



Heavy Metal Removal By Chitosan And Chitosan Composites

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SUMMERY

Radiation grafting of diethyl aminoethyl methacrylate (DEAEMA) on chitosan to impart ion exchange properties and to be used for the sorption of metal ions from waste water, was carried out. The effect of experimental conditions such as monomer concentration and the radiation dose on grafting were studied. On using chitosan, grafted chitosan and some chitosan composites in removing some metal cations, they show high up-take capacity for Cu^{2+} and lower uptake capacities for the other divalent metal cations used (Zn^{2+} and Co^{2+}). Competitive study, performed with solutions containing mixture of metal salts, showed high selectivity for Cu^{2+} than the other metal cations. Grafting of DEAEMA onto the chitosan backbone improves the sorption performance.

1-INTRODUCTION

Chitin is the second most important natural polysaccharide after cellulose⁽¹⁾. Chitin is poly [β -(1 \rightarrow 4)-2-acetamido-deoxy-2-D-glucopyranose]. The principal derivative of chitin is chitosan, produced by alkaline deacetylation of chitin. Chitosan is poly [2-amino-2-deoxy-(1-4)- β -D-glucopyranose] and also occurs naturally in some fungi but its occurrence is much less widespread than is that of chitin⁽²⁾.

Chitosan is a well known absorber of metal ions in dilute effluents^(3,4). The metal ion sorption occurs by a precipitation mechanism or deposition of metal aggregate, by complexation or by simple sorption^(1,3,5,6). The data presented by Yoshinari & Subramanion⁽⁴⁾ confirm that all these processes are important in varying degree for each individual metal ion.

The data published support the concept that chitosan-metal ion complex formation occurs primarily through the amine group functioning as ligands, so that the extend of deacetylation of the chitosan is a critical factor in controlling the level of metal ion uptake, i.e., adsorption capacity for metal ions depends strongly on the concentration of accessible amine groups^(7,8,9).

The nature of the anions present in the solution carrying metal cations to be collected on chitosan is very important; chloride can depress the collection extent, while sulphate can enhance it, as chitosan forms an insoluble sulphate.

The present work deals with the preparation of grafted chitosan, chitosan composite and $\text{SiO}_2/\text{TiO}_2$ chitosan supported composites, and their characterization to be used for sorption of metal cations. The direct radiation grafting technique was used. The major advantages of the radiation grafting are: (a) the reaction is carried out at lower temperature than in chemical operation, (b) grafting is carried out from gaseous vapour- and liquid phases of the monomer, and (c) the modified material is



free from residuals of initiator or catalyst. The study is extended to define the selectivity of the prepared samples for sorption of metal ions when two or more ions are present together in the solution under examination. Titanium dioxide and synthetic silicon dioxide (pyrogenic silica) have been attracted considerable attention as an ion exchanger owing to their high sorption selectivity for certain metal ions. Many reports have described their basic characteristics and sorption properties of these materials; also the sorption behaviour of TiO₂-polyacrylonitrile composite for removal of some hazardous radionuclides has been studied and it shows high sorption affinity for ions^(10, 11).

2- EXPERIMENTAL

2.1. Materials:

Chitosan (high molecular weight) was supplied by Fluka Chemie GmbH, Sigma-Aldrich Chemie GmbH, Switzerland. Diethylaminoethyl methacrylate (DEAEMA) was supplied by Fluka Chemie GmbH, Switzerland. Cupric sulfate was supplied by s.d.fine-chem. Ltd, India. Cobalt sulfate was supplied by Sisco Research Lab. PVT. Ltd, India. Zin sulfate heptahydrate was supplied by Merk, Germany. Other reagents were of laboratory grade chemicals.

2.2. Grafting Process:

The direct radiation grafting method was used as a technique in which glass ampoules -containing a mixture of chitosan and the calculated amount of water and DEAEMA monomer- were subjected to Co-60 gamma rays at National Center for Radiation Research and Technology, Cairo^(12, 13).

2.3. Preparation of Chitosan-Poly (DEAEMA)/SiO₂/TiO₂ Composites (C-CH-Si/Ti):

Not all physical mixture of polymer and oxides will form a desired composite; the compatibility between the two phases is important. Hence, chitosan was first swollen in the monomer/water mixture, SiO₂ or TiO₂ was then added, well mixed and subjected to react under radiation.

When DEAEMA monomer is polymerized in the presence of chitosan and oxides (SiO₂ or TiO₂) using gamma radiation as initiator, different products may be formed, such as, unimpaird chitosan or DEAEMA grafted chitosan, homopolymer, unreacted monomer and silicon or titanium oxide. When present all together, these products will be referred to as composite.

