Synthesis and characterization of chitosan based graft co polymer: an efficient adsorbent for dyeing industry waste water

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ABSTRACT

N- Maleilated chitosan was synthesized by reaction of chitosan with maleic anhydride (MA) in N, N-dimethyl formamide. N-Maleilated chitosan – g – (methyl methacrylate) co-polymer was prepared via free radical polymerization using ceric ammonium nitrate (CAN) as the initiator. The effect of polymerization variables including initiator concentration, monomer concentration and reaction temperature on grafting percentage were studied. It was found that the grafting yield and grafting efficiency were increased with increasing the polymerization variables and then decreased. The grafting was maximum at 1.6g of initiator (CAN), 2g of the monomer (Methyl methacrylate) at 70^0c. The co-polymer obtained was confirmed by FTIR, XRD, TGA, DSC analysis. This graft co-polymer was used as an adsorbent in dye effluent treatment. It was more efficient than parent chitosan. Equilibrium sorption experiments were carried out. The experimental data was successfully fitted to the Langmuir adsorption isotherm.

Introduction

Contamination of water by heavy metals, dyes and other particulate has become an increasing problem to the environment and health. Metal ions such as chromium, copper and cadmium among others are commonly detected in both natural and industrial effluents. The heavy metals can accumulate in living organisms, causing several disorders and diseases (Crini, 2006; Aksu, 2005; Forgacs, 2004).Metals can be distinguished from other toxic pollutants since they undergo chemical transformations, are non-biodegradable and have great environmental, economical and public health impacts (Kozlowski and Walkowiak, 2002).These toxic pollutants are caused by industries like electroplating, leather tanning, cement, preservatives, paints, pigments, textiles, steel fabrication and canning industry.

One of the ugly faces of industrialization is generation of large quantity of solid and hazardous wastes which need to be managed in an environmentally sound manner. Conventional methods applied for the removal of heavy metals are mainly chemical precipitation, filtration, oxidation/reduction, ion exchange, membrane separation and adsorption. Adsorption is the most frequently applied technique. Activated carbon is one of the most popular adsorbents for removal of metal ions. Current investigations tend toward achieving high removal efficiencies with much cheaper non-conventional materials which are mostly cheap and abundant biological matter (Mohan and Pittman 2006; Nomanbhay and Palanisamy 2005; Babel and Kurniawan 2003; Ansar Ali et al., 2011).

Recently, the removal of metals from solutions by biological materials is recognized as an extension to adsorption and is named as biosorption (Boddu et al., 2003). Chitosan a bio polymer prepared from chitin through the deacetylation method. Chitin is the second most abundant bio polymer next to cellulose (Muzzarelli, 1973). Chitin is a white, hard, inelastic nitrogenous

polysaccharide (Ravikumar, 2000). It is one of the principal ingredients of the carapaces, crusts and shells of crustacea. Only limited attention has been paid to chitin. Despite its huge annual production and easy accessibility, chitin still remains an unutilized biomass resource primarily because of its intractable bulk structure (Kurita, 2001). Chitin because of its insolubility is rarely subjected to chemical reactions except for the preparation of chitosan by deacetylation. Khor has stated that 21st century can be the century of chitin taking a place as an extra ordinary material because chitin and its derivatives have exhibited high potential in a wide variety of fields(Medical, pharmaceutical, cosmetics, food industry, agriculture, environmental protection) (Khor, 2002; VanLuyen and Huong, 1996; Kas, 1997; Kurita, 1998; Peter,2002;Hirano,1999;Ravikumar, 2000).
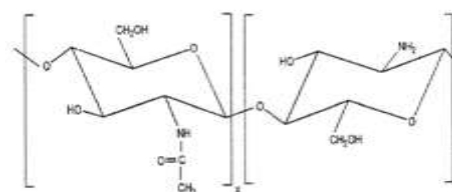

Figure. 1. Structure of chitosan

Chitosan can be dissolved in only acidic solutions through the interaction between H^+ and $-NH_2$, but it is insoluble under higher pH conditions. It is also of limited solubility in organic solvents. In order to sort the above problems, chemical modification affords a wide range of novel chitosan derivatives. Among the various methods of modification graft copolymerization is an attractive technique to modify the chemical and physical properties of chitosan (Crini, 2005)

Grafting of chitosan allows the formation of functional derivatives by covalent binding of a molecule, the graft, on to the chitosan backbone. Chitosan has two types of reactive groups such as free amino groups and hydroxyl groups that can

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be grafted (Alves and Mano 2008). Two major types of grafting may be considered:

(i) Grafting with single monomer.

(ii) Grafting with two monomers.

The first type usually occurs in a single step, and the second may occur with either the simultaneous (or) sequential use of the monomers (Bhattachariya and Misra 2004).

In the present study, we have synthesized graft co- polymer chitosan-g - maleic anhydride- g-(methyl methacrylate) using ceric ammonium nitrate as the initiator. The prepared graft co-polymer was subjected to various analytical techniques such as FTIR, XRD, TGA, and DSC to confirm the grafting. Also we investigated the polymerization variables such as initiator concentration, monomer concentration and reaction temperature. This graft co-polymer will be highly useful for various application fields including drug delivery and wastewater treatment. In present work efficacy of chitosan-g-maleic anhydride-g-(methyl methacrylate) for treating dye industry effluent was attempted and found successful.

Experimental

Materials

Chitosan was purchased from India sea foods Cochin, Kerala, India. Maleic anhydride and methyl methacrylate were of analytical grade and obtained from the company, Merck. All other chemicals were of analytical grade and used without any purification.

Preparation of chitosan –g-maleic anhydride -g-(Methyl methacrylate) co-polymer

Preparation of chitosan- g- Maleic anhydride

Chitosan (2g) and maleic anhydride (6g) were dissolved in 100 ml of dimethyl formamide (DMF), and then the mixture was stirred at 130^0c for 3hrs under nitrogen atmosphere.

The resulatant solution was cooled to room temperature and poured in to ice water to precipitate the product. The product was collected by filtration, washed with diethyl ether for three times and then dried in vacuum at 40^0c. The grayish white powder of N-maleilated chitosan was obtained. (Jinchen Fan et al., 2009).

Chitosan-g-maleic anhydride-g-(Methyl methacrylate)

The graft co-polymer was homogeneously synthesized in aqueous solution by using ceric ammonium nitrate as initiator. A mixture of 0.5g of maleilated chitosan and 1.6g CAN/10ml of HNO_3 was stirred followed by the addition of methacrylate (2g). The reaction was performed at 70^0c for 1hr. the contents of the flask were cooled to room temperature and poured into 10%NaOH solution to precipitate the graft co-polymer.

