Simultaneous Grafting of Poly(Acrylic Acid) and Poly(Ethylene Glycol) onto Chitosan using Gamma Radiation: Polymer Networks for Removal of Textile Dyes

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ABSTRACT

Chitosan is a bio-based polyelectrolyte with high potential for wastewater treatment. Chitosan can remove anionic dyes by adsorption but it has low performance in the removal of cationic dyes. In this work, we report the synthesis of chitosan-based graft-copolymers using gamma radiation. Acrylic acid and poly(ethylene glycol) were grafted successfully onto chitosan applying a radiation dose of 12 kGy at a dose rate of 8 kGyh^{-1}. The grafted-copolymers have improved adsorptive properties for the removal of basic dyes reaching a maximum adsorption capacity higher than 300 mgg^{-1}. The Lanmguir's isotherm model described satisfactorily the interaction between the grafted copolymers and basic dyes. Freundlich's isotherm model described the adsorption of anionic dye acid orange 52. The grafted copolymers removed successfully textile dyes from wastewater of the dyeing process. The best results were obtained in the removal of direct and basic dyes. Further, poly(ethylene glycol) grafted on the copolymer conferred better swelling behavior making easy the separation of the adsorbent after dye removal. The results showed that the adsorbent materials synthesized by radiochemical graft-copolymerization are more efficient than the beads, composite materials, and blends of chitosan.

1. Introduction

Chitosan is a cationic polyelectrolyte obtained by deacetylation of chitin. This polysaccharidecan interact with a wide variety of substances with acid or anionic character due to the presence of amino groups covalently bonded to the backbone. Although the high adsorption capacity of chitosan, several attempts try to enhance the adsorption performance of this bio-based polyelectrolyte. For example, Qiu et al. reported that is possible to increase the adsorption capacity by high-energy ball milling [1]. However, this material has a low affinity towards textile dyes with cationic character. To develop adsorbents able to remove dyes with anionic and cationic character, several transformations have been performed on chitosan.

Blending is an easy way to improve the adsorption capacity of chitosan. Kekes and co-workers improved the adsorption capacity of chitosan beads by a 50% incorporating cyclodextrin in the beads [2]. Gu et al. blended chitosan with lignosulfonate to adsorbing anionic and cationic dyes such as Congo red and Rhodamine B [3]. Zhao and co-workers blended chitosan with carboxymethyl cellulose obtaining hydrogels suitable for the adsorption of anionic and cationic dyes [4].

The formulation of chitosan-based composite materials incorporating inorganic fills is another approach to improve the adsorption performance of chitosan. Materials such as TiO_2[5], Magadiite [6], and $Fe(OH)_3$ were incorporated in chitosan matrixes to improve the adsorption capacity [7]. Further, nanomaterials are useful for preparing chitosan-based nanocomposites with improved adsorption performance. Graphene oxide is a nanomaterial with anionic character which increases the removal efficiency of cationic dyes of chitosan nanocomposites [8].

The adsorption performance of chitosan has been improved by chemical modification. Bondock and co-workers increased the adsorption performance of chitosan by 90% by chemical modification with N-allylthiourea for removal of arsenazo III dye [9]. León and co-workers introduced anionic groups in chitosan by chemical

oxidation using $KMnO_4/NaHSO_3$, $(NH_4)_2S_2O_8/NaHSO_3$, and $K_2Cr_2O_7/NaHSO_3$ to adsorb cationic dyes such as basic blue 9 [10].

Finally, graft-polymerization by radiochemical methods is a promising alternative to improve the adsorptive properties of chitosan. Graft-copolymerization allows linking specific monomers to a backbone polymer chain. This technique improves the properties of polymers and allows achieving the desired applications [11]. Da Silva and co-workers synthesized hydrogels by graft-polymerization of acrylamide onto chitosan under microwave irradiation [12]. Similarly, Yusof et al. improved the adsorption capacity of chitosan for the removal of acid red 27 grafting polyethylene imine using microwave radiation [13]. Radiation is suitable for activating polymers during graft-copolymerization since polymeric free radicals arise under irradiation and these are active in initiating polymerization [14]. Further, polymerization induced by gamma radiation does not require the use of initiators or crosslinking agents. Also, this type of radiation does not leave radioactive residues in the irradiated materials. Therefore, it meets some criteria of green chemistry [15, 16, 17].

