of the adsorption capacity towards the

Nigrosin acid dye. The adsorption of the Nigrosin acid dye is chemical in nature, as shown in Scheme 2.

In Figure 5 (b), it can be remarked that the adsorption capacity increased significantly with an increase in the initial concentration of the dye solution. This may be due to the propulsion force of the concentration gradient at a higher initial dye concentration. Moreover, the hydrogel network with large pores at pH 2 allows the dye molecules to diffuse into the hydrogel and react with its chains.³⁷



Scheme 2: Preparation of Poly(CS/AAm) hydrogel (1) and uptake of Nigrosin acid dye (2)

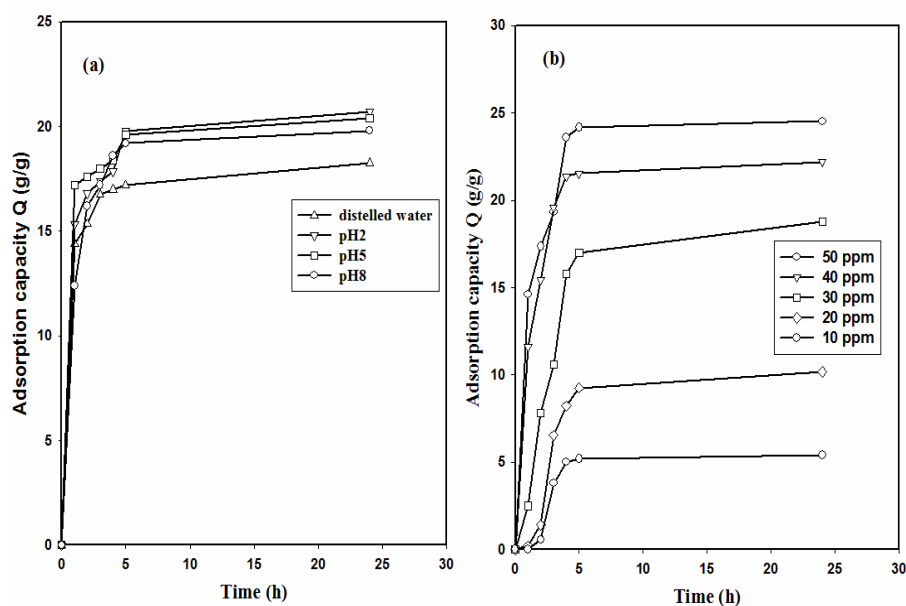


Figure 5: Effects of (a) different pH values (at an initial Nigrosin dye concentration of 50 ppm) and (b) of different initial concentrations of Nigrosin dye, on the adsorption capacity of the Poly(CS/AAm) hydrogel

Table 2
Comparison of adsorption capacities of different adsorbents towards acid dyes

Adsorbent	Adsorbate dye	Adsorption capacity (g/g)	Ref.
Rice wine lees	Acid Red 73	0.1874	[38]
Porous Fe-based composites	Acid Red 66	0.155	[39]
Laccase-modified zeolite	Acid Fuchsin	0.031	[40]
Functionalized DVB-co-GMA polymeric microspheres	Acid Green 16	0.1424	[41]
Poly(CS/AAm)	Nigrosin acid dye	25	This study

The adsorption capacity of the Poly(CS/AAm) hydrogel towards Nigrosin acid dye was compared with those of other adsorbents reported in the literature towards different acid dyes, as illustrated in Table 2. It is observed that the Poly(CS/AAm) developed in the present study has a good adsorption capacity for the uptake of Nigrosin acid dye, compared with other adsorbents.

CONCLUSION

The preparation of Poly(CS/AAm) hydrogels based on chitosan, as a cost-effective and non-toxic bio-adsorbent, was efficiently carried out using the direct gamma radiation graft copolymerization process. The FTIR analysis confirmed the successful preparation of the Poly(CS/AAm) hydrogels with different contents of AAm. The gelation % increased up to 1/10 wt% of CS/AAm, and decreased at higher concentration of AAm. The higher gelation can be probably explained by increased crosslinking among the polymer chains during the irradiation graft copolymerization up to the CS/AAm of 1/10 wt%. However, further increasing the content of AAm (1/20 wt%) restricts the grafting of AAm onto CS, increasing the formation of AAm homopolymer, which leads to a decrease in gelation (%). Also, it has been observed that the adsorption capacity of the prepared hydrogel is directly dependent on its composition, as well as on the initial dye concentration and the pH of the medium.

The findings have revealed that the 1/10 wt% Poly(CS/AAm) hydrogel has good hydrophilic properties and high adsorption capacity to remove Nigrosin acid dye from aqueous medium. This hydrogel formulation can be considered pH-sensitive, pH 2 being the optimal value for its maximum adsorption capacity. The outstanding adsorption properties of the selected Poly(CS/AAm) hydrogel recommend it as a

necessary bioadsorbent for the bioremediation of acid dye polluted wastewaters.

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