The effect of initiator concentration, monomer concentration and reaction temperature on the grafting yield and grafting efficiency were investigated. The grafting efficiency (GE %) and grafting yield (G %) were calculated as follows,

GE% = Wg/Wg + Wi *100.

GY% = Wg – Wi/Wi *100.

G% = Wg/Wa *100.

Where,

Wa = Weight of monomer.

Wi = Weight of chitosan – g-Maleic anhydride.

Wg= Weight of N-Maleilated chitosan-g-(Methyl methacrylate).

Characterization

FTIR

FTIR spectra of the grafted co-polymer products were determined by Perkin Elmer spectrophotometer and in a wide range wavelength between 400 cm^{-1} - 4000 cm^{-1} and in solid state using KBr pelletisation.

X – Ray Diffraction

X – Ray diffraction were obtained with a D\max - 2200 X-ray diffractometer using graphite - monochromatized Cu Kα radiation (K = 1.54178A^0)

Thermo gravimetric analysis

The thermal properties of samples were measured by NET Z SCH - Geratebau GmbH thermal analyzer. Samples were dried in vaccum desiccator and powdered in a standard Aluminium panel. 2.0mg of this sample was heated about 30^0C - 350^0C at a heating rate of 10^0C per min under N_2 atm in the DSC analysis.

TGA were recorded with 2.0mg of this sample was heated from 30^0C - 870^0C at a heating rate of 10^0C / min at N_2 atm.

Dyeing industry effluent

Dyeing industry effluent was collected from an effluent canal outside a leather dyeing unit of Ranipet Industrial area, India in a polythene container. pH and Temperature were noted on the spot

Physico- chemical characterization of effluents

Physico-chemical factors such as pH, Electrical Conductivity, Dissolved Oxygen, Biochemical Oxygen Demand, Chemical Oxygen Demand, Total Dissolved Solids, Total Solids, Alkalinity, Chloride, Hardness, Sodium and Heavy Metals such as Copper, Cobalt, Chromium and Zinc were analyzed as per the methods of APHA 1992,Heavy metals were anzalysed using varian AA200 Atomic absorption spectrophotometer(AAS) in air-acetylene flame

Results and Discussions

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 chitosan and graft copolymers.

FTIR spectrum of pure chitosan (figure.2a) shows a broad peak at 3429 cm^{-1} due to -NH stretching and -OH stretching peak at 1640 cm^{-1} 1592 cm^{-1} due to Amide I and Amide II groups. Peak at 1087 cm^{-1} indicates C-O-stretching, 1485 cm^{-1} peak due to C-N stretching.
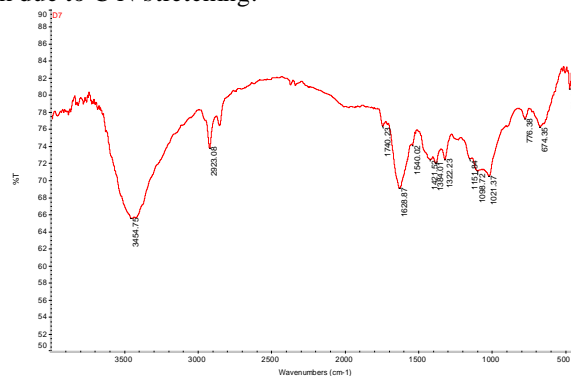

Figure. 2a FTIR of chitosan.

FTIR of Chitosan-g-Maleic anhydride shows in Figure.2b, strong peak at 1596 cm^{-1} indicating C=C bond. This confirmed the grafting of maleic anhydride group on to chitosan (Tian Ying GUO et al., 2004)

Maleilated chitosan when grafted further with methyl methacrylate formed Chitosan-g-Maleic anhydride-g-(Methyl methacrylate) copolymer.
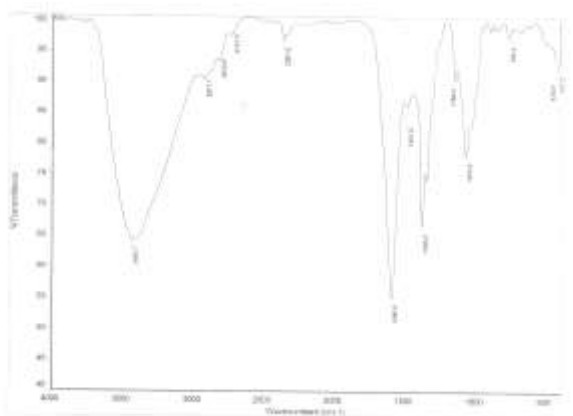
Figure.2b. FTIR of chitosan-g-Maleic anhydride

The FTIR spectrum (figure.2c) had additional sharp absorption peaks at 1731 cm^{-1}, 2950cm^{-1}, 2996 cm^{-1} due to carbonyl stretching and symmetrical and asymmetrical stretching of the methyl group respectively. This provided a substantial evidence of grafting methyl methacrylate to maleilated chitosan. (Singh et al., 2009)
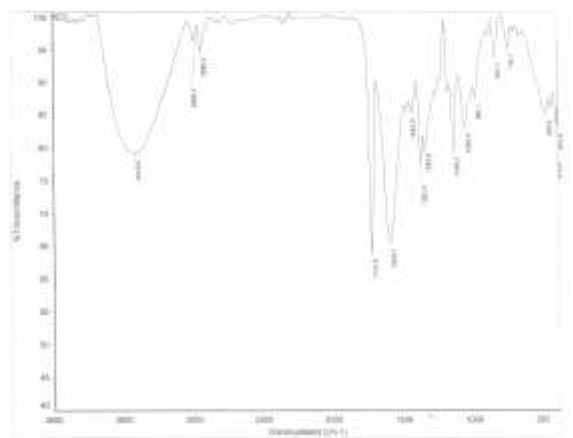

Figure. 2c. FTIR of chitosan-g-Maleic anhydride-g- (methyl methacrylate)

XRD

The XRD spectrum of chitosan (figure.3a) has low crystallinity and the characteristic peak at $2\theta=11^0$ and 20^0. In comparison with chitosan, maleilated chitosan-g-(Methyl methacrylate) (figure.3b) does not have the peak at $2\theta=11^0$, and the intensity of the peak, $2\theta=28^0$, descends sharply. Hence crystallanity of the grafted copolymer had decreased much.

