

# Graft copolymerization of methyl acrylate on chitosan: Adsorptive removal of Cu (II)

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**Abstract:** Chitosan is a natural based polymer obtained by alkaline deacetylation of chitin, exhibiting excellent biological properties such as biodegradation in the human body, and immunological, antibacterial, and wound-healing activity. Chitosan has also been found to be a good candidate as a support material for gene delivery, cell culture and tissue engineering. For a breakthrough in utilization, graft copolymerization onto chitosan will be a key point, which will introduce desired properties and enlarge the field of the potential applications of chitosan by choosing various types of side chains. Methyl acrylate was grafted onto chitosan by using the ceric ammonium nitrate as initiator. The grafted and un-grafted samples were characterized using Fourier (FTIR), and (SEM) methods. Evidence of grafting was confirmed by FTIR. The morphology of both biosorbents was evaluated by SEM. Both grafted and un-grafted chitosan were used for the removal of copper ions from aqueous solutions. The effects of pH of solution, initial copper ion concentrations, dose of biosorbent and contact time on percentage removal of Cu (II) using both biosorbents were studied. Grafted chitosan has been found to have higher adsorption capacity than un-grafted one.

**Key words:** Biosorption, Chitosan, Copolymerization, Copper (II), Grafting.

## 1 INTRODUCTION

The continuously increasing demand for the commodities produces by chemical industries has triggered heavy metals accumulation in the eco system. Water is polluted in many ways like effluent of leather and chemical industries, electroplating industries and dye industries [1]. Contamination of aquatic media by heavy metals is a serious environmental problem [2,3]. Heavy metals are highly toxic even at low concentrations and can accumulate in living organisms, causing several disorders and diseases [4,5,6]. Copper for example is used extensively in the electrical industry and manufacture of fungicides. Although copper can be an essential element for human beings in trace amount due to the fact that human body can regulate the trace level haem statically, it can also be toxic when large dosage is ingested [7]. The maximum contaminant level for Cu (II) in industrial effluent as suggested by United States Environmental Protection Agency (USEPA) is 1.3 mg/l [8]. Several methods are used for the removal of heavy metals from aqueous solution such as, chemical precipitation, oxidation/ reduction, filtration, ion exchange, membrane separation and adsorption [9].

Biosorption is a feasible option because it is both efficient and cheap compared to other conventional methods for removing toxic metals from effluents [10]. The

biomaterials that are used for sorption are complex a number of mechanisms could be occurring simultaneously [11]. There are several chemical groups in biomass that could potentially attract and sequester metal ions: acetamido groups in chitin, amino and phosphate groups in nucleic acids, amino, amido, sulfhydryl and carboxyl groups in proteins and hydroxyls in polysaccharides [12]. Biosorbents, include: fungi [13], algae [14], seaweeds [15,16], microorganisms [17,18], and chitosan.

Chitosan is a linear polysaccharide derived from chitin, the second most abundant organic compounds only next to cellulose in the nature. Chitin can be found in the shells of marine invertebrates (crabs, crustaceans, etc.), fungi, insects and yeasts. Depending on the source, it generally functions as an exoskeleton, providing structural integrity, commonly embedded in a matrix of proteins, minerals and at times various other polysaccharides. Chitin is a homopolymer comprised of 2-acetamido-2-deoxy- $\beta$ -D-glucopyranose units; however, some units exist in the deacetylated form as 2-amino-2-deoxy-  $\beta$  -D-glucopyranose. When chitin is deacetylated to at least 50%, it is referred to as chitosan, in other words this is essentially the N-deacetylated derivative of chitin. Chitosan has many interesting biological and chemical properties. The excellent features such as biocompatibility, ecologically safe biodegradability (degradation products of chitosan are non-toxic, non-immunogenic and noncar-

