Chapter 2

Adsorption of Chromium from aqueous solutions using Chitosan-modified Diethylenetriaminepentaacetic acid and Trimesic Acid

2.1 Introduction

Bio-adsorption using agro-waste/biomass and biopolymers has been adopted as an effective method to remove chromium and other toxic metals from aqueous environment (Abdel-ghani & El-chaghaby, 2014; Ngah, Endud, & Mayanar, 2002; Qian, Huang, Jiang, He, & Wang, 2000). During the past three decades, the use of Chitosan (CH) as a bio-adsorbent has been gaining increased attention (Dash, Chiellini, Ottenbrite, & Chiellini, 2011). because of abundant free amino and hydroxyl groups on its backbone (Bhatnagar & Sillanpää, 2009). Further, various functional groups could be flexibly grafted onto chitosan by functionalization or derivatization (Kyzas, Kostoglou, & Lazaridis, 2009) for more effective adsorption of target pollutants. For instance, CH has been modified by different ligands such as barbituric acid, oxine, glycine, iminodiaceticacid (IDA), Ethyleneglycol-bis (2-aminoethylether)-N,N,N,N-tetraacetic acid (EGTA), Ethylenediaminetetraacetic acid (EDTA) and Diethylenetri-aminepentaacetic acid (DTPA) (Inoue, Yoshizuka, & Ohto, 1999; Kushwaha & Sudhakar, 2011; Oshita, Sabarudin, Takayanagi, Oshima, & Motomizu, 2009; Rani, Agarwal, & Negi, 2011; Repo, Warchol, Agustiono, & Sillanpää, 2010; Roosen & Binnemans, 2014; Shimizu, Izumi, Saito, & Yamaoka, 2004; Yoshizuka, 1998; Zhao, Repo, Yin, & Sillanpää, 2013).

Evelina Repo et al. have used EDTA-modified CH for the removal of Co^{2+} in the presence of EDTA and other interfering species from aqueous solutions (Repo, Koivula, Harjula, & Sillanpää, 2013). They also had modified CH-silica hybrid with EDTA and used it as adsorbent for the removal of cobalt, nickel, cadmium and lead ions from aqueous solutions (Repo, Warchoł, Bhatnagar, & Sillanpää, 2011). They further had reviewed the use of amino polycarboxylic acid functionalized adsorbents for the removal of heavy metals from water (Repo, Warchoł, Bhatnagar, Mudhoo, & Sillanpää, 2013). CH grafted with poly(ethylene imine) and cross-linked with epichlorohydrin has been used by Kyzas et al. for the simultaneous removal of a reactive dye and Cr^{6+} (Kyzas, Lazaridis, & Kostoglou, 2013). They also had investigated the potential of N-(2-carboxybenzyl) grafted CH for the removal of both toxic metal cations (Cu^{2+}, Ni^{2+}) and metal anions (Cr^{6+}, As^{5+}) from aqueous solutions as well as succinyl grafted CH for the removal of zinc and cationic dye

from binary mixtures (Kyzas, Kostoglou, Lazaridis, & Bikiaris, 2013; Kyzas, Siafaka, Pavlidou, Chrissafis, & Bikiaris, 2015).

DTPA also known as pentetic acid has been used as the calcium, zinc or trisodium salt to exchange calcium or zinc ions for almost all metals with a higher binding capacity (G. Anderegg, 1977; Giorgio Anderegg, 1982; De Stefano, Gianguzza, Milea, Pettignano, & Sammartano, 2006; Martell, Smith, & Motekaitis, 2004; Pettit & Powell, 1997; Stefano, Gianguzza, Pettignano, & Sammartano, 2011). The salts are USFDA approved reagents and have been used in Europe and USA (Menetrier et al., 2005) as chelating agents for heavy metals and as decorporation agents for radio nuclides.

Zarebsiki used DTPA for the determination of trace levels of Cr^{3+} using several polarographic techniques (Bobrowski, Krolicka, & Zarebski, 2009). This method has been improved using a hanging mercury drop electrode (HMDE) for the speciation analysis of chromium in different media. The complexation of Cr^{3+} and Cr^{6+} with diethylenetriaminepentaacetic acid (DTPA), the redox behaviour of these complexes and their adsorption on the mercury electrode surface were investigated by Sander et al. using electrochemical techniques and UV-Vis spectroscopy (Sander, Navrátil, & Novotný, 2003). DTPA-modified CH (CD) as well as silica gel have been used by Evelina Repo et al. for the removal of cobalt as its EDTA complex (Repo, Malinen, Koivula, Harjula, & Sillanpää, 2011). However, the adsorption potential of CD for chromium has not been studied earlier. Bearing these factors in mind it was felt that chemical modification of CH with Diethylentriaminepentaacetic acid (DTPA) may result in an adsorbent for Chromium with interesting binding properties. Our objective was thus to modify chitosan using DTPA (CD) and study its potential for adsorption of Cr^{6+} as well its reduction to Cr^{3+}.

Coordination polymeric frame works with their intriguing variety of architectures and topologies, as well as potential applications in luminescence, nonlinear optics, porous materials, gas storage and catalysis (Batten & Robson, 1998; Braga, 2003; Cu et al., 2002; Eddaoudi et al., 2001; Hagrman, Hagrman, & Zubieta, 1999; James, 2003; Leininger, Olenyuk, & Stang, 2000; Moulton & Zaworotko, 2001; Subramanian & Zaworotko, 1994) have been of current interest to researchers. The construction of molecular architecture depends on the combination of several factors, such as the solvent systems, the templates, the temperatures, the counter ions, the ratio of ligands to metal ions, coordination geometries of central metals and organic ligands (Carlucci, Ciani, W. v. Gudenberg, Dorothea Proserpio, & Sironi, 1997; Hirsch, Wilson, Moore, Avenue, & February, 1997;

Munakata, Wu, Kuroda-sowa, & Maekawa, 1997; Suenaga et al., 1998). In this regard, the organic anions play important roles in directing the final structures and topologies of their coordination polymers. Benzoic multi carboxylate ligands are versatile building blocks for the construction of polymeric structures (Choi & Suh, 1998; Cotton et al., 1999; Yaghi, Li, & Li, 1995).