From the above, in this research we aimed to synthesize chitosan-based polymer networks using gamma radiation to improving the adsorptive properties of chitosan for the removal of cationic dyes. Acrylic acid and poly(ethylene glycol) were grafted on chitosan simultaneously and the grafted-copolymers were tested in the adsorption of methylene blue and malachite green. These dyes have cationic character and they are widely used for dyeing processes. We analyze the effect of the ratio between acrylic acid, poly(ethyleneglycol) and chitosan on the adsorptive properties of the copolymers. Further, the adsorption of one anionic dye, methyl orange was analyzed. The experimental data were analyzed applying the Langmuir and Freundlich models. Finally, the grafted copolymers were tested for the removal of textile dyes on wastewater from the dyeing process. The grafted-copolymers were highly efficient in the removal of basic and direct dyes from wastewater. Further, they removed disperse dyes from wastewater. In summary, grafted copolymers of chitosan obtained by gamma irradiation could be applied successfully in wastewater treatment from the dyeing process.

2. Experimental Section

2.1. Materials

Chitosan, acrylic acid and poly(ethylene glycol) were purchased from Sigma Aldrich Company and. They were used as received. Chitosan has a degree of *N*-acetylation of 3.57% and a viscosity-molecular weight of 663.909

kDa. The acetylation degree was calculated by FTIR-ATR according to the procedure reported in [18]. Molecular weight was obtained by viscometry using an Ubbelohde viscometer. Samples were prepared in acetic acid 0.25 M and sodium acetate 0.25 M at 25°C. The values of K and α constant for the Mark-Houwink-Sakurada equation were taken from the reference [19].

2.1. Graft Polymerization

Grafting of acrylic acid (AA) and poly (ethylene glycol) (PEG) was realized by the simultaneous irradiation method. The appropriate amounts of chitosan, AA and PEG (see Table 1) were mixed in 10 mL of deionizing water obtaining a homogeneous solution. The solutions were bubbled with argon for 5 minutes to displace the oxygen. Choi et al. reported that the depolymerization of chitosan exposed to gamma radiation takes place at radiation doses higher than 10 kGy [20]. However, the decrease of the molecular weight of chitosan can be avoided grafting and crosslinking of the polysaccharide. From the above, we select a radiation dose of 2, 6, or 12 kGy for the irradiation experiments. Samples were irradiated with a Gamma beam 651 PT irradiator at a dose rate of 8 kGyh^{-1}.

Table 1: Composition of polymerizable formulations.

	Chitosan (g)	Acrylic acid (mL)	Poly(ethylene glycol) (mL)
Copolymer 1	0.2	1	0.5
Copolymer 2	0.2	2	1
Copolymer 3	0.2	3	1.5

After irradiation, we obtained heterogeneous mixtures containing a solid and a liquid phase. The solid phase corresponds to the grafted-copolymer and the liquid phase corresponds to water and unreacted materials. The liquid phase was decanted and the graft polymer was treated with 50 mL water, ethanol, acetone, and chloroform (30 min with each solvent). The copolymers were dried at 70 °C and the grafted percentage was calculated with Equation 1.

$$\text{Grafted percentaje} = \frac{\text{w}_{\text{copolymer}} - \text{w}_{\text{chitosan}}}{\text{w}_{\text{(AA+PEG)}}} \times 100 \qquad (1)$$

Where $\text{w}_{\text{copolymer}}$ is the final weight of the grafted-copolymer, $\text{w}_{\text{chitosan}}$ is the weight of chitosan, and $\text{w}_{\text{(AA+PEG)}}$ is the sum of acrylic acid and PEG weights.

FTIR spectra were recorded with a Perkin-Elmer Spectrum Two with an Attenuated Totally Reflectance (ATR) accessory. The point of zero-charge (pH_{pzc}) was determinate following the procedure reported by Faria et al. [21]. To determinate the swelling behavior of copolymers,

0.1 g of the copolymer was placed in contact with 5 mL of water in a glass vial. The copolymers remained in contact with water for 24 h at 30°C. After that, the copolymers were extracted and the excess of solvent was dried with absorbent paper and the weight of the swelled copolymer was registered. The swelling percentage was calculated with Equation 2:

$$\text{Swelling percentage} = \frac{w_i - w_0}{w_0} \times 100 \qquad (2)$$

Table 2: Selected dyes and their characteristics.

Where w_i is the final weight of the grafted-copolymer, and w_0 is the weight of the dried copolymer.