2.4. Crosslinking of Chitosan Composites:

At the end of polymerization, crosslinked chitosan composites were prepared by adding 0.4 ml of glutaraldehyde/1g chitosan composite. The reaction mixture was stirred for 4 hours at 50°C. At the end of crosslinking, the resulting samples were filtered and washed thoroughly with distilled water. Finally the crosslinked samples were washed with acetone and dried at for 50°C 24 hours.



2.5. Analysis:

Graft yield (GY %) was determined from the gain in weight of chitosan due to graft polymerization after removing ungrafted polymer by extraction with the proper solvent (DMF). Total conversion (TC %) was obtained via quantitative estimation.

Graft yield (%GY) = dry wt of grafted sample – dry wt of chitosan used X 100 / dry wt of chitosan used.

Total conversion (%TC) = wt of grafted polymer + wt of homopolymer X 100 / wt of monomer used.

Percent of homopolymer (%HP) = dry wt of homopolymer X 100 / wt of monomer used.

Nitrogen content was estimated by kjeldahl method⁽¹⁴⁾.

Chitosan based samples were examined by the electron microscope, as it is a powerful technique to study structures.

2.6. Removal of Heavy Metal Cations:

For a given material, the maximum amount of cations that can be taken up is constant and is known as the cation-exhaustion capacity. It is measured in mill-equivalents per gram sample (meq/g sample) or measured in mg/g sample. Cation-exhaustion capacity measurements are performed at a neutral pH 7.

0.5 gram of the prepared chitosan products was added to 50 ml solution containing either Cu²⁺ or Co²⁺ or Zn²⁺ ions at a concentration of 0.1 M/l. After 24 hours, the solutions were filtered and the concentration of residual metal ions in the filtrate was measured using Atomic Absorption Spectrophotometry (Perkin Elmer 1100 B, Germany), Unit of Analysis and Central Scientific Services, National Research Centre.

$$\text{Exhaustion capacity} = x_0 - x \times v / w \quad \text{mg/1 g sample}$$

Where x_0 and x are the concentration (mg/l) of the cations before and after treatment with samples under investigation, v is the volume used in liter and w is the weight of the tested sample in grams.

3- RESULTS AND DISCUSSION

3.1. Tentative Mechanism:

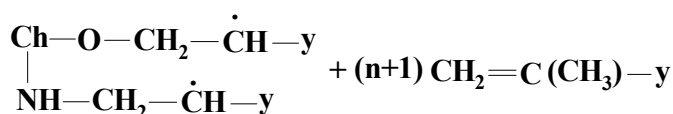
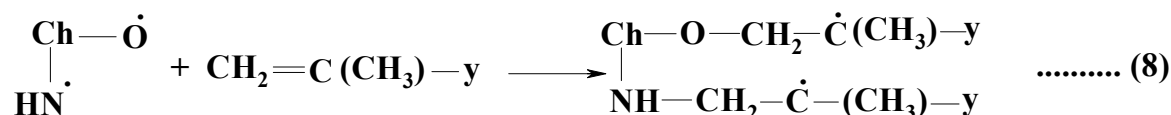
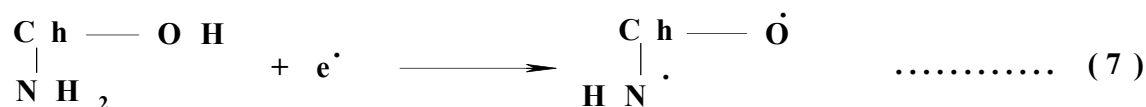
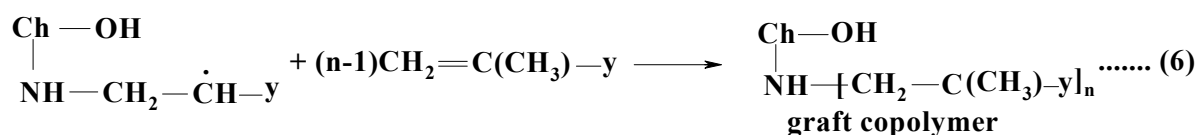
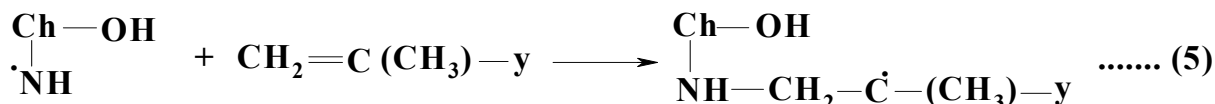
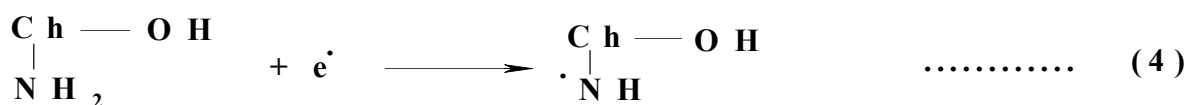
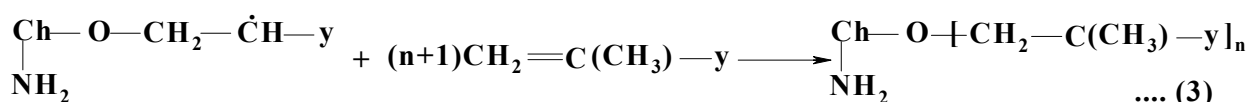
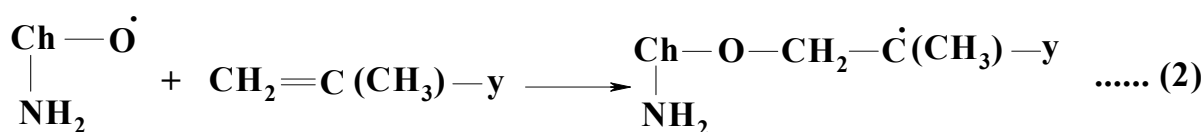
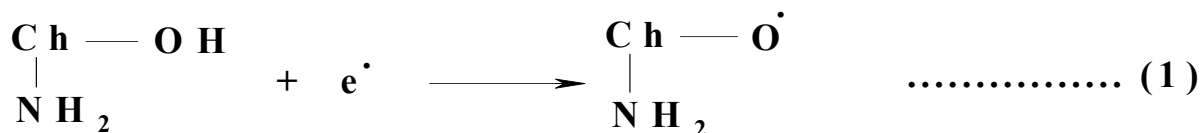
The most probable mechanism involving the following steps⁽¹⁵⁾:

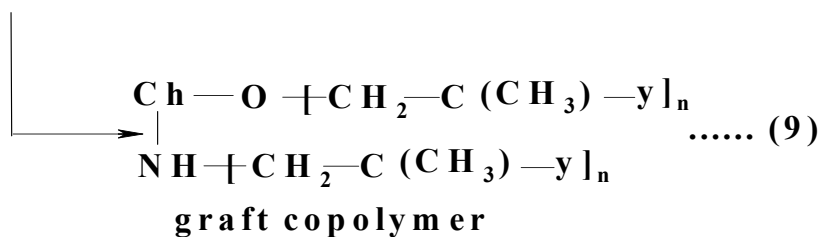
Abstraction of hydrogen atoms from chitosan (amino or hydroxyl groups) by radiation leads to formation of chitosan macroradical, as shown in the reaction suggested by equations 1,4,7. The presence of a vinyl monomer (DEAEMA), grafting occurs via addition of the chitosan macroradical to the double bond of the monomer (equations 2,5,8), followed by subsequent addition of monomer molecules, (equations 3,6,9).



The products can be obtained from the previous method are:

- chitosan-graft-poly (DEAEMA): g-CH
- chitosan-poly (DEAEMA) composite: C-CH consist of: unreacted chitosan, grafted chitosan, DEAEMA homopolymer and unreacted monomer.





where $y = -\text{COO}(\text{CH}_2)_2\text{N}(\text{C}_2\text{H}_5)_2$ in DEAEMA

3.2. Gamma Radiation-Induced Grafting of DEAEMA onto Chitosan:

3.2.1. DEAEMA Concentration:

Figure 1 shows the effect of DEAEMA concentration on %GY, %HP and %TC when the polymerization was carried out using the irradiation technique.

It can be depicted from the data (Fig 1) that increasing DEAEMA concentration is accompanied by a significant increase in the graft yield. The enhancement in the grafting reaction could be associated with increasing the availability of DEAEMA in the vicinity of chitosan active sites.

3.2.2. Irradiation Dose:

Figure 2 shows the effect of irradiation dose on the %GY, %HP and %TC. Increasing the irradiation dose to 2.5 kGY brought about a significant enhancement in %GY, %HP and %TC. Results show that %GY exhibit higher values than %HP, regardless of the irradiation dose used. While the increase of the irradiation dose improves the graft yield, it had a very marginal effect on the %GY and %TC. This indicates that the irradiation system under investigation is suitable for grafting of DEAEMA onto chitosan.