Trimesic acid (1,3,5-benzenetricarboxylic acid) TMA, a planar and highly symmetrical trifunctional compound having three equally spaced carboxylate groups with a 120° angle between two carboxylic groups, is a suitable candidate for the formation of hydrogen-bond networks in metal-organic coordination polymers because it can act as both hydrogen-bond donor and acceptor via three carboxylic acid groups at the same time (D. Cheng, Khan, & Houser, 2001; Dai et al., 2002; Ding et al., 2005; Kepert, Prior, & Rosseinsky, 2000; Ko, Min, & Suh, 2002; H. Li, Eddaoudi, O'Keeffe, & Yaghi, 1999; Pan et al., 2001). TMA can exhibit different types of binding modes, resulting in various 3D structures (Holmes, Kelly, and Elsegood 2004; Wanru Zhang. Sandra Bruda, christopher P. Landee, Judith L. patent 2003; Ying and Mao 2005).

Trimesic acid has proved to be a widely used in metal-organic framework research. Due to its rigidity and strong co-ordination ability of three equally spaced carboxylate groups, metal centres can strongly bind with it. TMA thus acts as a multidentate ligand for various divalent and trivalent metal ions (Ying & Mao, 2005). The co-ordination behaviour of TMA with Cu^{2+} ion has been reported by Zhang et al. (W. Zhang et al., 2003). A great deal of effort has been devoted to the synthesis of coordination polymers, porous metal-organic frameworks assembled from H_3BTC and metal cations (Ying and Mao 2005, Chui et al. 1999; Luo, Che, and Zheng 2008; Yaghi, Li, and Groy 1996). MIL-100(Cr) ($Cr_3F(H_2O)_3O[C_6H_3\text{-}(CO_2)_3]_2 \cdot nH_2O$ (n~28)), with a zeolite-type architecture built up from carboxylate moieties (benzene-1,3,5-tricarboxylate (btc)) and trimeric Cr^{3+} octahedral clusters, were synthesized by Ferey et al. (Férey et al., 2004).

In this series, chromium could be replaced by Fe to isolate the isostructural solid MIL-100(Fe) (Horcajada et al., 2007). The preparation and structure of analogues of MIL-96 structural type (MIL-96(Al), MIL-96(Ga), MIL-96(In)) were first described by Loiseau in 2006 and later Volkringer et al (Loiseau et al., 2006; Volkringer et al., 2007).

Recently TMA was used as an adsorbent for toxic cations and gaseous pollutants. P. Long et al. (Long et al., 2011) used alumina supported by benzene-1,3,5-tricarboxylic acid (trimesic acid, TMA) as an adsorbent material for the adsorption of toxic Cu^{2+} ion. Saha et

al. used this aromatic acid as an adsorbent for divalent toxic Cu^{2+} ions from wastewater after coating trimesic acid onto the surface of basic alumina as solid support (B. Saha, Chakraborty, & Das, 2008). More recently Wang et al prepared a cauliflower-like MIL-100(Cr), through simple reflux and used it for simultaneous determination of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} (D. Wang et al., 2015).

Cu-BTC as MOFs have attracted attention due to its amenable features as a sorbent for the extraction of pollutants in aqueous solution, such as high surface area, uniform pore size, accessible coordinative unsaturated sites, and excellent chemical and solvent stability Cu-BTC has been used for gas adsorption and removal of chromium (Maleki, Hayati, Naghizadeh, & Joo, 2015).

However there are no reports on the modification of biopolymer with trimesic acid its use for uptake of chromium. We thus also directed our efforts towards modification of chitosan with trimesic acid(CTMA) and investigation of its potential for the removal of chromium.

2.2 Materials and Methods.

2.2.1 Materials

All the reagents used were of AR grade. CH around 87% deacetylated (Sigma Aldrich, USA), DTPA (National Chemicals, INDIA) and Trimesic Acid (Sigma Aldrich, USA) were used as such without further grinding and sieving.

2.2.2 Synthesis of the adsorbents CD and CTMA

A 100 ml of 1% CH in 1% acetic acid solution was added to 100 ml of 0.5 M solution of DTPA/0.1 M solution of TMA dissolved in 0.41 M NaOH and stirred for 24 hrs for the formation of CD/CTMA. The pH was 12. A white gel material was formed which was then filtered, washed with double distilled water to neutral and dried overnight in vacuum oven at 30°C. The material was then crushed well and sieved with mesh size of 180 microns for obtaining uniform size of adsorbent.

2.2.3 Preparation of adsorbate solutions

Stock solution of 1000ppm Cr^{6+} was prepared by dissolving 5.6653g of AR grade potassium dichromate (99.92% assay) in 1L of double distilled water. Working standards were prepared by diluting different volumes of the stock solution to obtain the desired concentration.

2.2.4 Batch sorption Experiments

Batch adsorption experiments were conducted at 30°C by agitating 0.05 g of adsorbent under study(CD/ CTMA) with 25mL of Cr^{6+} solution of desired concentration at optimum pH in 100mL stoppered conical flask in a thermostated rotary mechanical shaker at 200 rpm for fixed time interval except for pH optimization experiments. The pH range at which the maximum chromium uptake occurred was determined by varying the initial pH of the solution in the range 1 to 11 using NaOH and H_2S0_4. The optimum equilibrium time was determined by varying the contact time in the range of 60 to 300 min. In each experiment, after agitation the contents of the flasks were filtered. The concentration of Cr^{6+} remaining in the solution was determined by UV Spectrophotometer (Jasco V630model) after complexation with 1,5-diphenylcarbazide (Rodman, Carrington, & Xue, 2006). The uptake of Cr^{6+} was calculated according to Eq.:

$$Q_e = \frac{(C_i - C_e)}{m}$$

where Qe represents the amount of Cr^{6+} adsorbed per gram of adsorbent and m represents the mass of adsorbent in g/L. C_i and C_e (ppm) are the initial and equilibrium (after adsorption) concentrations of Cr^{6+} in solution, respectively.

2.2.5 Equilibrium Sorption Studies

Adsorption isotherms were determined by the treatment of 0.05 g of adsorbent under study with 50ppm-1000ppm Cr^{6+} in a rotary mechanical shaker. After agitation the contents of the flasks were filtered. The concentration of metal remaining in the solution was determined. The results of experimental measurements were plotted in the form of adsorption isotherms. Attempts were made to fit the equilibrium metal sorption isotherm data to a number of well-known models like Freundlich, Langmuir, Temkin, Flory-Huggins and Halsey for the better understanding of the processes governing adsorption.