2.2. Adsorption of Textile Dyes

Table 2 shows the selected dye for the adsorption studies and their characteristics. The quantification of adsorbed dyes was realized by UV-V is spectrophotometry with a Perkin-Elmer Lambda 35 spectrophotometer. Calibration curves were constructed using the maximum absorbance wavelength as the wavelength detection.

Dye (Colour index)	Key	Character	Molecular weight (g mol^{-1})	λ_{max} (nm)	Calibration curve	R^2
Methylene blue (Basic blue 9)	BB9	Cationic	319.85	664	$C = \dfrac{0.1578}{A}$	0.9959
Malachite green (Basic green 4)	BG4	Cationic	364.91	617	$C = \dfrac{0.0926}{A}$	0.9907
Methyl orange (Acid orange 52)	AO52	Anionic	327.33	473	$C = \dfrac{0.0536}{A}$	0.9990

The interaction between the grafted-copolymer and textile dyes was studied by batch adsorption experiments. The adsorption was performed at 303K using an adsorbent dose of 5 g dm^{-3}. Kinetic studies were realized to stablish the adsorption equilibrium and the experimental data were analyzed applying the pseudo-first order and pseudo-second order models. We constructed adsorption isotherms using aqueous solutions containing BB9 and BV10 dyes with an initial concentration ranging between 300 and 1500 mg g^{-1}. The experimental data were interpreted applying the equations of Langmuir and Freundlich isotherm models. The adsorption of textile dyes from wastewater was performed using the conditions described above. The removal percentage was calculated with the Equation 3:

$$\text{Removal \%} = \left(1 - \frac{A_T}{A_{ww}}\right) \times 100 \qquad (3)$$

where A_{ww} is the absorbance of the wastewater and A_T is the absorbance of the wastewater after the treatment of adsorption.

3. Results and Discussion

3.1. Characterization of Grafted-Copolymers

Graft-polymerization was carried out in aqueous solution using gamma radiation as an energy source for the initiation of the polymerization reaction. It is well known, that chitosan is insoluble in water, but it is soluble in aqueous solutions of acetic acid. Acrylic acid and acetic acid have similar values of pK$_a$ (4.2 and 4.75 respectively). Thus, acrylic acid helps to dissolve chitosan in water by protonation of amino groups and it can replace the acetic acid while acts as a monomer. Further, the polymerization reaction was carried out without free-radical initiator and crosslinking agent because the reaction was activated with gamma radiation. This way, we reduced the number of chemicals in the polymerizable mixture. Poly(acrylic acid) and poly(ethylene glycol) were successfully grafted onto chitosan using gamma radiation asthe energy source. Figure 2 shows the graft-percentage of chitosan-based copolymers as function of the radiation dose. The grafted-percentage obtained for the first polymerizable formulation is unaffected by the radiation dose. The graft percentage is almost the same for the copolymers obtained at 2, 6, and 12 kGy. However, the graft-percentage of copolymer 2 increased significantly as the radiation dose increased. For the copolymer 3, the grafted-percentage does not increase noticeably with a radiation dose higher than 6 kGy. Figure 5 shows the swelling percentage of the copolymers after being in contact with water for 24 h. Copolymer C3 has the highest swelling percentage because it contains a higher amount of hydrophilic segments.
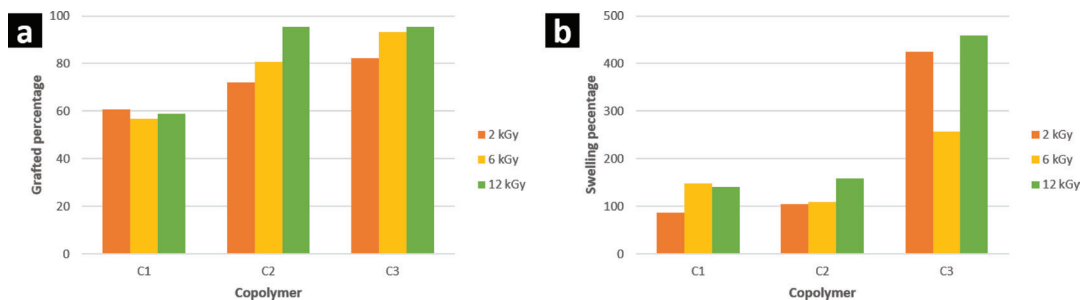
Figure 1: a) Graft-percentage, and b) swelling percentage of copolymers as a function of the radiation dose.