3.3. Removal of Metal Cations:

3.3.1. Removal Capacity:

It is obvious that the metal cations uptake was measured as a function of metal concentration in the solution. The results show that metal cations uptake not only depends on the nature of the sample prepared material used, but also on the metal cation type.

Table 1 shows the efficiency of the different prepared chitosan based samples on the removal of Cu^{2+} , Co^{2+} and Zn^{2+} cations. The behaviour is not the same for all samples, as they indicate that the uptake capacities for Co^{2+} and Zn^{2+} are lower than that for Cu^{2+} . The order of the ion uptake by the samples under investigation is: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$.

Results in Table 1 show that the removal capacity of metal ions depends strongly on the nature of the prepared samples. We can conclude that the order of the removal capacity of metal ions is:



g.CH (low GY)>CH>g.CH(high GY)>C.CH>C.CH-Si/Ti

The greater effectiveness of g.CH (low GY) and CH for metal removal may be due in part to the greater basicity of the aliphatic-primary and/ or tertiary amino groups and due to the appearance of new absorbing functions⁽¹⁶⁾. The nitrogen electrons present in the amine and substituted amino groups can establish bonds with metal ions, especially in case of g.CH(low GY) and CH, where free amino groups are particularly abundant.

The decrease in the adsorption capacity of g.CH with high GY% and C.CH for metal ions (Cu^{2+} , Zn^{2+} , Co^{2+}) may be ascribed to: (a) the increased swellability of adsorbents which inhibits the diffusion of Cu^{2+} , Zn^{2+} and Co^{2+} ions from the aqueous phase onto the active sites of the adsorbents, and (b) competition between protons and Cu^{2+} , Zn^{2+} , Co^{2+} cations.

From the above results given in Table 1, it is clear that the presence of silicon or titanium oxide in the composite decreases significantly the magnitude of adsorption capacity. However, adsorption capacity relatively increases as the oxide content increases up to 50% (ows), but an obvious decrease of the adsorption capacity was recorded at 100% (ows) oxide content. Generally, it can be suggested that limited addition of SiO_2 or TiO_2 upto 50% (ows) will permit reasonable ion up-take capacity through porous composite system, while using 100% (ows) oxide content will reduce metal ion uptake due to restriction of the swelling and blocking of the composite pores which make the penetration of ions into the polymeric chains rather difficult as well as the low quantity of the solution absorbed by the composite.

Previous studies⁽¹⁷⁾ show that the use of organic crosslinker plays an important role in determining the property of the preparation of metal removal polymers. The results in Table (1) show that the ion uptake capacity decreases with the use of crosslinker. The decrease in the capacity can be attributed to the increase in the degree of crosslinking between the polymeric chains. This leads to a decrease in the number of free amine groups and thus a decrease in the interaction with metal ions consequently, the ion uptake capacity decreases.

3.3.2. Removal Selectivity:

Recently, there has been growing interest in the selective chelating ion exchangers⁽¹⁸⁾. This interest originates from their possible application in industry and in solving problems in environmental chemistry. Most of the commercial resins tested in waste-water treatment show high ion uptake capacity, but quite poor selectivity for different metal ions.

From results in Table 2, it is clear that adsorption selectivity depends on the prepared sample nature and also on the type of metal cations mixed in the solution. From the results we can conclude that the sequence of adsorption selectivity is the same like that of ion uptake capacity (3.3.1).

Generally, the data in Table 2 show high selectivity for copper ions than the other metal cations (Zn^{2+} & Co^{2+}) regardless of the time of treatment.

As a result of the obtained data the presence of more than two metal ions (Cu^{2+} , Co^{2+} , Zn^{2+}) in the solution under examination, with a quantity of the prepared samples based on chitosan insufficient for the complete collection of metal ions present, the Cu^{2+} cations which forms the most stable complex with the sample under



investigation will be collected leaving most of the other cations (Co^{2+} , Zn^{2+}) in solution, i.e. copper depresses most appreciably the collection of cobalt and zinc.

3.4. Visual Evaluation (Scanning Electron Microscopy):

Visual evaluation of the chitosan-based derivatives was performed by scanning electron micrography to show the change in morphological feature of the different prepared samples. The micrographs of the surface view of the samples were shown in Figures 3 and 4.

Fig 3a shows the morphology of ungrafted chitosan, it can be seen that the surface is very smooth and very clear.

The surface morphology of grafted chitosan (g-CH) given in Fig 3b, c shows that the surface of the samples was coated with the graft polymer.

From the micrograph of C-CH-SiO₂/TiO₂ (fig 3d), it is clear that SiO₂ or TiO₂ is not trapped inside or linked with the constituents of the polymer composite.