2.2.5.1 Freundlich model

The empirical Freundlich isotherm is based on the equilibrium relationship between heterogeneous surfaces. The Freundlich isotherm model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface (H.M.F. Freundlich, 1906). This equation has the following form :

$$q_e = K_f C_e^{1/n}$$

which can also be expressed in the linear logarithmic form as

$$logq_e = logK_f + \frac{1}{n} logC_e$$

Where, q_e is amount of adsorbate adsorbed at equilibrium (mg/g), C_e is Cr^{6+} concentration in solution at equilibrium (mg/L), K_f (L/mg) and *1/n* are adsorption capacity at unit concentration and adsorption intensity, respectively. In this model, the mechanism and the rate of adsorption are functions of the constants 1/n and K_F (L/g). The plot of $logq_e$ versus $logC_e$ has a slope with a value of $1/n$ and an intercept of magnitude $logK_F$. $logK_F$ is equivalent to $logq_e$ when C_e equals unity. *1/n* values indicates whether the adsorption process is irreversible ($1/n=0$), favourable ($0<1/n<1$) or unfavourable ($1/n>1$) (Bell, 1998). Larger values of *n* implies stronger interaction between adsorbent and adsorbate while $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites. This model often gives a better fit particularly for adsorption from liquids

2.2.5.2 Langmuir model

Langmuir adsorption isotherm model is usually adopted for homogenous adsorption and it is used successfully in monomolecular adsorption processes (Irving Langmuir, 1918). The Langmuir adsorption isotherm is based on the assumption that all sites possess equal affinity for the adsorbate. It may be represented in the linear form as follows (Langmuir, 1916; Schiewer & Patil, 2008):

$$q_e = \frac{K q_{max} C_e}{1 + K C_e}$$

rearranged to

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}}$$

Where q_{max} is the maximum metal uptake, mg/g, K_L the Langmuir adsorption constant, L/mg.). The linear plot of C_e/q_e *versus* C_e and the constants q_{max} and K_L can be calculated from slope and intercept of the plot. The monolayer saturation capacity is indicated by Qm. Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. This isotherm is based on three assumptions, namely adsorption is limited to monolayer coverage, all surface sites are alike and only can accommodate one adsorbed atom and the ability of a molecule to be adsorbed on a given site is independent of its neighbouring sites occupancy. The decrease of K_L value with temperature rise signifies the exothermic nature of the adsorption process (physical adsorption) (Djeribi and Hamdaoui 2008), while the opposite trend signifies chemisorption (Aydin, Bulut, and Yerlikaya 2008; Deng et al. 2006). In physical adsorption, the bonding between adsorbate and active sites of the adsorbent weakens at higher temperature while in chemisorption bonding becomes stronger.

2.2.5.3 Temkin model

Temkin considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. He suggested that, because of these interactions and ignoring very low and very large values of concentration, the heat of adsorption of all molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interaction (Vijayaraghavan, Padmesh, Palanivelu, & Velan, 2006) rather than logarithmic, as implied in the Freundlich equation. Furthermore, the Temkin isotherm model predicts a uniform distribution of binding energies over the surface binding adsorption sites (Tan, Ergene, Ada, & Katircioglu, 2008). The Temkin isotherm has generally been applied in the following linear form (M.J. Tempkin, 1940):

$$\frac{q_e}{q_m} = \frac{R_T}{\Delta Q}\mathrm{Ln}(K_T C_e)$$

$$q_e = BTlnK_t + BTlnC_e$$

where K_t (L/g) is Temkin isotherm constant, B_T (J/mol) is a constant related to heat of sorption, R is the gas constant (8.314J/mol K). A plot of q_e versus lnC_e enables the determination of the K_t and B_T from the intercept and slope. K_t is the equilibrium binding constant corresponding to the maximum binding energy and constant B_t is related to the heat of adsorption

2.2.5.4 Halsey model

This model explains multilayer adsorption. Halsey proposed an expression for condensation of a multilayer at a relatively large distance from the surface (George Halsey, 1948).

$$q_e = K_H / C_e^{1/n_H}$$

Where, k_H is Halsey constant. and the fitting of the experimental data to this equation confirms to the hetero porous nature of the adsorbent.

2.2.5.5 Flory-Huggins model

The Flory-Huggins (F-H) isotherm is chosen to account for the surface coverage characteristic degree of the sorbate on the sorbent (Vijayaraghavan et al., 2006). It expresses the feasibility and spontaneous nature of an adsorption process

$$\mathrm{Log}\frac{\theta}{C_0} = \mathrm{Log}K_{FH} + n_{FH}\mathrm{Log}(1-\theta)$$

Where, θ = (1-Ce/Co) is the degree of surface coverage, K_{FH}=Equilibrium constant, n_{FH} is the model exponent. K_{FH} and n_{FH} can be determined by plotting ln (θ/Co) versus ln (1-θ)

2.2.5.6 Elovich model

The Elovich model is based on a kinetic principle according to the assumption that the adsorption sites increase exponentially with adsorption, which implies multi-layered adsorption (S.Y. Elovich, 1962).

$$\frac{q_e}{q_m} = K_E C_e \exp - \left(\frac{q_e}{q_m}\right)$$

where k_E is Elovich equilibrium constant, qm is the Elovich maximum adsorption capacity.

2.2.6 Sorption Dynamics

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process (Kalavathy, Karthikeyan, Rajgopal, & Miranda, 2005). Information about the rate-controlling step of the adsorption process, including chemical reaction, diffusion or mass transfer, can be used to predict adsorption rate at any desired conditions which can then be used in designing and modeling of industrial adsorption operations.

The adsorption rate is known to be controlled by several factors corresponding to different processes including: (1) diffusion of the solute from the bulk of the solution to the film surrounding the absorbent particle, (2) diffusion from the film toward the particle surface (external diffusion), (3) diffusion from the surface to the internal sites (surface or pore diffusion) and (4) uptake of the adsorbate which can involve several reaction steps (Igwe & Abia, 2006).