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cinogenic) and low toxicity with versatile biological activities (chitosan has antimicrobial activity and low immunogenicity) recommends this biopolymer for applications in biomedicine [19-22]. In addition, chitosan is very efficient for interaction with the anionic solutes including dyes in acidic solutions due to the reactive groups, such as  $-OH$  and  $-NH_2$ . This property has been widely used for the removal of the water-soluble dyes, as an alternative to the conventional sorbents and flocculants [23, 24]. However, due to inter- and intramolecular H-bonding, chitosan is only soluble in few dilute acid solutions (depending on the molecular weight), which limits its applications. As a result, many attempts have been made in chemical modification of chitosan, aiming at improving its water solubility. Among these an ideal way is the graft modification of chitosan [25, 26]. The main advantage in the grafting efforts is the high degree of functionality of chitosan - the molecule backbone contains two hydroxyl groups and one primary amine group per repeat unit. The active primary amino groups on the molecule being reactive provide sites for the attachment of different side groups employing mild reaction conditions. In this way versatile materials based on chitosan with specific functionality can be obtained. Grafting vinyl monomers onto chitosan [27, 28] is one of the most effective methods to improve the performances of chitosan without sacrificing its properties and also is a challenging field of research with unlimited future prospects. Vinyl graft copolymerization can be described as the modification of a preexisting polymer chain (trunk polymer). Graft copolymers are synthesized to improve physicochemical properties of synthetic/natural polymers for applications in agriculture, biomedicine and other fields.

The aim of this study was to conduct a kind of chemical modification of chitosan by graft polymerization of methyl acrylate onto the backbone of chitosan. The grafted polymer (chitosan-g-methyl acrylate) was characterized by FTIR and SEM, which elucidated the structure changes in comparison with chitosan. In the present work, the chitosan-g-methyl acrylate was applied for the removal of copper (II) ions from aqueous solution. It was found that the copolymer was a promising matrix for the biosorption of metal ions. The effect of biosorption parameters such as contact time, initial heavy metal concentration, pH of solution, and biosorbent dosage was investigated.

## 2 MATERIALS AND METHODS:

### 2.1 Materials:

Chitosan (Degree of Deacetylation = 95% and Molecular Weight (100,000 -300,000)) was supplied by ACROS ORGANICS CO, Ltd., Japan. Acetic acid, Methyl Acrylate, ceric ammonium nitrate, and other chemicals of analytical grade were used without fur-

ther purification. Analytical grade  $CuSO_4 \cdot 5H_2O$  was used to make all copper standard solutions used in the experiments. A stock solution of 1000 mg/L was prepared by dissolving the powder in reagent grade water. Working standards ranging from 20 mg/L to 100 mg/L were then prepared by appropriately diluting the stock solution. The pH of the metal solution was adjusted to that required by the experiment using 1M HCl and 1M NaOH.

### 2.2 Graft copolymerization:

Chitosan aqueous solution of 2 wt % was prepared by dissolving 2 g of chitosan powder in 100 mL of acetic acid solution (1%, v/v). After chitosan was fully dissolved, ceric ammonium nitrate with known concentration of  $0.06 \text{ Mol L}^{-1}$  in 0.5 M nitric acid solution was then loaded into the reactor under continuous stirring. Then Methyl Acrylate ( $0.12 \text{ Mol L}^{-1}$ ) was injected into the reactor. The reactor is a three necked round bottomed flask (1000 ml), equipped with a magnetic stirrer, thermometer, and reflux condenser in a temperature-controlled water bath. The reaction was assumed to have started at the moment the monomer was injected. Temperature of the system was strictly controlled at  $35^\circ \text{ C}$  for 3 hr. After completion of the reaction, the reaction mixture was immediately poured into methanol in the ratio of 1:5 of material to liquor for precipitation. The precipitated product was recovered by centrifugation and washed with pure methanol ( $2 \times 50 \text{ mL}$ ).

The crude copolymer thus obtained was dried till constant weight under vacuum (7.6 mm Hg) for 24 h at  $40^\circ \text{ C}$ . The crude copolymer thus obtained was dried till constant weight under vacuum (7.6 mm Hg) for 24 h at  $40^\circ \text{ C}$ . The dried product was extracted with dimethylformamide for 48 h and washed with methanol to remove the homopolymer (polyacrylonitrile). The grafted Chitosan (Chitosan-g-MA) was dried to a constant weight under vacuum (7.6 mm Hg) for 24 h at  $40^\circ \text{ C}$  [29].