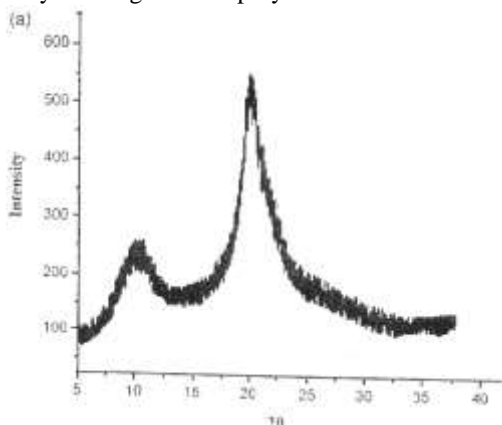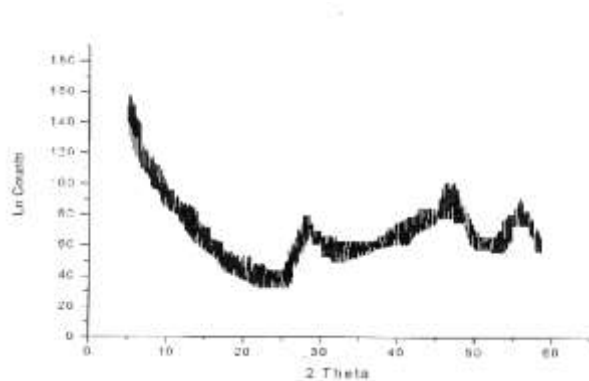**Figure.3a. XRD of chitosan**

Figure.3b. XRD of chitosan-g-maleic anhydride -g-(methyl methacrylate)

Thermo gravimetric Analysis

The TGA curve of chitosan figure.4a has two degradation temperatures which the temperature lower than 100^0c indicating the loss of water. The temperature at 100^0c indicates the decomposition of pyranose ring structure. The TGA of grafted co-polymer (figure.4b&4c) shows five decomposition temperatures. Maximum decomposition was observed around from 220^0c, which may be due to the the decomposition of side chains grafted on to the chitosan backbone.
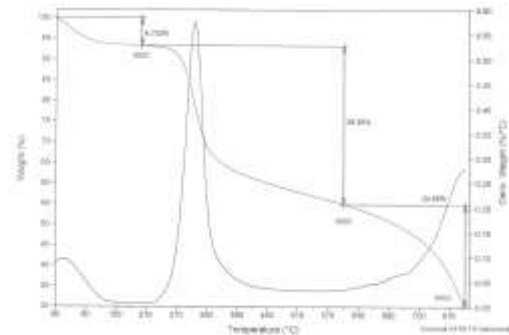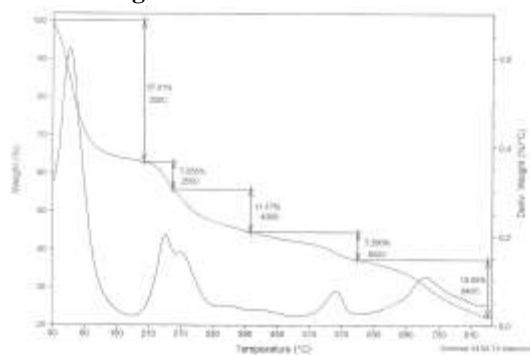

Figure. 4a. TGA of chitosan

Figure. 4b. TGA of chitosan -g- maleic anhydride
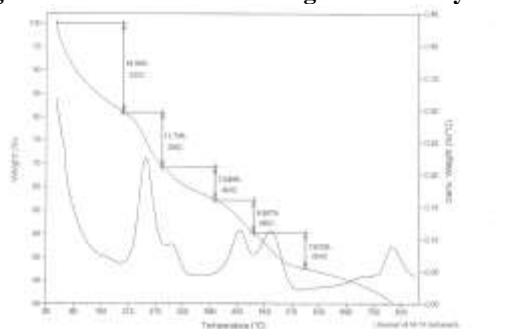

Figure. 4c. Chitosan-g- maleic anhydride-g-(methyl methacrylate)

DSC

DSC curves of chitosan (figure.5a) showed one endothermic and one exothermic peak. Endothermic peak can be attributed to the loss of water from chitosan. While the exothermic peak indicates the decomposition of side chains. DSC curve of grafted co polymer (figure 5b&5c) showed the single Tg value which confirms the grafting of methylmethacrylate to the maleilated chitosan backbone.
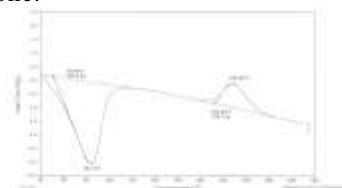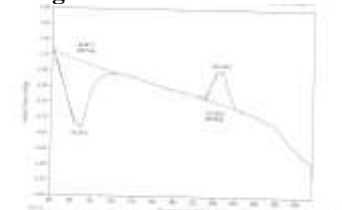

Figure.5a.DSC of chitosan

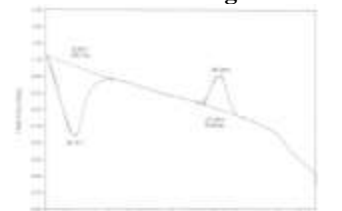**Figure.5b. DSC of Chitosan-g- Maleic anhydride**

Figure.5c. DSC of chitosan-g- Maleic anhydride-g-(methyl methacrylate)

Effect of polymerization variables on grafting parameters of chitosan -g – Maleic anhydride – g - (Methyl methacrylate)
Initiator concentration

Figure.6.Shows the effect of concentration of ceric ammonium nitrate (CAN) on the graft co-polymerization methyl methacrylate on to maleilated chitosan by keeping other reaction variables constant. Both grafting percentage and grafting efficiency showed an increase at first, followed by a decrease with the increase of the initiator concentration.

The increase of grafting percentage may be ascribed to the increase of macro radicals generated by the attack of more CAN for the saccharide unit of maleilated chitosan and therefore, the more active sites of maleilated chitosan reacting with methyl methacrylate. When the concentration of CAN was further increased more than 1.6g/10ml HNO_3, the concentration of radicals increased and consequently initiated more of the homopolymerization of a methyl methacrylate, which was resulted in the decrease of both GP% and GE%.
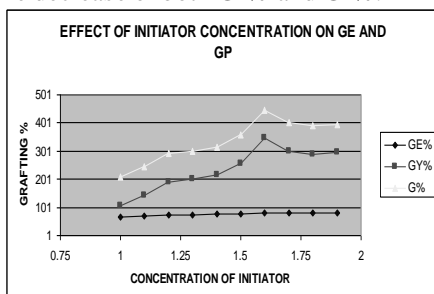

Figure.6. Effect of initiator concentration

Effect of Monomer concentration

The effect of monomer concentration on grafting parameters GE and GY shows in figure.7, which indicates an initial increase, followed by a decrease with the increase of monomer charged.