For kinetic experiment, the Cr^{6+} solutions were equilibrated at pH 2.0 for different time intervals(30 - 300 min) for CD and CTMA respectively. The efficiency of the adsorption process was also assessed by treating the kinetic sorption data of Cr^{6+} onto CD and CTMA with pseudo-first-order, pseudo-second-order, intraparticle diffusion, Bangham and Liquid film diffusion models. The values of co-relation coefficients and standard deviation were used to compare the models. Linear regression was used to determine the best-fitting kinetic rate equation (Yuh Shan Ho, 2006).

2.2.6.1 Pseudo-first-order model

For a batch process the pseudo-first order equation (Lagergren) assumes that the rate of sorption of metal on to the adsorbent surface is proportional to the amount of metal adsorbed from the solution phase. The Pseudo-first order equation of Lagergren (Lagergren, 1898) is generally expressed as follows:

$$\frac{dq_t}{dt} = K_1(q_e - q_t)$$

where, *qe* is the amount of metal adsorbed (Uptake) at equilibrium (mg/g), q_t is the amount adsorbed (Uptake) at time *t* (mg/g), K_1 is the rate constant of first order adsorption (min^{-1}). After integration and applying boundary conditions, $t = 0$ to *t* and $q = 0$ to q_e ; the integrated form of equation (2) becomes:

$$\log(q_e - q_t) = log q_e - \frac{K_1 t}{2.303}$$

Values of adsorption rate constant (K_1) for adsorption process was determined from the straight line plot of $\log(q_e - q_t)$ against *t*. The pseudo-first-order kinetics equation can describe the initial phase in adsorption process and with the progress of adsorption, the adsorption data may deviate the fitted curve.

The equation, applicable to experimental results, generally differs from a true first-order equation in two ways (Aharoni, Levinson, Ravina, & Sparks, 1991): i) the parameter $K_1(q_e - q_t)$ does not represent the number of available sites; and ii) the parameter log q_e is an adjustable parameter which is often not equal to the intercept of a plot of $\log(q_e - q_t)$ versus *t*, whereas for a true first-order process logq_e should be equal to the intercept of a plot of $\log(q_e - q_t)$ versus *t*.

In most cases in the literature, the pseudo-first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the sorption process.

2.2.6.2 Pseudo-second-order model

The pseudo-second order kinetic model assumes that the rate of adsorption is dependent on the amount of solute adsorbed on the adsorbent surface at a time t and equilibrium as given by

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$$

Where, K_2 is the pseudo-second-order rate coefficient (g/mg min). Integrating eq. and linear equation is obtained:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e{}^2)} + \frac{t}{q_e}$$

Where $K_2 q_e^2 = h$ can be regarded as the initial sorption rate as $qt/t \rightarrow 0$

Where K_2 and *h* values were determined from the slope and intercept of the plots of *t*/*q* against *t*. the value of k_2 often depends on the applied operating conditions, namely,

initial metal concentration, pH of solution, temperature and agitation rate etc Furthermore, it is in agreement with chemisorption being the rate controlling step (Ho Yuh-Shan, 1995;):

As such, in comparison to pseudo-first-order kinetic this model is considered more appropriate to represent the kinetic data in bio-sorption systems. This tendency comes as an indication that the rate limiting step in bio-sorption of heavy metals are chemisorption involving valence forces through the sharing or exchange of electrons between sorbent and adsorbate (Bhainsa and D'Souza 2008) complexation, coordination and/or chelation (Lu & Gibb, 2008).

2.2.6.3 Intra-Particle Diffusion Study

The most commonly used technique for identifying the mechanism involved in the adsorption process is by using intra-particle diffusion model (Weber & Morris, 1963). According to intraparticle diffusion model, the adsorption process can be differentiated into three steps: external surface adsorption, intraparticle diffusion which is the rate-limiting step, and the final equilibrium which is very fast:

$$q_t = K_i t^{0.5} + I$$

Where K_i is the intra-particle diffusion rate constant which indicate enhancement in the rate of adsorption and I is the intercept. If intra-particle diffusion occurs, then q_t against $t_{0.5}$ will be linear and the line will pass through the origin if the intra-particle diffusion was the only rate limiting parameter controlling the process. Otherwise, some other mechanism is also involved. Values of I give an idea about the thickness of the boundary layer. i.e**.,** the larger the intercept the greater is the boundary layer effect (Kannan & Sundaram, 2001). The deviation of straight lines from the origin may be because of the difference between the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step (Poots et al., 1978). Simultaneously, external mass transfer resistance should also be considered although this resistance is only significant for the initial period of time (Mall, Srivastava, & Agarwal, 2006). When the active sites are internally located in the porous adsorbent and the external resistance to diffusive transport process is much less than internal resistance then adsorption is controlled by Intra particles diffusion (Weber & Morris, 1963).

2.2.6.4 Elovich model

Elovich equation is used to describe the rate of adsorption that decreases exponentially with an increase in the amount of adsorbate but does not provide any mechanistic information about adsorption:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$$

The integration of the rate equation with the same boundary conditions as the pseudo first- and second-order equations becomes the Elovich equation.

$$q_t = \frac{1}{\beta}\mathrm{Ln}(\alpha\beta) + \frac{1}{\beta}\mathrm{Ln}t$$

where α is the initial sorption rate (mg/g min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

In this case, a linear relationship was obtained between metal adsorbed, *qt*, and ln *t* over the whole adsorption period. The Elovich equation has proved suitable for highly heterogeneous systems of which the adsorption of metal onto adsorbents is an example (Ornek, Ozacar, & Sengil, 2007).

2.2.6.5 Liquid Film Diffusion model

If diffusion within an adsorbent particle is very rapid or if the adsorbent is nonporous, adsorption can be considered to occur only on the external surface, while diffusion through the laminar film surrounding a particle controls diffusion. The liquid film diffusion model is given by :(Boyd, Adamson, & Myers, 1947)

$$\mathrm{Ln}\left(1 - \frac{q_t}{q_e}\right) = -K_{FD}t$$

LFD is applicable when flow of the reaction from the bulk liquid to the surface of the adsorbent determines the rate constant. Here, F is described as the fractional attainment of equilibrium (=q_t/q_e), and K_{Fd} is the adsorption rate constant, whether the main resistance to mass transfer is in the thin film surrounding the adsorbent particle or in the resistance to diffusion inside the pores. determines the rate constant (Boyd et al., 1947).