The grafting of acrylic acid and PEG onto chitosan was confirmed by FTIR spectroscopy. Figure 2 shows the FTIR spectra of chitosan, acrylic acid, PEG and the copolymer C1. The spectra of copolymers C2 and C3 are very similar to the spectrum of C1 and they are not shown. The spectrum of the copolymer shows some characteristic absorption bands from chitosan, acrylic acid, and PEG. They give evidence of the obtaining of the expected copolymer. The bands that come from chitosan are the bands at 3397 and 1557 cm^{-1} due to ν_{asym} NH$_2$ and δN-H vibration of the amino group. The spectrum of the copolymer shows a band at 1706 cm^{-1} due to νC=O vibration of the carboxylic acid group. Further, the bands at 3174, 1243, 1163 616, 514 cm^{-1} are related to the carboxylic acid group. They were attributed to νO-H, δO-H, νC-O, δCO, and rocking vibration respectively. The bands that come from PEG in the FTIR spectrum of the copolymer were observed at 1451 and 1350 cm^{-1}, and they were attributed to δCH$_2$ and the deformation in of the plane of O-H vibration of PEG. Further, the bands at 945 and 886 cm^{-1} were assigned to the CH$_2$ twisting vibrations from the PEG backbone. Finally, the spectrum of the copolymer shows a band at 1080 cm^{-1} attributed to ν_{asym} C-O-C of ether group. This band appears in the spectra of chitosan and PEG at 1065 and 1098 cm^{-1} respectively. Thus, the band observed in the spectrum of the copolymer has the contribution of the ether groups from chitosan and PEG.
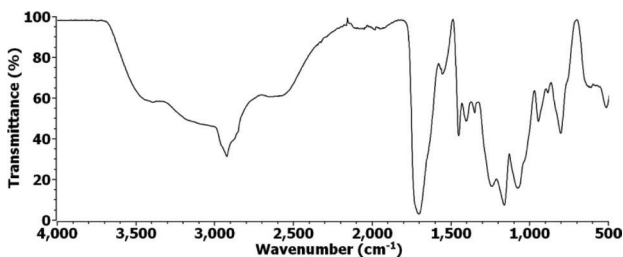

Figure 2: FTIR spectra of the grafted-copolymer C1.

The pH$_{pzc}$ of copolymers C1, C2, and C3 is 3.09, 3.39 and 3.18 respectively. The surface of the copolymers has acid character due to the high percentage of acrylic acid grafted in the copolymer. Thus, the three copolymers are suitable for the adsorption of basic dyes with cationic character.

3.2. Dye Absorption

3.2.1. Kinetic Study of the Adsorption

Figure 3 shows the concentration profiles of BB9 for the adsorption of this dye on the copolymers C1-C3. They show that the concentration of BB9 in the solution decreased rapidly during the first 120 min (2 h) of contact. Then, the concentration of BB9 decreased slowly until reaching the equilibrium at 1440 min (24 h) of contact. After that, the amount of adsorbed dye did not change significantly. From the above, we established 24 h as the optimal contact time for the adsorption of textile dyes. The experimental data fit the pseudo-second-order kinetic model and thus the diffusion controls the adsorption process. Table 3 shows the values of k$_2$ calculated from the experimental data and the amount of adsorbed dye at the equilibrium. According to the values of k$_2$, the adsorption velocity of BB9 on the copolymers decreases in the order C1>C3>C2. However, at the end of the adsorption, the amount of adsorbed dye at the equilibrium (a$_e$) is almost the same for the three copolymers.
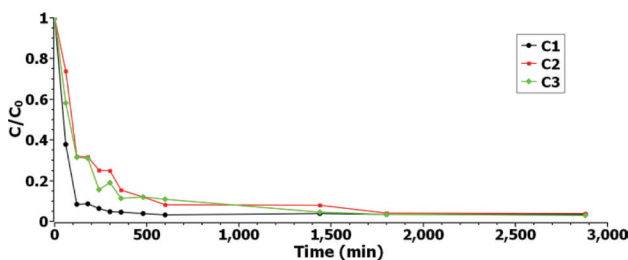

Figure 3: Concentration profiles for the adsorption of BB9.

Table 3: Kinetic parameters of the adsorption of BB9.