### 2.3 Characterization of grafted polymer:

#### 2.3.1 FTIR spectroscopy studies:

The Fourier Transform Infrared Spectrum (FTIR) of chitosan and also grafted chitosan samples were

analyzed in wide range wavelength between 400 cm<sup>-1</sup> and 4000 cm<sup>-1</sup> by FTIR- 8400 S Shimadzu.

### 2.3.2 SEM (Scanning electron microscope):

Scanning electron microscopy images were obtained for Chitosan and grafted chitosan (chitosan-g-MA) by SEM "JEOL JSM 6360 LA."

### 2.4. Adsorption isotherm experiment:

Batch adsorption experiments were performed with different concentrations of copper sulfate (CuSO<sub>4</sub>.5H<sub>2</sub>O) to investigate the extent of adsorption. The extent of removal of Cu (II) was investigated by changing the adsorbent dose, pH of the solution, time of shaking, initial concentration of Cu (II) solution. The pH of each solution was adjusted to different values with either NaOH or HCl. The stoppered bottles were stirred (at 30°C) at fixed speed, 160 rpm for various time intervals. The adsorbate was separated using centrifuge technique and supernatant liquid was analyzed for residual concentration of the metals by UV/DR2010 spectrophotometer. The mixture was stirred until it reached equilibrium stage. The mixture was separated by means of centrifuge field and the residual concentration of Cu (II) ion in solution was determined by UV-DR2010 spectroscopy at 560 nm, the maximum adsorption wavelength for copper ions.

The percentage removal of metal ions was calculated using the following equation :

$$\% \text{ removal} = (C_i - C_e) / C_i * 100 \quad (1)$$

The amount of Cu (II) adsorbed using chitosan and grafted chitosan at equilibrium, q<sub>e</sub> (mg/g) was calculated by the following mass balance relationship:

$$q_e = (C_i - C_e) * V / m \quad (2)$$

Where C<sub>i</sub> and C<sub>e</sub> are the initial and equilibrium liquid-phase concentration of copper, respectively (mg/l), V the volume of the solution (l), and W is the weight of the adsorbent used (g).

### 3.1 Infrared Spectroscopy (FTIR):

FTIR is a promising tool to identify unknown substances and to determine the amount of components in a given sample. This test was performed to get authenticated information about the vibrational origin of the amide, carbonyl and alcoholic groups of both chitosan and grafted chitosan. Spectrophotometric observation of both chitosan and grafted chitosan was in the range of 400-4000 cm<sup>-1</sup>, and served as a direct mean for the identification of the organic function on the surface. An examination of both chitosan and grafted chitosan possibly provided information regarding the specific functional groups that might have participated in the adsorption reaction and also indicated the surface sites on which biosorption can take place which indicated the possibility of using chitosan and grafted chitosan as biosorbents. FTIR spectrum of chitosan is shown in Figure 1 (curve A (red color)). It showed a broad peak at 3429 cm<sup>-1</sup> due to -NH stretching and -OH stretching peak at 1640 cm<sup>-1</sup>, 1592 cm<sup>-1</sup> peak due to the presence of amide groups. Peak at 1087 cm<sup>-1</sup> indicated C-O stretching, and 1485 cm<sup>-1</sup> peak is due to -CN stretching. On the other hand, FTIR of grafted chitosan (chitosan-g-MA), (curve B (blue color)) showed strong peaks at 1720 cm<sup>-1</sup> indicating C=O, and C-O stretching vibrations at 1180 cm<sup>-1</sup>.

This observation confirmed the grafting on chitosan. This result was in agreement with the experimental results of Wu and Zhang [30] compared with the spectra of chitosan and grafted chitosan (chitosan-g-MA), the observed biosorption peaks at 1720 cm<sup>-1</sup> and 1180 cm<sup>-1</sup>.