2.2.6.6 Bangham model

Bangham model can be used to verify whether pore diffusion is or not the only rate-controlling step in the adsorption process by kinetic data regression using Bangham's equation (Aharoni, C, Sideman, S, Hoffer, 1979):

$$\mathrm{LogLog}\left(\frac{C_0}{C_0 - q_t m}\right) = \mathrm{Log}\left(\frac{km}{2.303V} + \propto \mathrm{Log}t\right)$$

where V is the volume of solution, α (<1) and k are constants. If, the double logarithmic plot did not yield satisfactory linear curves for the removal of metal on adsorbent (r^2 < 0.88) it indicates that the film diffusion is not the only rate controlling parameter and that the film and pore diffusion were important to different extents in the removal process (Gupta & Ali, 2000).

2.2.7 Thermodynamics of Sorption Studies

The thermodynamic parameters of adsorption, Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) provide information concerning the type and mechanism of the adsorption process concerning the type and mechanism of the adsorption process. The Gibbs free energy change in adsorption (ΔG^0) indicates whether it is spontaneous and a higher negative value indicates more energetically favourable cases. The thermodynamic parameters of the adsorption process could be determined from the experimental data obtained at various temperatures using the equations:

$$K_d = \frac{q_e}{C_e}$$

$$lnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$lnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

The values of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the plots of $\ln K_d$ against 1/T. A negative enthalpy value change (ΔH^0) indicates an exothermic process.

2.2.8 Characterization techniques

2.2.8.1 Zeta potential

Charge Measurement was done by Zeta sizer ZetaPlus 90Plus/BI-MAS Brrok Haven model and range of measured potential is -150mV to +150mV.

2.2.8.2 CHNS

Thermo Finnigan EA 1112 Series Flash Elemental Analyzer was used for CHNS elemental analysis. The products of combustion (Temp. up to 900°C) are sent through a packed chromatographic column. The column converts the products into combination of NO_2, CO_2, SO_2, and H_2O. These simple compounds are then measured using a thermal conductivity detector. The calibration is performed by analyzing standard compounds with K-factors calculations. The analysis of all elements in the CHNS group is performed

simultaneously. Key components of CHNS are auto sampler, combustion reactors, chromatographic column, and T.C.D. detector.

2.2.8.3 Fourier Transform Infra-red Spectroscopy

FTIR was used to determine the changes in vibrational frequencies of the functional groups in the adsorbents to enable better understanding of the surface features. The spectra were collected by a Perkin Elmer RX1 model within the wave number range of 400-4000 cm^{-1}. Specimens of samples were first mixed with KBr and then ground in an agate mortar at an appropriate ratio of 1/100 for the preparation of the pellets. Resulting mixture was pressed at 10 tons for 5 min. sixteen scans and 8 cm^{-1} resolution were applied in recording spectra. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. It is necessary to collect a background spectrum in order to remove instrument and atmospheric contributions from the sample spectra.

2.2.8.4 Raman Analysis

Using an argon ion laser with an incident wavelength of 514 nm as the excitation source room temperature FT Raman spectra (RS) were measured in the 4000-150 cm^{-1} spectral range using a MiniRam Portable Raman Spectrometer from B&W Tek, with an operating spectral resolution of 3 cm^{-1} and a laser power output of 100 mW. A double analysis per 400 scans was carried out for each sample. An average Raman spectrum was formed afterwards and the spectrum was vector-normalised using the operating spectroscopy software OPUS Ver. 6.5 (Bruker Optics).

2.2.8.5 BET Surface area measurements

Surface area of the adsorbents was determined using Micromeritics Surface area Analyzer SMART SORB 93. by means of adsorption of ultra purity nitrogen at -196°C. It is useful to derive the total area of surface for active adsorption of metal. When the sample exposed to Nitrogen gas at liquid Nitrogen temperature adsorbs Nitrogen and forms a single molecular layer of Nitrogen on the surface of the powder Surface area can be calculated by measuring the volume of Nitrogen adsorbed using a modified single point BET equation as proposed by Brunauer, Emmet and Teller.

$$\frac{1}{v\left[\left(p_0/p\right)-1\right]}=\frac{c-1}{v_m c}\left(\frac{p}{p_0}\right)+\frac{1}{v_m c}$$

p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity (in volume units), and v_m is the monolayer adsorbed gas quantity. c is the BET constant, which is expressed by :

$$c = exp\left(\frac{E_1 - E_L}{RT}\right)$$

E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction.

2.2.8.6. Thermal Analysis

2.2.8.6.1 Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. Thermo gravimetric analysis was done using EXSTAR6000 TG/DTA 6300 model instrument. The measurements were carried out under nitrogen atmosphere. Samples weighing in the range of 5-10 mg were taken in the sample pan and the temperature was raised from 30 to 900°C at a heating rate of 10 °C per minute. The mass of the sample pan was continuously recorded as a function of temperature.

2.2.8.6.2. Differential Scanning Calorimetry Technique

The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. The DSC thermograms were recorded from 30 to 500°C at a ramp of 10°C min^{-1} in a nitrogen stream of 50 mL/min using 822EN Mettler Toledo Model instrument. The positive sign of the DSC curve (mW/mg) indicated that the reaction in the spectrum was endothermic.

2.2.8.7 SEM & EDAX

Scanning electron microscopy (SEM) (model JEOL JSM-5610LV) was used to observe the surface morphology of CH, CD and CTMA. A dried sample was placed on metal stub with adhesive and coated with gold using a JEOL auto fine coater-JEOL 1600. The accelerating voltage was -10-20keV. Energy Dispersive X-ray Analysis (EDAX) technique was used for performing chemical analysis in conjunction with Scanning Electron Microscopy (SEM).The intensity or area of a peak in an EDAX spectrum is proportional to the concentration of the corresponding element in the specimen. For determining elemental content, the electron-beam current is assumed to be uniform throughout the specimen and electron channelling is avoided by avoiding strong diffraction conditions.

2.2.8.8 X-ray Diffraction (XRD)

X-ray diffraction is versatile and non-destructive technique for characterizing the crystalline samples including nano materials. XRD measurements of the powder samples were performed with a PANalytical Diffractometer (Bruker) with Cu-Kα radiation (λ= 0.15418 nm) at a voltage of 45 kV and with a scanning range of 2 theta 0°-90°.