It is easy to observe discreet phases of these composites when immersed in water, the two components were separated, this behaviour confirms the previous observation.

Figs. 3, 4 show that the surface of samples under investigation before metal ion uptake is smooth and a homogeneous colour is characteristic for each sample; but the surface after metal ion uptake became tough and the colour of the samples is not homogenous as there are small white spots on the surface.

CONCLUSIONS

- DEAEMA has been grafted onto chitosan using gamma radiation, grafting percentage up to 80% have been reached.
- Chitosan and grafted chitosan was found to be able to form complexes with various divalent cations and the extent of metal ions uptake was found to follow the following order: $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$.
- To certain extent grafting of DEAEMA polymer (containing specific functional groups) onto the chitosan backbone improves the sorption performance due to the appearance of new absorbing functions.
- SiO₂ and TiO₂ could be supported on chitosan-poly (DEAEMA) upto 50% (ows) increase their adsorption capacity and adsorption selectivity.



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Table 1: Adsorption of metal cations from its solution by the prepared chitosan derivatives.

Substrate	Index	Adsorption capacity(mg/1g sample)		
		Cu ²⁺	Zn ²⁺	Co ²⁺
chitosan	CH	167	162	160
chitosan-g-poly(DEAEMA)*45%GY	g.CH*(45%GY)	252	180	180
chitosan-g-poly(DEAEMA)*79%GY	g.CH*(79%GY)	159	139	120
chitosan-poly(DEAEMA) composite*	C-CH*	99.9	97	95
chitosan-poly(DEAEMA) composite	C-CH	85.7	85	85
chitosan-poly(DEAEMA) composite +25% SiO ₂ (ows)	C-CH/25%SiO ₂	77	71.3	71.1
chitosan-poly(DEAEMA) composite +50% SiO ₂ (ows)	C-CH/50%SiO ₂	84	81.8	80
chitosan-poly(DEAEMA) composite +100% SiO ₂ (ows)	C-CH/100%SiO ₂	82.2	72.9	70
chitosan-poly(DEAEMA) composite +25% TiO ₂ (ows)	C-CH/25%TiO ₂	81.3	67.2	67
chitosan-poly(DEAEMA) composite +50% TiO ₂ (ows)	C-CH/50%TiO ₂	89.4	82.4	82
chitosan-poly(DEAEMA) composite +100% TiO ₂ (ows)	C-CH/100%TiO ₂	70.7	67.3	65.5

(*) Samples without crosslinking

-Adsorption conditions: initial concentration of metal ions, 0.1 M/l
time, 24 hours at room temperature (25°C), M/l ratio, 1:50.

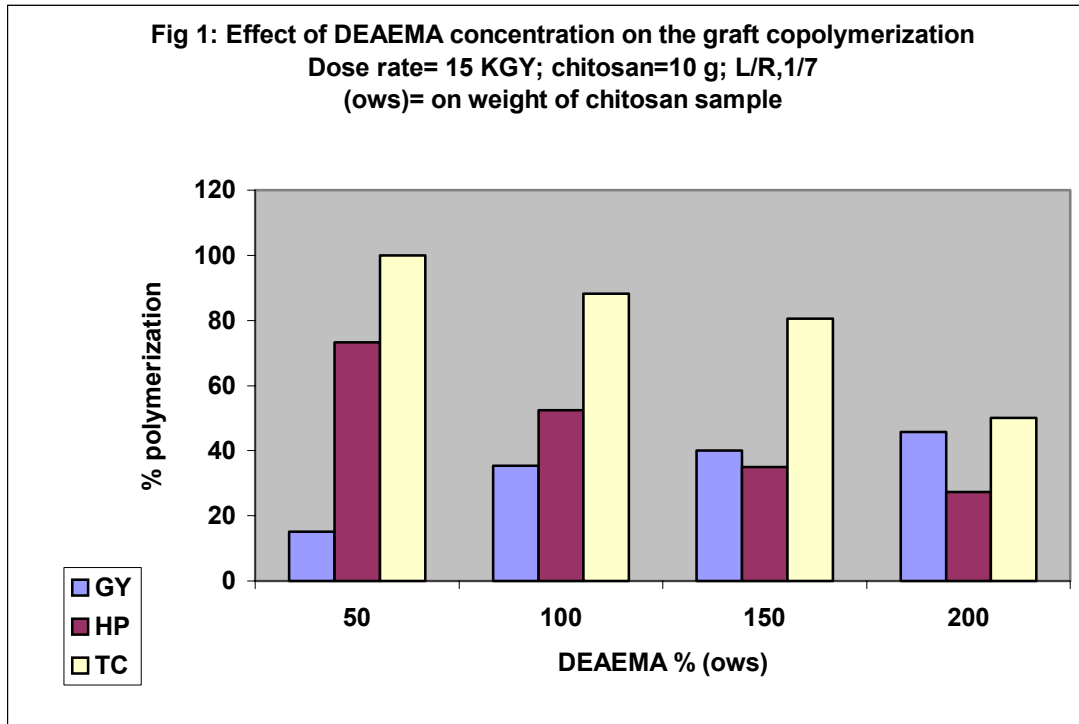
Table2: Adsorption selectivity of the prepared chitosan derivatives.