### 3. Results and Discussions

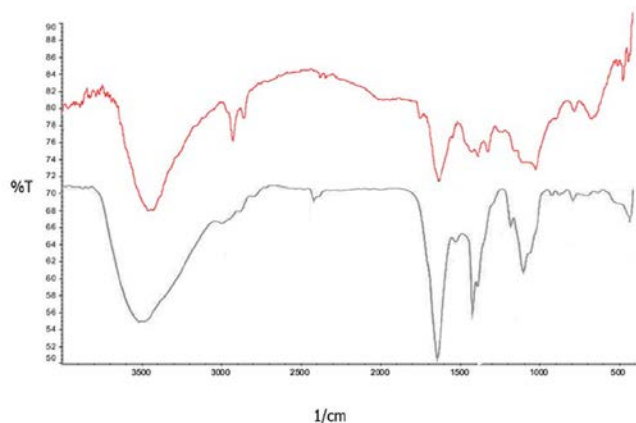


Fig.1. (A) (red color): FTIR spectra of chitosan.

Fig.1. (B): (blue color) FTIR spectra of grafted chitosan

### 3.2 Scanning Electronic Microscopy (SEM):

Figure 2 (a) presented SEM image of the surface morphology of chitosan (external surface). As shown in the figure, there is a little texture of roughness on the surface. The internal surface of chitosan is shown in Figure 2 (b). A number of small pores can be seen in the figure, which resulted in enhancing the biosorption properties of chitosan for trapping Cu (II) ions. The natural polymer had different particle sizes with a rough surface. On the other hand, Figure 2 (c) presented SEM micrographs of the surface of grafted chitosan (chitosan-g-methyl acrylate). It can be seen that the external surface had a large number of rough textures with heterogeneous surfaces which resulted in enhancing the biosorption properties of grafted chitosan. Strong interactions between chitosan and methyl acrylate produced grafted chitosan with larger surface area than the un-grafted one, which enhanced the biosorption of Cu(II). The internal surface of grafted chitosan is shown in Figure 2 (d).

As shown in the figure, there is an increase in the number of pores compared to that of the un-grafted chitosan. Consequently, a well-developed porous network in pore size ranges resulted in improved biosorption properties of grafted chitosan.

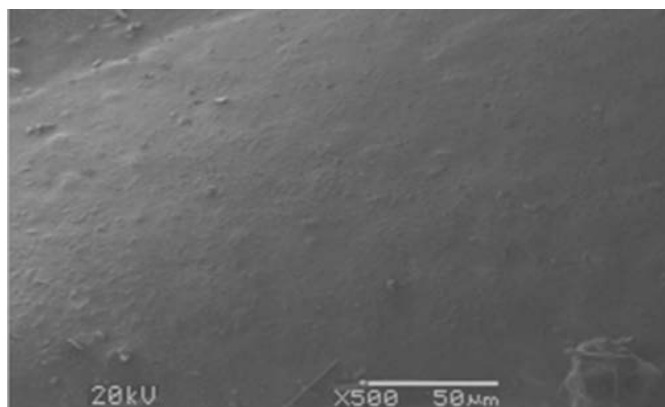


Fig. 2. (a)

SEM image of the external surface morphology of chitosan

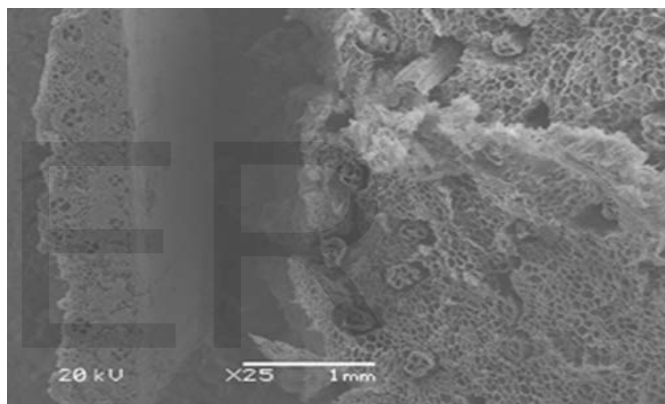


Fig. 2. (b)