2.2.8.9 ESR

To check the oxidation state of the chromium in the adsorbents under study after adsorption, an EPR spectrum was also recorded on a JEO, Japan. JES-FA200 ESR Spectrometer with X and Q band.

2.2.8.10 XPS

X-ray photoelectron spectroscopy (XPS) is useful for determination of bonding energies of C, O and N on the surface of CH and CTMA and their metal chelates and is effective for determination of the coordination number of the respective metal complex. The KRATOS AXIS Ultra HSA n X-ray photoelectron spectrometer was used for recording X-ray photoelectron spectra of CD and CTMA before and after adsorption of Cr^{6+}. Using the 165mm radius hemispherical analyzer (HSA), The X-ray power supply was run at 15 kV NS 5 mA. The pressure of the analysis chamber during the scan was 10^{9}Torr. Peak fitting and presentation output are produced by an integrated VISION control and information system. The de-convolution process of C 1s spectra as well as the elemental composition evaluation may result in an error of up to 5%. All spectra are presented charge balanced and energy referenced to C1s at 284.6eV. Chemical states of O, N and C species were determined from the charge corrected hi-resolution scans. The atomic concentrations were estimated based on comparisons of integrated peak intensities normalized by the atomic sensitivity factors.

2.2.8.11 Inductive Couple Plasma (ICP)

The teledyne Leemn lab pro DG high dispersion ICP having Solid-state detector technology was used for estimation of total chromium content

2.2.8.12 UV Spectrophotometer

Jasco V630model used for quantitative analysis of Cr^{6+} by 1,5-diphenylcarbazide method. And used for UV spectra for nano material samples which included in Chapter 5.

2.2.9 Desorption

For desorption studies, 0.05 g of CD and CTMA preloaded with Cr^{6+} was equilibrated with 25 ml solutions of 0.1 M of NaOH, H_2SO_4, HCl and HNO_3 for 120 min.

The contents of the flasks were filtered and the chromium content in the filtrate was determined by ICP. Three consecutive adsorption-desorption cycles were carried out to test the reusability of CD and CTMA.

2.3. Results and Discussion

2.3.1 Zeta Potential Analysis

Figure 2.1 Zeta Potential of CD and CTMA

As shown in Fig. 2.1 pzc was found to be 7 and 9.4, for CD and CTMA respectively. Because –OH, –NH, and –COOH are protonated at low pH, a high concentration of these functional groups leads to a positively charged surface, the highest being at pH 2 (Figure 2.1) amenable for uptake of Cr^{6+}.

2.3.2 FTIR Analysis

2.3.2.1 FTIR Analysis of CD

The FTIR spectra of CH, CD before and after adsorption of Cr^{6+} are shown in Figure 2.2 and the assignments for all absorption frequencies of CH and CD before and after adsorption of Cr^{6+} are tabulated in Table 2.1.

The FT-IR spectrum of CH showed characteristic bands corresponding to O-H and N-H stretching vibrations at 3619 and 3420 cm^{-1} respectively, peaks at 2929 and 2857 cm^{-1} are from the stretching vibrations of C-H bond. Absorption peaks around 1697, 1650 and 1393 cm^{-1} can be assigned to amide band I, amide band II and CH_3 symmetrical angular deformation, respectively (Monier, Ayad, Wei, & Sarhan, 2010). The large band around 1051 cm^{-1} is due to vibration of C-O bond of alcohol and to -C-O-C- vibration of the monosaccharide unit (Justi, Fávere, Laranjeira, Neves, & Casellato, 2005). The IR spectra of DTPA presents bands at 1699 and 1634 cm^{-1}, corresponding to the C=O bending of

COOH. The characteristic absorption bands at 1204 cm^{-1} attributed to C-N stretching can be observed.

In CD the band of C=O bond stretch of DTPA is at 1620 cm^{-1} and the band due to C-O of alcohol and C-O-C are observed at 1051cm^{-1}. The band at 1398 cm^{-1} can be attributed to the COO^- function and has been observed in other CH-DTPA compounds where DTPA and CH are linked by electrostatic interactions (T. K. Saha, Ichikawa, & Fukumori, 2006). These changes could be attributed to the effective grafting of DTPA onto CH by forming ammonium carboxylates. However there are free carboxyl groups of DTPA that had not interacted with NH_3^+ of chitosan in CD.

Figure 2.2 FTIR Spectra of DTPA, CH, CD and $CDCr^{6+}$

After chromium adsorption characteristic peak due to Cr-O was observed in the IR spectrum region of 570 to 671 cm^{-1}. There was shifting of different carboxyl frequencies and negligible changes in the frequencies of amino groups suggesting that binding of chromium occurred at free carboxyl groups of DTPA and amino groups of chitosan in CD.

Table 2.1 FTIR Frequencies (in cm^{-1}) for CH, DTPA, CD and $CDCr^{6+}$

CH	DTPA	Chitosan DTPA	Cr^{+6} loaded Chitosan DTPA ($CDCr^{6+}$)	Inference
3859, 3747, 3619, 3420		3854, 3747	3854,3747	O-H, N-H Stretching vibration
	3018			-OH stretching of carboxylic acid
2929, 2857		2924, 2857,	2924,2857	C-H Stretching vibration
2364	2555	2364, 2336	2364, 2336	stretching vibration in –CH and –CH_2
1742		1734	1793,1734	Free carboxyl asymmetric stretching vibration
	1634			Carboxylate intermolecular
1697	1699	1697	1697	carboxyl asymmetric stretching vibration
1650		1653	1650	-NH_2 bending Vibration
		1560	1558	COO^- asymmetric stretching
1546, 1502		1541	1538,1504	C=O stretching vibrations
		1398	1420, 1395	COO^- symmetric stretching
1457	1353	1493, 1457	1490,1457	–CH symmetric bending vibrations in –CHOH
	1204			νC-N
1051	1145, 1091, 907	1051	1048	C-C-O , –CO stretching vibration in –COH
	961			CH_2 wagging a deformation vibration of R-O C-O group
	801			C-C stretch
875,822		875, 825	875,822	Glycosidic linkage
			671,570	Cr–O stretching Vibration