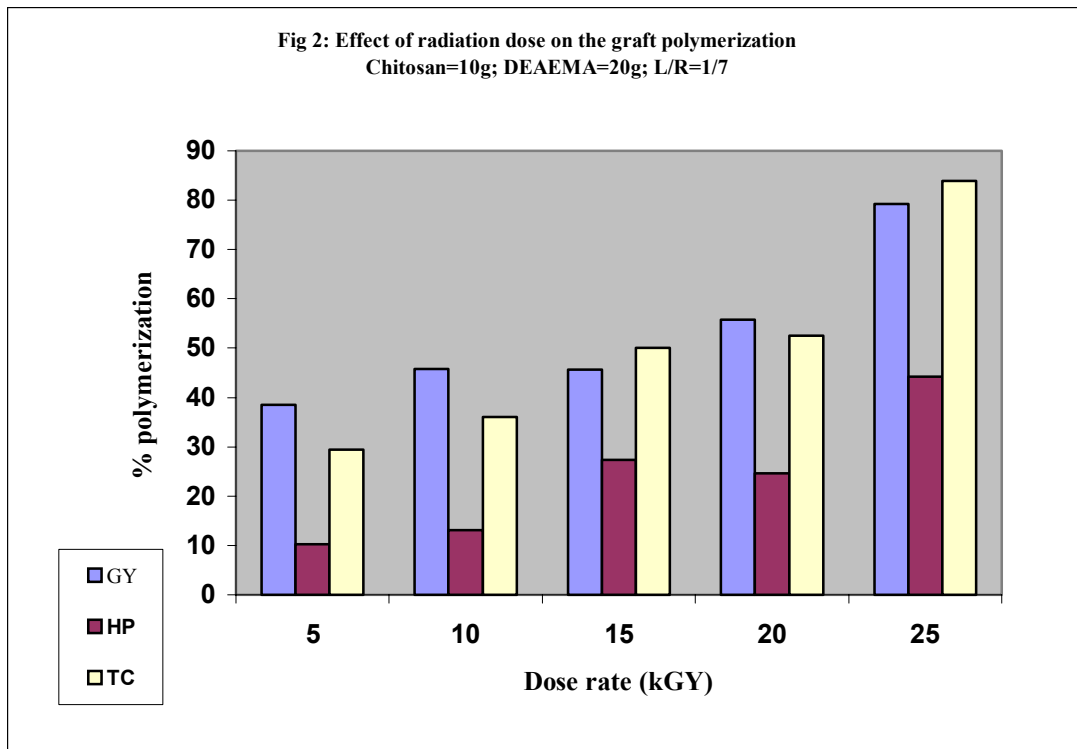
Index	Adsorption Capacity (mg/1g sample)											
	After 5 hrs			After 15 hrs			After 24 hrs					
	Cu ²⁺	Zn ²⁺	Co ²⁺	Cu ²⁺	Zn ²⁺	Co ²⁺	Cu ²⁺	Zn ²⁺	Co ²⁺	Cu ²⁺	Zn ²⁺	Co ²⁺
CH	92.9	62.5	61.3	93.2	68.6	66.7	97.2	73.2	67.5			
g-CH 79% GY	69.3	60.5	60.0	74.8	63.5	62.9	84.1	64.1	62.8			
C-CH	62.7	53.9	50.0	64.0	55.1	52.8	67.2	61.0	56.2			
	65.8	57.4	60.1	73.9	59.4	61.7	74.7	77.4	64.9			
	77.9	55.5	55.1	85.5	69.1	65.9	86.6	72.3	67.0			
	53.6	48.1	43.2	60.7	61.8	53.5	65.3	64.1	55.4			
	69.0	58.4	60.7	72.1	57.8	63.4	72.8	66.9	65.9			
	70.6	63.0	62.8	72.3	74.7	64.6	74.9	75.0	67.0			
	54.7	54.3	53.8	60.4	67.5	60.9	64.2	68.8	64.5			