The maximum is reached when the weight of methyl methacrylate is 2g. The increasing tendency is ascribed to the accumulation of monomer molecules in close proximity to the maleilated chitosan backbone due to the increase in monomer concentration. As the graft co-polymerization progress the depletion of the available monomer, as well as reduction in the active sites on the backbone, results in a decrease of both GE and GY.

The continuous decrease of GP with the increase of methyl methacrylate concentration could be associated with the fact that more monomer molecules are helpful for homo polymerization than for graft co polymerization.
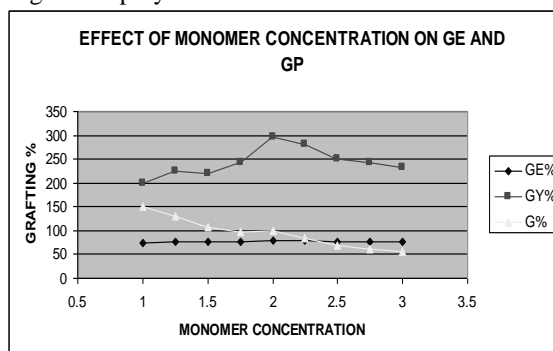

Figure.7. Effect of monomer concentration
Effect of Reaction temperature

The effect of reaction temperature on graft co-polymerization of methyl methacrylate on to maleilated chitosan was showed in figure.8 and investigated by changing the temperature from 40 to 90^0c, while keeping other reaction variables constant. It shows that both GP and GE reached a maximum at 70^0c. When the reaction temperature was low the graft co- polymerization was did not progress readily. A higher temperature was helpful in increasing the chance of collision for CAN and maleilated chitosan, which led to the increase of maleilated chitosan radicals and therefore enhanced the graft Co- polymerization. On the other hand, GP and GE decreased with a further increase in temperature, probably due to the greater possibilities of termination and chain transfer at a relatively higher reaction temperature.
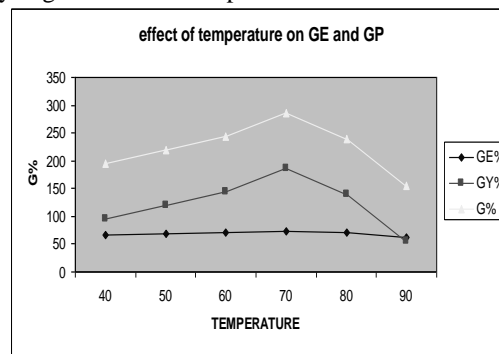

Fig.8. Effect of temperature

Table.1 represents the physico – chemical parameters and heavy metal content of the dyeing industry effluent collected from an industry from Ranipet industrial area. All the parameters along with the heavy metal contents were found to be high than the accepted limits.

Effect of Adsorbent dose in dye industry effluent treatment

Various dosages of the prepared chitosan - g - maleic anhydride - g – (methyl methacrylate) have been used to treat dye effluent. The parameters such as COD, TS, BOD, and ions such as chloride, sulphate and also heavy metals such as copper, chromium, cobalt and zinc have been decreased drastically with the increase in the adsorbent dosage. The purification of water has been found at minimum amount of sample required (5mg/L). Hence 5 mg was found to be the optimum dosage of graft co-polymer in treating the effluent time (Singh et al., 2009).

Effect of time in dye industry effluent treatment

Table.3 represents the effect of time on the treatment of dye effluent by the chitosan –g – maleic anhydride – g – (methyl methacrylate). On increasing the time the initial dye concentration reduces. After the treatment for 5 hrs all parameters reduced to the maximum extent. Hence 5 hrs was found to be an optimum treatment time (Guinesi and Cavalheiro, 2006).

Effect of pH in dye industry effluent treatment

Table. 4 represent the effect of pH on dye effluent treatment. The reduction of all the parameters in the effluent by the grafted co-polymer was found to be pH dependant. Results showed that the there was maximum adsorption of all the parameters in the effluent by chitosan- g- maleic anhydride- g – (methyl methacrylate) at pH 6.

Adsorption isotherm

The relationship between adsorbed metal concentration and concentration of the solution at equilibrium is described by isotherm models, of which Langmuir and freunlich are the most widely referred equations.langmuir model is a representative of monolayer adsorption occurring, on an energetically uniform surface on which the adsorbed molecules are not interactive (Baroni et al., 2008; Singh and Pant, 2004). Accordingly, equilibrium is attained once the monolayer is completely saturated (Dubey and Gopal, 2007).

The equilibrium studies were carried out for chitosan -g - maleic anhydride -g –(methyl methacrylate) toward copper and chromium ions in dye effluent at the pH value of optimum adsorption (pH = 6) and with the necessary contact time to reach the adsorption equilibrium of each metal. The linearization according to the Langmuir model of adsorption isotherm for copper and chromium ions by this graft co-polymer is shown in figure (9 –12). The results obtained from the adsorption isotherms according to the Langmuir model are given in table.5. The linearization according to the Langmuir model of adsorption isotherms for copper and chromium ions by this graft co-polymer show a good correlation

Langmuir sorption isotherm

The Langmuir model, which is one of the most widely used, was initially proposed for the adsorption of a gas on the surface of a solid, nevertheless it has been extended to include the sorption of solid at a solid – liquid interface. The Langmuir model suggests that the sorption occurs on the surface of the solid that is made up of elementary sites, each of which can adsorb one sorbate molecule, i.e. Monolayer sorption. It was also assumed that every sorption site is equivalent and the ability of sorbate to get bound there is independent of whether (or) not the neighboring sites are occupied (Langmuir, 1918).