(Kousalya, Rajiv Gandhi, & Meenakshi, 2010; J. S. Wang, Peng, Yang, Liu, & Hu, 2011; Zuo & Balasubramanian, 2013)

2.3.2.2 FTIR Analysis of CTMA

The recorded FTIR spectra for TMA and CTMA before and after Cr^{6+} adsorption are shown in Figure 2.3 and the assignments to their respective absorption frequencies are summarised in Table 2.2

Figure 2.3 FTIR Spectra of TMA, CTMA and Cr^{6+} Loaded CTMA

TMA shows the C=O, O–H, and C–O stretching vibration at 1728, 1455, and 1286 cm^{-1} respectively corresponding to the aromatic acid. the C=O, O–H, and C–O stretching vibration shift to 1721,1441, 1256 cm^{-1} in CTMA along with characteristics of chitosan. The presence of the coordinating carboxylate groups is demonstrated by the stretching vibrations at ~1640 cm^{-1} and 1476 cm^{-1}, respectively. The absorption at 755 cm^{-1} can be attributed to the C-H deformation vibration of the 1,3,5-substituted aromatic ring.

Table 2.2 FTIR Frequencies (in cm^{-1}) CH, TMA, CTMA and CTMACr

CH	TMA	CTMA	Cr^{6+} Loaded CTMA	Inference
3859, 3747, 3619, 3420	3423	3855, 3758, 3654, 3360, 3282, 3424	3448	O-H, N-H Stretching vibration
-	3090, 3018	3090	3075, 3018	-OH stretching of carboxylic acid
2929, 2857, 2364	2988, 2838	2945, 2919, 2849, 2807		–CH stretching vibration in –CH and $–CH_2$ and
1697, 1742	1728	1721, 1777	1693, 1700, 1758, 1735	C=O stretching vibration
1650	1607	1674, 1655	1678, 1659,	$-NH_2$ bending Vibration
		1621	1623,	NH_3^+ asymmetric deformation
			1640,	Asymmetric stretch of bound C-O group
		1560		COO^- stretch
		1523	1531	Symmetric NH_3^+ bending
1393	1402	1377	1397	Symmetric stretch of bound C-O group
	1327	1324	1351, 1313	C=O stretching vibration
1457	1455,1286, 1248	1441 1256	1442, 1298, 1242, 1202	–CH symmetric bending vibrations in –CHOH
		1477	1476	Symmetric stretch of bound C-O group
1051	1180, 1107, 919	1159, 1121, 1068	1178, 1146, 1092, 1045, 1012, 901	–CO stretching vibration in –COH
		989	991,961	C-H out-of-plane bending vibrations
			961	Cr=O
	785, 740	755	714	C–H deformation vibration
			584	Cr–O stretching Vibration
			556	Cr-N stretching

(Darras, Nelea, Winnik, & Buschmann, 2010; Kousalya et al., 2010; Singh, Suri, Tiwary, & Rana, 2013; J. S. Wang et al., 2011; Zuo & Balasubramanian, 2013)

IR spectroscopy has also proven to be useful for the recognition of proton transfer compounds (Lynch, Thomas, Smith, Byriel, & Kennard, 1998; Smith & White, 2001). The most distinct feature in the IR spectrum of proton transfer compounds are the presence of strong asymmetrical and symmetrical carboxylate stretching frequencies at 1560-1621 cm^{-1} and 1324-1441 cm^{-1} (Jin, Liu, Wang, & Guo, 2011). The characteristic Cr-O stretching frequencies are observed in chromium loaded CTMA spectrum.

2.3.3 Raman Analysis

The Raman spectra of CH, TMA, CD and CTMA before and after adsorption of Cr^{6+} are shown in Figure 2.4 and the detailed attribution of Raman vibrational modes are tabulated in Table 2.3.

Chitosan shows characteristic bands of intense CH_3 absorption of acetamide groups (1378 cm^{-1}) and the amidic carbonyl band (1673 cm^{-1}). The weak amidic N–H stretch (3367 cm^{-1}) is observed only after adsorption of chromium onto CD.. It can be seen that the most significant Raman vibration mode are O=C-O and C-O-H stretching vibration, benzene ring breathing vibration, symmetric stretching vibration of C=O, C-O-H asymmetric stretching vibration, O-C=O wagging vibration, COOH out-of-plane vibration, and C-C symmetric stretching mode in TMA CTMA and Cr^{6+} CTMA (J. Li, Zhao, Ren, Sun, & Zhou, 2016). The intense peaks at 1409 cm^{-1} correspond to the stretching vibrations of (OH) in DTPA. In CD and $CDCr^{6+}$ the peaks at 1600-1690 are enhanced as compared to DTPA. The triplet in the 2500 to 2850 cm^{-1} region suggests C-H, C-N and C-O respectively in CD Cr^{6+}.

In the Raman spectrum of TMA, the C-C ring stretching vibration was observed at 1608 cm^{-1}. The frequencies are higher in CTMA and Cr-CTMA due to a reduction of intermolecular distances, thus the intermolecular coupling becomes stronger. C-O-H stretching mode was seen to have changed significantly as a result of the strengthening of the hydrogen bond mode in CTMA and Cr-CTMA. C-H in-plane bending modes of H_3BTC are assigned to 1163 cm^{-1} frequency. The peak at 843.46 cm^{-1} is due to Cr species in Cr-CTMA.