Adsorbent	Dye	k$_2$ (g mg^{-1} min^{-1})	a$_e$ (mg g^{-1})	R^2
C1	BB9	5.7263	58.21	0.9999
C2	BB9	0.0139	55.64	0.9986
C3	BB9	0.0173	57.79	0.9998

3.2.2. Adsorption Isotherms

The adsorption capacity of the grafted-copolymers was analyzed by the construction of adsorption isotherms. Figure 5 shows the adsorption isotherms of BB9, BG4, and AO52. The points represent the experimental data and the continuous lines represent the theoretical behavior according to the equations of Langmuir or Freundlich. The experimental data of the adsorption of cationic BB9 and BG4 dyes fit the Langmuir's model. The maximum

adsorption capacity (a_m) shows that the BG4 dye was adsorbed in a higher amount than BB9. The adsorption capacity of the copolymers is higher than 200 mg g^{-1} and after adding NaOH increased up to 312.5 mg g^{-1}. The adsorption capacity of the copolymers increases significantly in the presence of NaOH because carboxylate groups dissociate fully while carboxylic acid groups dissociate partially. Previously, Herrera-González et al. reported the increase of the adsorption capacity of basic dyes of chitosan-based polyelectrolytes in the presence of NaOH [22].
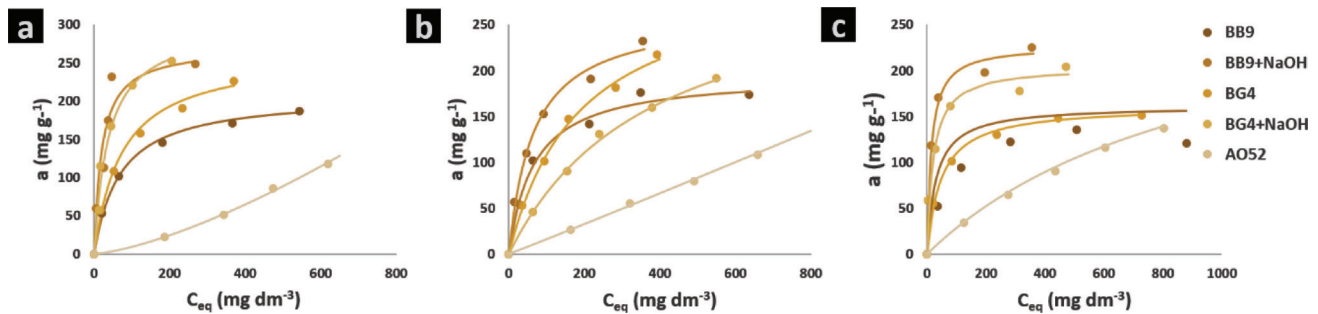

Figure 4: Adsorption isotherms of BB9, BG4, and AO52 onto grafted copolymers a) C1, b) C2, and c) C3.

Table 4: Langmuir's parameters for the adsorption of basic dyes.

Adsorbent	Dye	a_m (mg g^{-1})		K_L (dm^3 mg^{-1})		R^2		R_L	
C1	BB9	208.3	270.3*	0.0146	0.0500*	0.9984	0.9908*	0.0437	0.0132*
C1	BG4	263.2	303.0*	0.0138	0.0267*	0.9924	0.9902*	0.0461	0.0244*
C2	BB9	196.1	263.2*	0.0150	0.0154*	0.9947	0.9907*	0.0426	0.0414*
C2	BG4	312.5	322.6*	0.0053	0.0026*	0.9903	0.9925*	0.1113	0.2028*
C3	BB9	129.9	227.3*	0.0331	0.0696*	0.9902	0.9960*	0.0197	0.0095*
C3	BG4	161.3	204.1*	0.0214	0.0485*	0.9995	0.9925*	0.0302	0.0136*

*pH was modified adding 0.1 cm^3 of 0.1 M NaOH.

The Langmuir's model did not describe satisfactorily the adsorption of the anionic dye AO52. However, Freundlich's model described successfully adsorption behavior. This implies multilayer adsorption on a heterogeneous surface. The adsorption of AO52 is less favored than the adsorption of cationic dyes due to the electrostatic repulsion between the surface of the copolymers and the dye. Thus, the adsorption equilibrium of AO52 was reached at a higher concentration. Table 5 shows the Freundich's parameters obtained from the experimental data.

Table 5: Freundlich's parameters for the adsorption of AO52.

Adsorbent	Dye	K_F (mg g^{-1})	n	R^2
C1	AO52	0.0139	0.7094	0.9981
C2	AO52	0.1446	0.9779	0.9974
C3	AO52	0.9580	1.3405	0.9903

Table 6 shows the adsorption capacity for BB9 and BG4 dyes of some chitosan-based materials reported in the literature. The table shows that grafted-copolymers of chitosan has a better performance than some polymeric beads and composite materials for the removal of basic dyes.