The Langmuir model is given as follows,

$$Qe = Q^0bCe/1+bCe \qquad \text{---------- (1)}$$

The linearised form is,

$$Ce/qe = 1/Q^0b + Ce/Q^0 \qquad \text{------------- (2)}$$

Where, qe (mg/g) and Ce (mg/L) are the sorbed metal ion on the sorbent and the metal ion concentration in the solution at equilibrium b (L/mg) is the constant related to the affinity of binding sites. Q^0 (mg/g) is known as the Langmuir constant, which represents the monolayer sorption capacity. In general for good sorbents, high values of Q^0 and low values of b are required (Kratochvil and Volesky, 1998). The calculated values are reported in the table.5
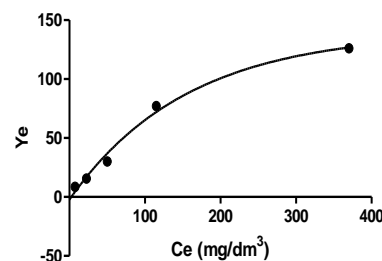
Figure.9. Effect of initial concentration on the adsorption of Copper by chitosan – g – Maleic anhydride – g – (Methyl methacrylate)
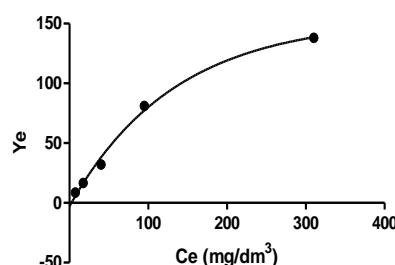
Figure.10. Effect of initial concentration on the adsorption of Chromium by chitosan – g – Maleic anhydride – g – (Methyl methacrylate)
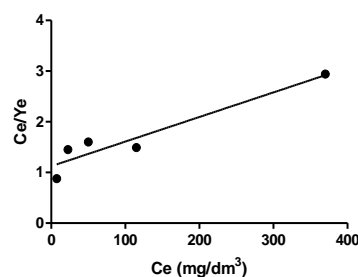
Figure.11. Langmuir adsorption of Copper by chitosan – g – Maleic anhydride – g – (Methyl methacrylate)

The affinity between adsorbate and adsorbent can be predicted using the Langmuir parameter to form the dimensionless separation factor R_L

$$R_L = 1/1+bC_o. \qquad \text{---------------- (3)}$$

Where C_o is the initial metal ion concentration and b is the Langmuir isotherm constant, the adsorption process as a function of R_L.

Figure.12. Langmuir adsorption of Chromium by chitosan – g – Maleic anhydride – g – (Methyl methacrylate)

Freundlich sorption isotherm

The freundlich isotherm model, which is also very widely used. The freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, and/ or interactions between sorbed species (Freundlich, 1907).

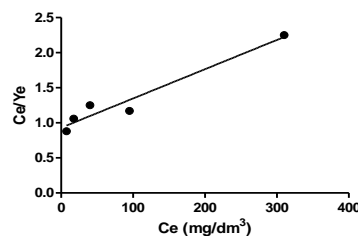The freundlich model can be expressed by,

$$Qe = K_F Ce^{1/n.} \qquad \text{---------------} \quad (4)$$

$$\log qe = \log K_F + 1/n \log Ce. \qquad \text{--------} \quad (5)$$

Where, K_F and n represent the freunlich constants. K_F is indicative of the relative sorption capacity, where n is the measure of the nature and strength of the sorption process and the distribution of active sites. Using mathematical calculation that n values between 1 and 10 represent beneficial sorption (Febrianto et al., 2009).
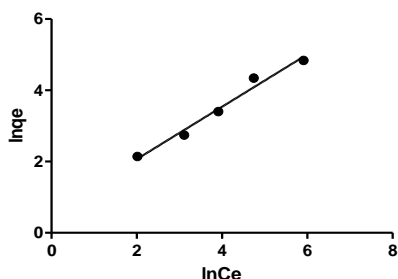

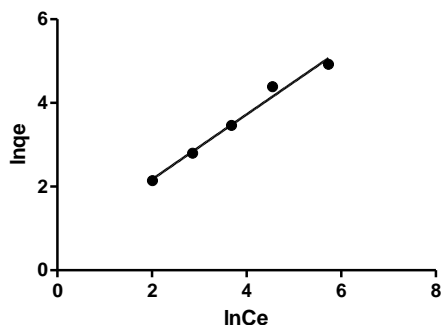**Figure.13. Freundlich adsorption isotherm for copper**

Figure.14. Freundlich adsorption isotherm for chromium

According to the regression coefficients proved that the correlation of freunlich model was strong with respect to the Langmuir model.

Dubinin – Radushkevich sorption isotherm

Dubinin – Radushkevich model (Dubinin and Radushkevich, 1947) is postulated within a sorption space close to the sorbent surface to evaluate the sorption free energy and to help to determine the nature of bonding either physisorption (or) chemisorptions. The D – R model can be expressed,

$$qe = qm \exp (-k\varepsilon^2) \qquad \text{------------} \quad (6)$$

$$\ln qe = \ln qm - k\varepsilon^2 \qquad \text{------------} \quad (7)$$

Where, qm is the maximum adsorption capacity (mg/g). K is a constant related to the energy of adsorption and ε is the Polanyi potential which is calculated (Sarin and Pant, 2006; Ramnani and Sabharwal, 2006; Quintelas et al., 2008).

$$\varepsilon = RT \ln (1+ 1/Ce) \qquad \text{--------} \quad (8)$$

R is the gas constant (0.08314 KJ/mol/K) and T is the absolute temperature in Kelvin. From figure.15&16 the isotherm constants qm and k were calculated from the slope and intercept of the plot of lnqe Vs ε^2. The value of k was calculated as mean free energy of adsorption (E) was calculated using the value of k.

$$E = (2k)^{-0.5} \qquad \text{-------------} \quad (9)$$
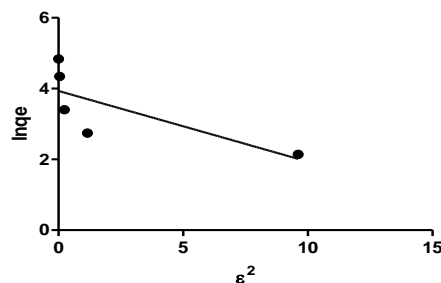
Figure.15. D – R adsorption isotherm for copper
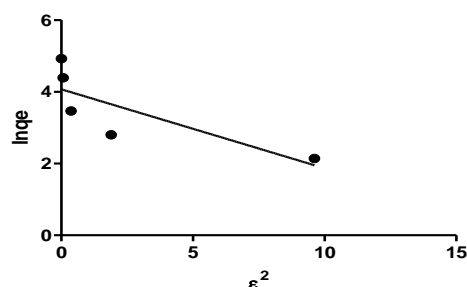
Figure.16. D – R adsorption isotherm for chromium

Accordingly, the value of E for copper and chromium are 0.3565 and 0.3503KJ/mol respectively. The common regard about E is that it depicts adsorption by ion exchange, when its value is between 8 and 15 KJ/mol. The value of E calculated in this study is substantially lower than 8KJ/mol, indicating that the adsorption of copper and chromium on chitosan graft co polymer occurs via physisorption due to vanderwaals forces (Sari and Tuzen, 2008; Singh and Pant, 2008).