SEM image of the internal surface morphology of Chitosan

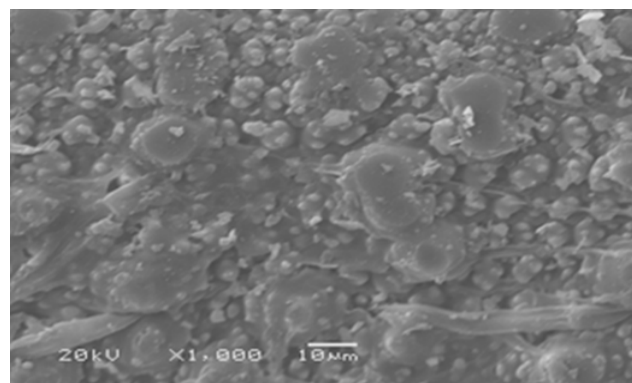


Fig. 2. (c)



SEM image of the external surface morphology of grafted chitosan

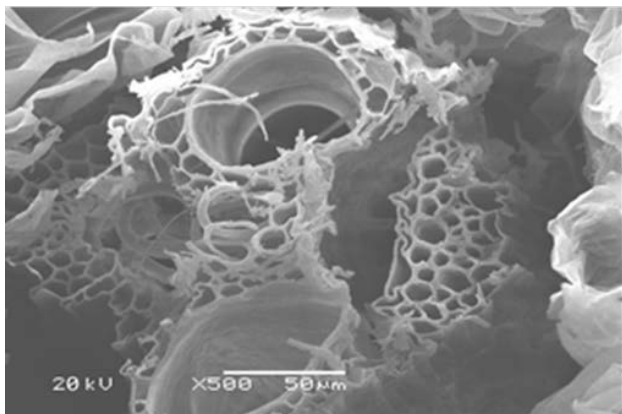


Fig. 2. (d)

SEM image of the internal surface morphology of grafted chitosan

**3.3 Factors influencing the biosorption of Cu(II) ions:**

The influences of several operational parameters such as initial concentration of Cu (II) ions, dose of biosorbent, pH of solution, and contact time were investigated for grafted and un-grafted chitosan.

**3.3.1 Effect of contact time:**

Figure (5) indicated that % removal of copper was increased with increasing contact time before equilibrium was reached.

This is probably due to larger surface area of the biosorbent available at the beginning for adsorption of Cu (II) ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transferred from the exterior to the interior sites of the adsorbent particles. The effect of contact time on metallic biosorption was measured for times of 1, 2, 3, 4, and 5 hours. Typically 40-70% of the ultimate biosorption capacity occurs within two hours of contact for Cu (II) ions. Equilibrium occurs at time of 180 min for both grafted and un-grafted chitosan in which maximum removal percent of copper was attained.

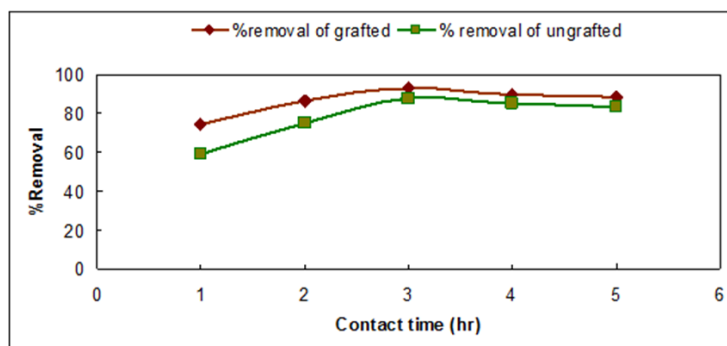


Fig. 5.

Effect of contact time on Cu (II) percentage removal

**3.3.2 Effect of initial concentration of Cu(II) ions:**

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases [31]. The biosorption of Cu (II) ions onto pure and grafted chitosan was carried out at different initial Cu (II) ion concentrations ranging from 20 to 100 mg/l. Fig. 3 clearly shows that by increasing the concentration gradually there is a decrease in the percentage removal for both biosorbents. As the ratio of sportive surface to ion concentration decreased with increasing metal ion concentration and so metal ion removal was reduced. At low initial concentration of metal ions, more binding sites are available. But as the concentration increases, the number of ions competing for available binding sites in the biomass increased [31].