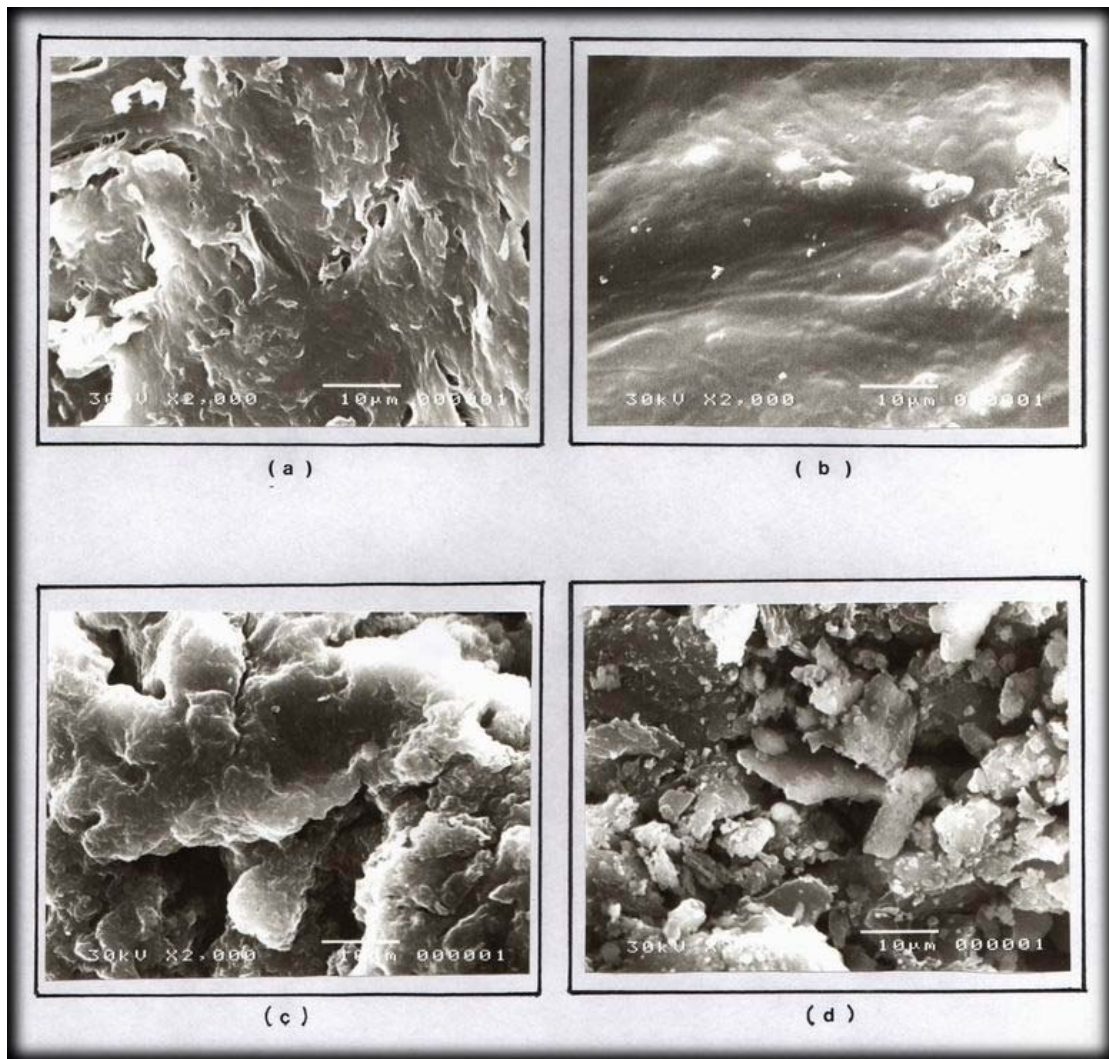
Concentration of metal ions in one liter of mixed solution before adsorption: 0.1 M/l.
(*) samples without crosslinking.

Substrate	Chitosan	Chitosan-g-poly(DEAEMA)* GY 79%	Chitosan-poly(DEAEMA) composite	Chitosan-poly(DEAEMA) composite +25%SiO ₂ (ows)	Chitosan-poly(DEAEMA) composite +50%SiO ₂ (ows)	Chitosan-poly(DEAEMA) composite +100%SiO ₂ (ows)	Chitosan-poly(DEAEMA) composite +25%TiO ₂ (ows)	Chitosan-poly(DEAEMA) composite +50%TiO ₂ (ows)	Chitosan-poly(DEAEMA) composite +100%TiO ₂ (ows)
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Fig 1: Effect of DEAEMA concentration on the graft copolymerization
Dose rate= 15 KGY; chitosan=10 g; L/R,1/7
(ows)= on weight of chitosan sample







Fig(3): Scanning Electron micrographs before metal uptake.