Temkin adsorption isotherm

The temkin isotherm equation (Temkin and Pyzher, 1940) contains a factor that explicitly takes in to account adsorbing species – adsorbate interactions. It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate – adsorbate repulsions and the adsorption involves a uniform distribution of maximum binding energy. In addition, it assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the freundlich equation. The temkin isotherm has commonly been written in the following form,

$$q = RT/b_{Te} \ln (a_{Te}C_e) \qquad \text{--------------} \quad (10)$$

$$q = RT/b_{Te} \ln a_{Te} + RT/b_{Te} \ln C_e \qquad \text{--------------} (11)$$

Where, T is the absolute temperature in Kelvin, and R is the universal constant. The constant b_{Te} is related to the heat of adsorption (J/mol), and a_{Te} is the equilibrium binding constant (L/g) corresponding to the maximum binding energy.

Figure.17. Temkin adsorption isotherm for copper

Figure.18. Temkin adsorption isotherm for chromium

The heat of adsorption (b_{Te}) for copper is 78.85J /mol and for chromium is 68.85 J/mol. The maximum binding energy (a_{Te}) for copper is 10.00 and for chromium is 9.36 L/g.

Intra particular diffusion

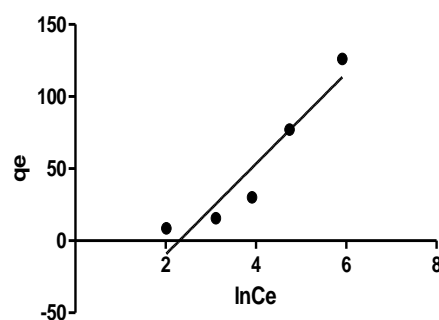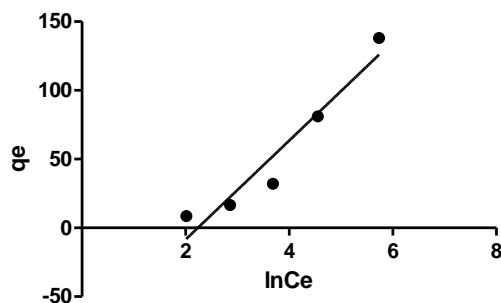In terms of kinetics numerous models have been investigated among which we have the Intraparticulate diffusivity model. Kinetics of adsorption is one of the important characteristics defining the efficiency of adsorption. The study of adsorption dynamics describes the solute uptake rate and evidently the rate control the resident time of adsorbate uptake at the solid-solution interface. The adsorption rate constant can be used to compare the performance of activated carbons (Demirbas *et al.,* 2005). Various adsorption kinetic models have been adopted to describe the behaviour of batch biosorption processes under different experimental conditions. Sorption kinetics are however controlled by different steps including solute transfer to the sorbent particle surface, transfer from the sorbent particle surface to the intra particle active sites and retention on these sites via sorption, complexation and intraparticle precipitation phenomena. Contribution of intra particle diffusion mechanism can be tested by applying the Weber and Morris equation. According to one of the intraparticle diffusion equation, for intra particle diffusion mechanism, the plot of qt versus $t^{0.5}$ should be linear. If the plots are not totally linear, and more so do not pass through the origin, then intraparticle diffusion could not be the only mechanism involved.

Sorption Efficiency

The distribution coefficient of an adsorbent is defined as the ratio of the metal ion adsorbed to the amount in the liquid phase. Values of the distribution coefficient lower than 1.0 shows low sorption efficiency. In this study the values of distribution coefficient is higher than 1.0 as presented in table.9&10. The estimated values of the distribution coefficient indicated high efficiency of the chitosan graft co polymer for the treatment of wastewater containing Cu (II) and Cr (VI) ions (Bamgbose et al., 2010).

Thermodynamics

The thermodynamic property, Gibbs free energy was calculated by the following,

$$\Delta G^0 = - 2.303 \; RT \; \log C_{ad}/C_{eq}. \qquad \text{------------ (12)}$$

The ΔG^0 value of Cu (II) and Cr (VI) were -168.55 and -214.68 respectively. The negative value of Gibbs free energy indicates the spontaneous nature of adsorption process (Hamadi et al., 2001).

Conclusion

The graft co-polymer of N -maleilated chitosan -g-(Methyl methacrylate) was synthesized through homogeneous graft co-polymerization of methyl methacrylate on to N- Maleilated chitosan in aqueous solution using ceric ammonium nitrate as initiator. The impact of polymerization variables including initiator concentration, monomer concentration and reaction temperature on grafting parameters were investigated.

FTIR, XRD, TGA, DSC analyses confirmed the introduction of the Methyl methacrylate side chain in to the N-maleilated chitosan backbone by graft co-polymerization. The effects of dosage, time and pH of the medium on adsorption efficiency of graft co-polymer were studied for wastewater dye effluent. A significant result has been found for the industrial application. Hence the chitosan-g-maleic anhydride-g- (methyl methacrylate) can be used for waste water treatment at industrial level.

References

Aksu Z. Application of biosorption for the removal of organic pollutants: a review. Process Biochem. 2005; 40: 997-1026.

Alves NM and Mano JF.Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications. International Journal of biological macromolecules.2008; 43: 401-414.

AnsarAli Z, Jeyachandran Venkatesan, Se Kwon Kim and Sudha PN.Beneficial effects of chitosan – g – polyacrylamide copolymer in removal of heavy metals from industry dye effluents. International Journal Environmental Science.2011; 1(5): 820-833.

Babel S and Kurniawan TA.Low-cost adsorbents for heavy metals uptake from contaminated water: a review. Journal of Hazardous Materials.2003; B97: 219-243.

Bamgbose JT, Adewuji S, Bamgbose O and Adetoye AA. Adsorption kinetics of cadmium and lead by chitosan. African Journal of Biotechnology.2010; 9(17): 2560 – 2565.

Baroni P, Vieira RS, Meneghetti E, Da Silva MGC and Beppu MM.Evalution of batch adsorption of chromium ions on natural and cross linked chitosan membranes.Journal of Hazardous Materials.2008;152:15-1163.