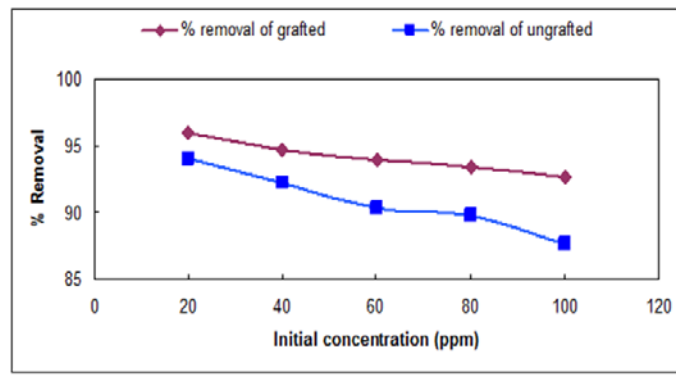


Fig. 3.

### Effect of initial copper concentration on Cu (II) percentage removal

#### 3.3.3 Effect of biosorbent dose:

The effect of the biosorbent dose was studied by varying the sorbent amounts from 1 to 5 g/100 ml. It is obvious from Figure (4) that the percentage removal of grafted and un-grafted chitosan increased by increasing their dosage. The Increase in biosorption could be attributed to the increase in biosorbent surface area and due to the availability of more biosorption sites [31]. The increase in percentage removal of grafted chitosan is higher that of un-grafted one, and this is due to the large surface area of grafted chitosan compared to that of un-grafted. As seen from SEM of grafted chitosan in figure 2 (c,d) there is an enhancement in the adsorption properties of grafted chitosan compared to un-grafted chitosan.

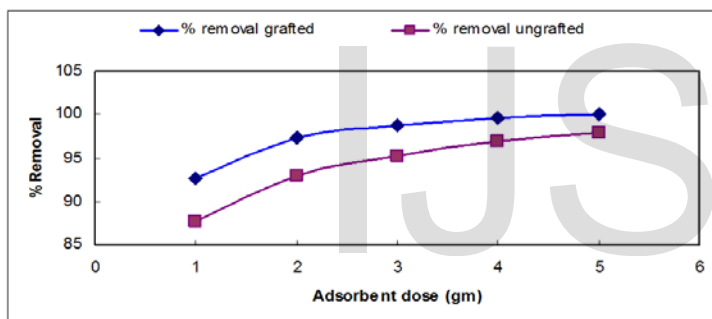


Fig .4.

### Effect of biosorbent dose on Cu (II) percentage removal

#### 3.3.4 Effect of pH

Figure (6) illustrated that pH obviously influenced the percentage removal of copper ions in the aqueous solution using adsorbent material (grafted and un-grafted chitosan). The results indicated that the role of hydrogen ion concentration was examined in solutions at different pH values (4-9). It was observed that with the increase in the pH of the solution, the extent of metal ions removal increased for both biosorbents until pH=8. The maximum percentage removal of Cu (II) was observed at pH= 8. At lower pH, hydrogen ions occupy most of the adsorption sites on the surface of the adsorbent and thus results to a very low biosorp-

tion of Cu (II) ions due to electrostatic repulsion. However, increasing the pH of the solutions results to a decrease in the competition of hydrogen ions with Cu(II) ions for biosorption sites and thus facilitating higher rate of removal of Cu(II) ions. Increasing pH above 8 resulted in the precipitation of insoluble copper hydroxide, causing a decrease in the removal of Cu(II) [31].