- (a) Chitosan
- (b) Poly(DEAEMA)-Chitosan graft copolymer
- (c) Chitosan-Poly(DEAEMA) composite
- (d) Chitosan-Poly(DEAEMA) composite-SiO₂/TiO₂

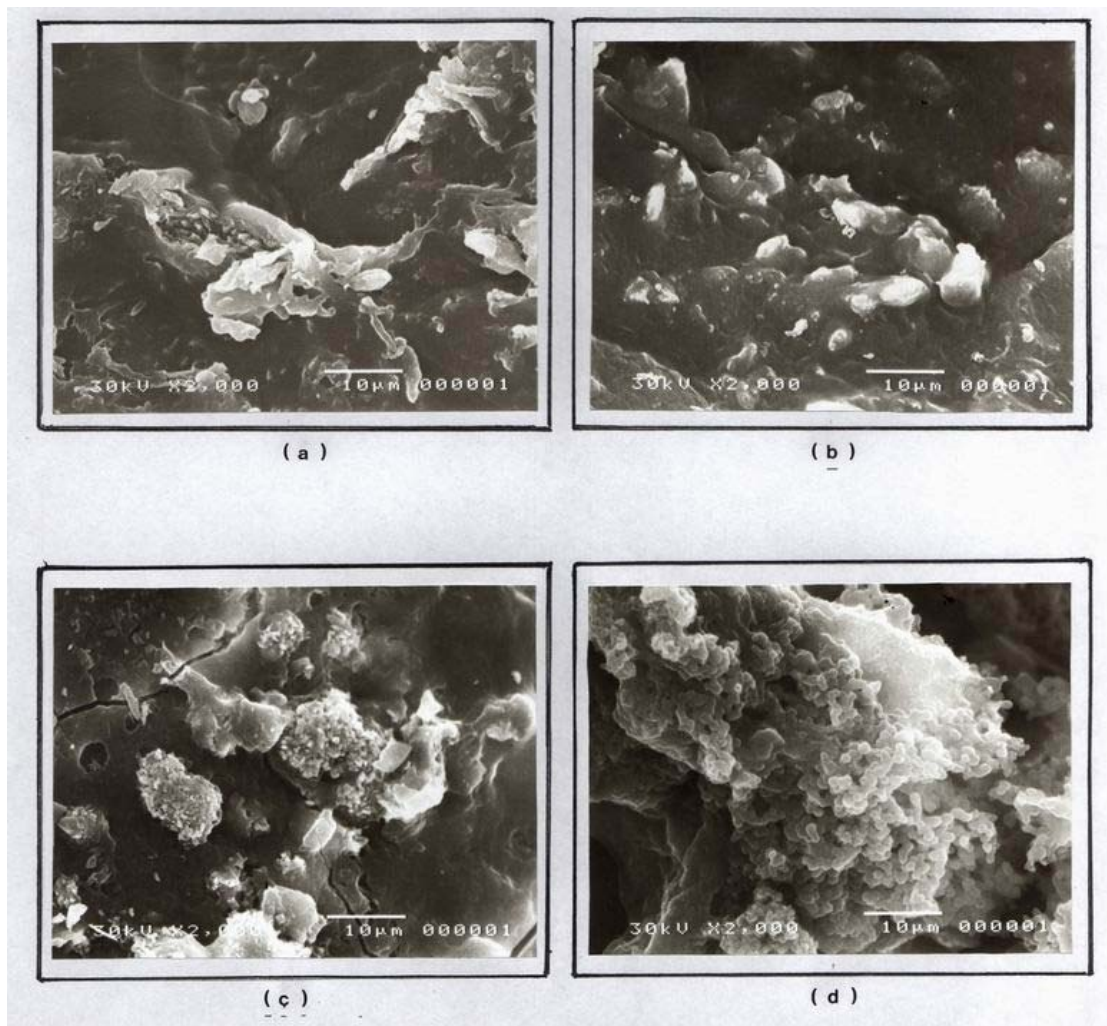


Fig (4): Scanning Electron micrographs after metal uptake.
(a) Chitosan
(b) Poly(DEAEMA)-Chitosan graft copolymer
(c) Chitosan-Poly(DEAEMA) composite
(d) Chitosan-Poly(DEAEMA) composite-SiO₂/TiO₂