Bhattachariya A and Misra BN.Grafting: A Versatile means to modify polymers techniques factors and applications. Programme Polymer Science.2004; 29: 767-814.

Boddu V, Abburi K, Talbott JL and Smith ED.Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent. Environmental Science Technology.2003; 37: 4449-4456.

Crini G. Recent developments in polysaccharide - based materials used as adsorbents in wastewater treatment. Programme Polymer Science.2005; 30: 38 -70.

Crini G. Non-Conventional low-cost adsorbents for dye removal; a review. Bioresource Technology.2006; 60: 67-75.

Demirbas A. Adsorption of Cr (III) and Cr (VI) ions from aqueous solutions on to modified lignin. Energy Sources.2005; 27(15); 1449-1455.

Dubey SP and Gopal K. Adsorption of chromium (VI) on low cost adsorbents derived from agricultural waste material: a comparative study. Journal of Hazardous Materials.2007; 145:465-470.

Dubinin MM and Radushkevich LV. Equation of the characteristics curve of activated charcoal. Chemisches Zentralblatt. 1947; 1:875 -889.

Febrinto J, Kosasih AN, Sunarso J, Jua, Yi- H, Indraswati N and Ismadiji S. Equilibrium and kinetics studies in adsorption of heavy metals using biosorbents: A summary of recent studies. Journal of Hazardous Materials. 2009; 162(2-3): 616- 645.

Forgacs E, Cserhati T and Oros G. Removal of synthetic dyes from wastewaters: a review. Environment International.2004; 30: 953-971.

Freundlich HMF. Uber die adsorption in losungen. Zeitschrift Fur Physikalische Chemie (Leipzig). 1907; A57: 385 – 470.

Guinesi LS and Cavalheiro ÉTG. The use of DSC curves to determine the acetylating degree of chitin/chitosan samples. Thermochimica Acta.2006; 444(2): 281-283.

Hamadi NK, Chena XD, Farid MM and Lub MGQ. Adsorption kinetics for the removal of chromium (VI) from aqueous by adsorbents derived from used tyres and sawdust. Chemical Engineering Journal. 2001; 84: 95- 105.

Hirano S.Chitin and chitosan as novel biotechnological materials. Polymer International.1999; 48:732 -734.

Jinchen Fan, Jie Chen, Liming Yang, HanLin and Fangqi Cao.Preparation of dual sensitive graft copolymer hydrogel based on N – Maleoyl – Chitosan and poly (N- iso propyl acrylamide) by electron beam radiation. Bulletin of Material Science.2009; 32 (5): 521 – 526.

Kas HS.Chitosan, Properties, preparation and applications to micro particulate system. Journal of Microencapsulation.1997; 14: 689 – 711.

Khor E. Chitin, A biomaterials in waiting, Current Opinion in solid state. Material Science. 2002; 6: 313 – 317.

Kozlowski CA and Walkowiak W. Removal of chromium (VI) from aqueous solutions by polymer inclusion membranes. Water Resource.2002; 36: 4870-4876.

Kratochvil D, Pimentel P and Volesky B. Removal of trivalent and hexavalent chromium by seaweeds: kinetics and mechanism studies. Environmental science and Technology. 1998; 32:2693 – 2698.

Kurita K, Kojima T, Munakata T, Akao H, Mori T and Nishiyama Y. Preparation of non natural branched chitin and chitosan. Chemistry Letters.1998; 27: 317 – 318.

Kurita K.Controlled functionalization of polysaccharide chitin. Programme Polymer Science.2006; 26: 1921 – 1974.

Langmuir I. Adsorption of gases on plane surface of glass, mica and platinum. Journal of American Chemical Society.1918; 40:1361 – 1403.

McKay G, Blair HS and Findon A. Equilibrium studies for the sorption of metal ions on to chitosan. International Journal of Chemistry.1989; A28:356-360.

Mohan D and Pittman Jr CU.Activated carbons and low cost adsorbents for remediation of tri and hexavalent chromium from water. Journal of Hazardous Materials.2006; B137: 762-811.

Muzzarelli RAA. Editor. Natural Chelating Polymers. Pergamon Press.1973; Newyork. 83.

Nomanbhay SM and Palanisamy K. Removal of heavy metals from industrial wastewater using chitosan coated oil palm shell charcoal.Elect.J.Biotechnol.2005; 8: 43-53.

Peter MG.Chitin and chitosan from animal sources, in; Biopolymers, (Polysaccharides II).2002; De Baets S., Vandamme E.J. and Steinbuchel .A, (Eds) Wiley – VCH, Weinheim, 2, ch. 15.

Quintelas C, Fernandez, Castro J, Figueiredo H and Tavaren, T.Biosorption of Cr (VI) Bacillus Coageelans bio film supported on granular activated carbon (GAC). Chemical Engineering Journal. 2008; 136: 195 – 203.

Ramnani SP and Sabharwal S. Adsorption behaviour of Cr (VI) onto radiation cross linked chitosan and its possible application for the treatment of wastewater containing Cr (VI). Reactive and Functional Polymers. 2006; 66:902-909.

Ravikumar MNV. A Review of chitin and chitosan applications. Reactive and Functional Polymers.2000; 46: 1-27.

Ravikumar MNV, Muzzarelli RAA, Muzarelli C, Sashiwa and Domb AJ.Chemical Reviews.2004; 104(12): 6017-6084.

Rio S and Delebarre A. Removal of mercury in aqueous solution by fluidized bed plant fly ash. Fuel.2003; 82:153-159.

Sanford PA. Skjak – Braek G, Anthonsen T and Sanford PA. (Eds). Chitin and chitosan - sources, chemistry, Biochemistry, Physical properties and Applications.1989; Elsvier, London.51-70.

Sari A and Tuzen M. Biosorption of total chromium from aqueous solution by red algae (Ceramium Virgatum): Equilibrium, kinetics and thermodynamic studies. Journal Hazardous Materials. 2008; 160(2-3): 349 – 355.

Sarin V and Pant K.K. Removal of chromium from industrial waste by using eucalyptus bark. Bioresource Technology. 2006; 97(1): 15 – 20.

Singh TS and Pant KK. Equilibrium, kinetics and thermodynamic studies for adsorption of As (III) on activated alumina. Separation and PurificationTechnology.2004; 36: 139-147.

Singh V, Sharma AK and Sanghi R.Poly (acrylamide) functionalized Chitosan: An efficient adsorbent for azo dyes from aqueous solutions. Journal of hazardous materials.2008; 166(1): 327-335.