#### 4. Conclusions:

Grafted and un-grafted chitosan had been used for Cu (II) removal from aqueous solutions. The graft copolymer of chitosan (Chitosan-g-MA) was synthesized through homogeneous graft copolymerization of methyl acrylate onto the backbone of chitosan in aqueous solution using ceric ammonium nitrate as initiator. The characterization of the grafted products by means of Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM) furnished evidence of grafting methyl acrylate onto chitosan and showed that the grafted copolymer had rougher surface with larger surface area, and large number of pores which resulted in enhancing its biosorption properties. It had been proved that the grafting copolymerization is one of the most effective methods to improve the performance of chitosan without sacrificing its properties and also is a challenging field of research with unlimited future prospects. Favorable removal for Cu (II) had been achieved. Hence the chitosan-g-MA can be used for waste water treatment. The effects of biosorbent dosage, contact time, initial copper ion concentrations, and pH of the medium on adsorption efficiency of both grafted and un-grafted chitosan were studied for Cu(II) removal. Grafted chitosan has been found to have higher adsorption capacity than un-grafted one. Hence the graft copolymer chitosan (Chitosan-g-MA) can be used for waste water treatment at industrial level.

#### REFERENCES:

[1] P. N. Sudha, Chitin, Chitosan, Oligosaccharides and Their Derivatives, Ed. SeKwon Kim, CRC Press, pp. 561-585,2010.  
 [2] Baraka A., Hall P. , Heslop J.J. , "Melamine-FormaldehydeNTA chelating gel resin; synthesis,

characterization and application for copper (II) ion removal from synthetic wastewater”, *Journal of hazardous materials*, vol 140, pp 86-94,2007.

[3] Bose P., Bose M. , Kumar S. , “Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper,zinc and cyanide”, *Advances in Environmental Research*, vol 7, pp 179-195,2002.

[4] Crini, G., “Nonconventional Low cost adsorbents for dye removal; a review”, *Bioresource Technology*, vol 60, pp 67-75, 2006.

[5] Aksu Z., “Application of biosorption for the removal of organic pollutants: a review”, *Process Biochemistry*, vol 40(34), pp 997-1026, 2005.

[6] Forgacs E., Cserhati T. , Oros G. , “Removal of synthetic dyes from wastewater; a review” *Environmental International*, vol 30, pp 953-971,2004.

[7] N. Li , R.Bai, “Copper adsorption on chitosan-cellulose hydrogel beads :behaviours and mechanisms, separation and purification technology”, *Journal of Applied Polymer Science*, vol 42, pp. 237-245, 2005.

[8] S.Hasan, T.K.Ghosha, D.S.Viswanath,V.M. Boddub,” Dispersion of chitosan on perlite for enhancement of copper (II) adsorption capacity”, *Journal of Hazardous Matter*,vol 152, pp.826-837, 2008.

[9] Mohan D. , Pittman Jr, C.U. , “Activated carbons and low cost adsorbents for remediation of tri and hexavalent chromium from water”, *Journal of Hazardous Materials*, B137, pp 762-811, 2006.

[10] B.Volesky ,” Detoxification of metal -bearing effluents: Biosorption for the next century”, *Hydrometallurgy*, vol 59, pp. 203-216, 2001.

[11] B. Volesky , Z.R. Holan ,” Biosorption of heavy metals”, *Biotechnology Progress*, vol 11,pp. 235-250, 1995.

[12] P. Uday Bhaskar, L. Iyengar, Prabhakar Rao, A. V. S. , “Hexavalent chromium interaction with chitosan”, *Journal of Applied Polymer Science*,vol 39, pp. 739-747, 1990.

[13] R.I. Acosta, X. Rodriguez, C. Gutierrez, G. Mottezuma, “Biosorption of chromium (VI) from aqueous solutions onto fungal biomass:, *Bioorganic Chemistry Application* , vol 2, pp.1-7, 2004.

[14] V.K.Gupta, A.K. Shrivastava, N. Jain, “Biosorption of chromium (VI) from aqueous solution by green algae *Spirogyra* species, *Water Resource*, vol 35, pp. 4079- 4085, 2001.

[15] R. Elangovan, L.Philip, K. Chandraraj, “Biosorption of chromium species by aquatic weeds: kinetics and mechanism studies”, *Journal of Hazardous Matter*, vol 152, pp.100-112, 2008.