Table 6: Adsorptive properties of chitosan-based materials for the removal of textile dyes.

Adsorbent	Dye	a_m (mg g^{-1})	Reference
Chitosan/coir pith activated carbon/dodecyl sulfate	Basic green 4	4.40	[23]
Chitosan/1-butyl-3-methylimidazolium beads	Basic green 4	8.07	[24]
Chitosan/zeoliticimidazolate composite	Basic green 4	62.11	[25]

Chitosan/magadiite composite	Basic blue 9	40.01	[6]
Chitosan/cellulose acetate/SWCNT/Fe_3O_4/ TiO_2 fibers	Basic blue 9	97.60	[26]
Magnetic chitosan-g-poly(methacrylic acid) microspheres	Basic blue 9	211.22	[27]

3.2.3. Removal of Textile Dyes in Wastewater

Figure 5a shows the removal percentages of textiles dyes in aqueous solutions using the grafted-copolymers C1-C3. The copolymers show adsorption percentages close to 100% for BB9 and BG4 dyes due to the high affinity of grafted-copolymers towards basic dyes. The best results

were obtained with copolymer C1 because the ratio of acid groups in the copolymer is higher for C1 than C2 and C3. Wastewaters obtained from the dyeing process containing disperse, basic or direct dyes were treated by adsorption using the copolymers C1-C3. Figure 5b shows the removal percentage of textile dyes from wastewaters. The best results were obtained for wastewaters containing basic dyes. As we mentioned before, basic dyes have cationic character and thus they are efficiently removed from wastewater due to the electrostatic attraction between the grafted polymers and dyes. Disperse dyes have neutral character and direct dyes have anionic character. Thus, the affinity between the grafted copolymers and this kind of dyes is lower as the removal percentage. For the wastewater containing basic violet dye the grafted copolymer removed up to 98% of dyes from the effluent.
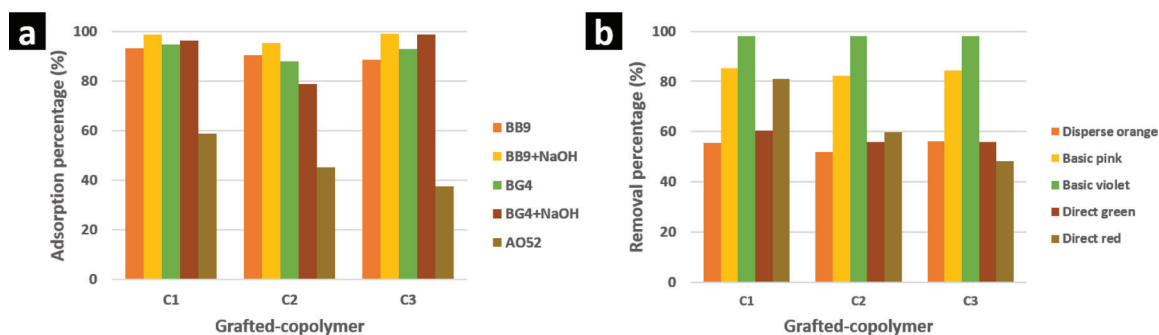

Figure 5 a) Adsorption percentage of textile dyes in aqueous solutions, and b) removal percentage of textile dyes from wastewater.

Conclusions

Poly(acrylic acid) and poly(ethylene glycol) were successfully grafted onto chitosan using gamma radiation. A radiation dose of 12 kGy is enough to obtain a graft-percentage close to 100%. Further, the grafting and crosslinking of chitosan with acrylic acid and poly(ethylene glycol) avoid the effect of depolymerization caused by the gamma radiation forming polymer networks with hydrogel properties. The graft-copolymerization improved the adsorption capacity of chitosan towards cationic dyes such as methylene blue and malachite green in aqueous solutions and wastewater from the dyeing process. Also, the grafted-copolymers adsorb direct and disperse dyes from wastewaters. The high adsorption capacity of the copolymers and their swelling behavior shows that these materials could be useful as adsorbent hydrogels for the removal of textile dyes. Hydrogels are better materials for wastewater treatment than others such as ultra filtration membranes because they can be employed easier. Finally, it is important to notice that graft-copolymerization induced by gamma radiation yields better chitosan-based adsorbent materials than others obtained by blending, chemical modification of chitosan.

Acknowledgments

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