Singh V, Sharma AK, Tripati DN and Sanghi R.poly (Methyl methacrylate) grafted chitosan; an efficient adsorbent for anionic azo dyes. Journal of Hazardous Materials.2009; 161: 955-956.

Temkin MJ and Pyzhev V.Kinetics of ammonia synthesis on promoted iron catalysts.Acta Physiochim.1940; URSS12: 217-222.

Tian Ying Guo, Yong Qing XIA Guang Jie Hao Bang Hua Zhang .Chemically modified chitosan beads as molecularly imprinted polymer matrix for adsorptive separation of proteins. Chinese Chemical Letters.2004; 15(11): 1339-1341.

Van Luyen D, Huong D – M.Chitin and Derivatives, in; Polymeric Materials Encyclopedia.1996; Salamone J.C. (Eds), CRC, Boca Raton (Florida), 2: 1208-1217.

Wan Ngah WS, Endud CS and Mayanar R.Removal of copper (II) ions from aqueous solution onto chitosan and cross linked chitosan beads. Reactive and functional polymers.2002; 50 (2): 181-190.

Table.1 Physico-chemical characteristics of the dyeing Industry effluent

Parameters	Dyeing effluent	Optimum levels (MINAS)
PH	7.8	7.0-9.0
EC dsm^{-1}	14.5	0.68
TDS mg/L	6750	462
TSS mg/L	1460	111
BOD mg/L	1475	400
COD mg/L	4575	421
K mg/L	745	100
Ca mg/L	740	26
Na mg/L	1450	200
Mg mg/L	1100	84
Zn mg/L	420	5.0
Cu mg/L	270	3.0
Co mg/L	76	0.2
Cr mg/L	650	2.0

Table.2. Effect of adsorbent dose of Chitosan – g – Maleic anhydride – g –(Methyl Methacrylate) on the physico-chemical factors and metals of the dyeing industry effluent

Parameters	Effluent	Adsorbent dose				
		1 g	2 g	3 g	4 g	5g
EC dsm^{-1}	14.5	11.2	9.4	7.4	5.6	3.1
TDS(mg/L)	6750	3215	1705	1115	840	310
TSS (mg/L)	1460	745	360	205	111	50
BOD (mg/L)	1475	635	411	215	96	75
COD (mg/L)	4575	1945	890	410	117	96
K (mg/L)	745	270	110	76	45	30
Ca (mg/L)	740	376	210	148	110	65
Na (mg/L)	1450	510	250	110	76	45
Mg (mg/L)	1100	650	410	275	115	59
Zn (mg/L)	420	375	114	81	50	25
Cu (mg/L)	270	119	74	35	15	9
Co (mg/L)	76	24	11	8	5.1	3.5
Cr (mg/L)	650	110	50	25	11	7

Table.3. Effect of contact time of Chitosan – g - Maleic anhydride - g – (methyl methacrylate) on the physico-chemical factors and metals of the dyeing industry effluent

Parameters	Effluent	Contact time in min				
		60	120	180	240	300
EC dsm^{-1}	14.5	8.5	5.2	3.1	1.6	1.5
TDS(mg/L)	6750	4200	2100	1175	750	254
TSS (mg/L)	1460	825	375	210	97	75
BOD (mg/L)	1475	750	450	175	135	130
COD (mg/L)	4575	2100	1050	750	210	150
K (mg/L)	745	300	120	70	45	40
Ca (mg/L)	740	350	250	150	120	100
Na (mg/L)	1450	270	150	121	75	62
Mg (mg/L)	1100	710	510	312	214	210
Zn (mg/L)	420	112	75	44	35	30
Cu (mg/L)	270	119	69	45	44	44
Co (mg/L)	76	35	20	11	9.5	9.0
Cr (mg/L)	650	110	65	35	19	12

Table.4. Effect of pH of Chitosan – g - Maleic anhydride - g – (methyl methacrylate) on the physico-chemical factors and metals of the dyeing industry effluent

Parameters	Effluent	pH				
		5	6	7	8	9
EC dsm^{-1}	14.5	8.0	2.3	2.7	3.7	5.9
TDS(mg/L)	6750	2740	235	790	1255	2100
TSS (mg/L)	1460	475	79	110	225	375
BOD (mg/L)	1475	440	175	155	190	450
COD (mg/L)	4575	1010	180	240	770	1050
K (mg/L)	745	220	70	82	95	120
Ca (mg/L)	740	310	110	140	175	250
Na (mg/L)	1450	210	70	85	145	150
Mg (mg/L)	1100	520	190	275	350	560
Zn (mg/L)	420	82	40	55	64	79
Cu (mg/L)	270	90	42	45	51	67
Co (mg/L)	76	35	9.2	19	21	35
Cr (mg/L)	650	90	15	25	37	72

Table.5. the Langmuir constants for Chitosan – g – Maleic anhydride – g – (Methyl methacrylate) co polymer for Chromium and Copper at equilibrium

Metal ion	Langmuir constants		
	$K_L (dm^3.g^{-1})$	$b (dm^3.mg^{-1})$	$C_{max} (mg.g^{-1})$
Copper(II)	1.123	0.004854	231
Chromium (VI)	0.9298	0.004172	222

Table.6 R_L values for copper

Initial concentration of Cu(II) in (mg/l)	R_L
200	0.5074
100	0.6732
40	0.8373
20	0.9115

Table.7. R_L values for chromium

Initial concentration of Cr(VI) in (mg/l)	R_L
200	0.5451
100	0.7056
40	0.8570
20	0.9229
10	0.9599

$R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable, $R_L = 0$ Irreversible.

Table. 8. Freundlich constants for copper and chromium

Metal ion	Freundlich constants		
	$K_f (mg/g)$	n	R^2
Copper(II)	3.9536	1.360	0.9779
Chromium (VI)	4.136	1.287	0.9840

Table.9. Equilibrium sorption of metal ions on chitosan – g – Maleic anhydride – g – (Methyl methacrylate) at 25^0c pH 6

Initial concentration of metal ions (mg/l)	Metal ion adsorbed (mg/l)	
	Cu(II)	Cr(VI)
200	126	138
100	77	81
40	30	32
20	15.5	16.5
10	8.5	8.5

Table.10 Distribution coefficient (Kd) of metal ions at 25^0c

Metal ions	Equilibrium concentration of metal ion (mg/l)	Distribution coefficient Kd
Cu(II)	74 – 1.5	1.7027 – 5.6666
Cr(VI)	62 – 1.5	2.2258 – 5.6666