[16] D. Kratochvil, P. Pimentel, B. Volesky, “ Removal of trivalent and hexavalent chromium by seaweeds: kinetics and mechanism studies”, *Environmental Science Technology*, vol 32, pp. 2693 – 2698, 1998.

[17] Y. Sahin, A. Ozturk, “Biosorption of chromium (VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*”, *Process Biochemistry*, vol 40, pp.1895-1901, 2005.

[18] T. Fan, Y. Liu, B. Feng, G. Zeng, C. Yang, M. Zhou, H. Zhou, Z. Tan, X.Wang, “Biosorption of cadmium (II), Zinc (II) and lead (II) by *Penicillium simplicissimum*: isotherms, kinetics and thermodynamics”, *Journal of Hazardous Matter*, vol 160 , pp. 655-661, 2008.

[19] Khan TA, Peh KK, Chang HS, “Mechanical, bioadhesive strength and biological evaluation of chitosan films for wound dressing”, *Journal of Pharmacy & Pharmaceutical Sciences*, vol 3, pp.303-311, 2000.

[20] Tashiro T,” Antibacterial and bacterium adsorbing Macromolecules”, *Macromolecular Materials and Engineering*, vol 286, pp.63-87, 2001.

[21] Aoi K, Takasu A, Okada M, “New chitin based polymer hydrids”, *Macromolecules*, vol 30, pp.6134-6138, 1997.

[22] Ignatova M, Manolova N, Rashkov I, “Novel antibacterial fibers of quaternized chitosan and poly (vi-

nyl pyrrolidone) prepared by electrospinning” Eurpian Polymer Journal, vol **43**, pp.1112-1122, 2007.

[23] Wang H, Li W, Lu Y, Wang Z, “Studies on chitosan and poly(acrylic acid) interpolymer complex”, *Journal of Applied Polymer Science*, vol 65, pp.1445-1450, 1997.

[24] Santos MA, Grazina R, Pinto M, Farkas E, “Transition metal complexes of two new iminohydroxamic acids”, *Inorganica Chimica Acta*, vol 321, pp.42-48, 2002.

[25] Hu SG, Jou CH, Yang MC, Surface grafting of polyester fiber with chitosan and the antibacterial activity of pathogenic bacteria, *J Appl Polym Sci*, **86**, 2977-2983, 2002.

[26] Liu L, Li Y, Liu H, Fang Y, “Synthesis and characterization of chitosan-graft polycaprolactone Copolymers”, *Eurpian Polymer Journal*, vol **40**, pp. 2739-2744, 2004.

[27] Jayakumara R, Prabaharana M, Reisa RL, Mano JF, “Graft copolymerized chitosan-present status and applications”, *Carbohydrate Polymer*, vol **62**, pp.142-158, 2005.

[28] Joshi JM, Sinha VK, “Ceric ammonium nitrate induced grafting of polyacrylamide onto carboxymethyl chitosan”, *Carbohydrate Polymer*, vol 67, pp.427-435, 2007

[29] Hemalatha. R , Chitra. R , Xavier Raja Rathinam , Sudha. P N, “Synthesizing and characterization of chitosan graft co polymer: adsorption studies for Cu (II) and Cr (VI)”, *International Journal of environmental sciences*, Vol 2(2), pp. 805-828, 2011.

[30] X. Zhang, Z. Wu, “PEG- grafted chitosan nanoparticles as an injectable carrier for sustained protein release”, *Journal of Materials Science: Materials in Medicine* , vol 19, pp.3525-3533, 2008.

[31] A. Shanmugapriya1, R. Ramya , S. Ramasubramaniam1 and P. N. Sudha, “Studies on removal of Cr(VI) and Cu(II) ions using Chitosangrafted- Polyacrylonitrile”, *Archives of Applied Science Research*, vol 3 (3), pp.424-435, 2011.

### List of symbols

Symbol	Description	Units
$C_e$	Equilibrium copper concentration	mg/L
$C_i$	Initial copper concentration	mg/L
m	Mass of adsorbent	g
$q_e$	amount of copper adsorbed at equilibrium	mg/g
V	Volume of solution	L



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