Figure 2.4 Raman Spectra of CH, DTPA, TMA, CD, CTMA, $CDCr^{6+}$ and $CTMACr^{6+}$

Table2.3 Raman vibration assignment for CH, DTPA, TMA, CD, CTMA, $CDCr^{6+}$ and $CTMACr^{6+}$

Adsorbent	Wavenumber (cm^{-1})	Inference
CH	414.9	γ OH and γ pyranoid ring
	561.81	δ pyranoid rings
	834.46	υ pyranoid and ρCH_2 υC-N
	1118.3	υC-O-C of glycosidic linkage, C–O stretching pyranose ring, υ(C-O-H), υ ($C-CH_2$), δ C-H, ρCH, ρCH_3, C–N, CC stretching
	1376.99	δ $C-H_2$, δ C-H, δ O-H, υ pyranoid CH bending, CH_2 wagging, CH_2 twisting, CH_3 of amide group
	1673.58	υ(C-O) amide I band (C=O stretching peptide linkages)
DTPA	908.69	υC-N NH_2 wagging
	1409.21	$\upsilon_s COO^-$ free
CD	565.07	δ pyranoid rings
	843.46	υ pyranoid and ρCH_2, υC-N
	929.15	υ_s(C- C) , NH_2 wagging
	1123.81	υ(C-O-C) of glycosidic linkage, C–O stretching pyranose ring, υ(C-O-H), υ($C-CH_2$), δ C-H, ρCH, ρCH_3 C–N, CC stretching
	1517.8	Ammonium (NH_3^+ symmetric bending) and amino (–NH_2) groups
	1624.24	υ(C-O) Amide I band NH_3^+ asymmetric bending and asymmetric COO^- stretch
	401.22	Cr-N
$CDCr^{6+}$	1339.32	$\upsilon_s COO^-$ CH_3 bending
	1655.75	Amide I band NH_3^+ asymmetric bending
	2823.45	υCH of complexed DTPA
TMA	214.87	δ COOH out of plane vibrations of benzene rings
	384.06	υ_s(C-O-H)
	733.72	ω (O-C=O)
	786.01	τ (C_6H_6)
	1001.16	υ_s(C- C) γ (COOH), CC stretching
	1608.34	υ_s(C- O)
	1653.52	υ_s(C= O), υ_s(C-O-H) and (C=O)
CTMA	411.48	υ_s(C-O-H)
	568.34	δ ring
	929.15	υ_s(C- C) γ (COOH) υC-N NH_2 wagging
	1096.38	υC-C C–O stretching pyranose ring, C–N, CC stretching, 3υ C-O-C of glycosidic linkage
	1356.96	υ C-C δ C-H, CH_3 bending, CH bending, CH_2 wagging, CH_2 twisting
	1527.24	Ammonium (NH_3^+ symmetric bending) groups
	1637.8	υ_s(C- O) and (C=O), υC-C δ C-H, amide I band NH_3^+ asymmetric bending and asymmetric COO^- stretch
	1786.3	(C=O) stretching, υCO, δ O-H , δ C-C
$CTMACr^{6+}$	384	Cr-O
	414.9	υ_s(C-O-H)
	574.85	δ ring
	671.09	CrO_6 Octahedron
	843.4	CrO_4 tetrahedron, υC-N NH_2 wagging
	1101.89	υ_s(C- C) γ (COOH), 3ν C-O-C of glycosidic linkage
	1356.9	CH_3 bending, CH bending, CH_2 wagging, CH_2 twisting
	1527.24	Ammonium (NH_3^+ symmetric bending) and amino (–NH_2) groups
	1657.99	υ_a(C- O) and (C=O) υ (C-O) amide I band NH_3^+ asymmetric bending and asymmetric COO^- stretch
	1786.3	(C=O) stretching

(Mahalakshmi & Balachandran, 2014; McConnell, Nuttall, & Stalker, 1978)

2.3.4 TGA and DSC

TGA curves of CH, CD and CTMA are shown in Figure 2 5. It is seen that there are two weight loss steps in all the three cases. The first one occurred at around 100°C corresponding to 5 and 8% loss, respectively, for CD and CTMA which can be attributed to the loss of adsorbed and bound water. This was followed by another weight loss starting at ~240°C for CH and ~255°C for CD which can be attributed to deacetylation of chitosan in CH and both degradation of DTPA/TMA and deacetylation in CD and CTMA .

The DSC curve in Figure 2.5 of CD shows two peaks: an endothermic peak at 77.18°C and an exothermic peak at 302.8°C which could be attributed to evaporation of water from the polymer and oxidative degradation as well as deacetylation (Qu, Wirsén, & Albertsson, 2000). The glass transition temperature of CD was observed to be at 300°C while for CH it was observed at 306°C. It was observed that there was a small increase in the decomposition temperature of CD as compared to chitosan. However in general the TGA results indicate that CD is less stable than CH.

DSC curve of CTMA shows the endothermic peak at 68.50°C could be attributed to evaporation of water Broad exothermic signal indicates degradation of CTMA due to depolymeriztion and oxidation where decomposition at 261.08°C. There was observed to be more reduction in crystallinity in CTMA as compared to CD and CH.

Figure 2.5 a) TGA & b) DSC of CH, CD and CTMA

2.3.5 Elemental Analysis and Surface Properties of CD, CTMA, CDCr^{6+}& CTMACr^{6+}

The Surface Area (Sq.m/gm) was measured to be 7.15, 9.03 and 8.20 for CH, CD and CTMA respectively Elemental analyses were conducted by CHN microanalysis and SEM EDX techniques and are presented in Table 2.4 and SEM images in Figure 2.6 while Surface area of the adsorbents under study were determined with a BET instrument.

Table 2.4 EDAX and CHN Elemental Analysis

	CD			$CDCr^{6+}$		
Element	**Weight%**	**Atomic%**	**CHN**	**Weight%**	**Atomic%**	**CHN**
Carbon	50.57	57.57	37.0278	37.86	47.58	26.8487
Nitrogen	1.58	1.54	6.2424	3.01	3.24	4.2841
Hydrogen	ND	ND	6.2467	ND	ND	5.2083
Oxygen	47.85	40.89	ND	48.99	46.23	ND
Chromium	ND	ND	ND	10.14	2.95	ND
	CTMA			**$CTMACr^{6+}$**		
Element	**Weight%**	**Atomic%**	**CHN**	**Weight%**	**Atomic%**	**CHN**
Carbon	10.99	13.85	39.7664	7.68	11.03	36.096
Nitrogen	14.49	15.56	6.3638	11.76	14.47	5.7507
Hydrogen	ND	ND	6.6515	ND	ND	6.2666
Oxygen	74.52	70.5	ND	64.04	69.02	ND
Chromium	ND	ND	ND	16.52	5.48	ND

From Figure 2.6 it is observed that CD did not look porous suggesting that the uptake of chromium could be mainly attributed to the functional groups on its surface while CTMA was porous in nature and Cr^{6+} loaded CTMA showed obvious chromium deposition on the adsorbent. The EDAX results affirm modification of chitosan with DTPA and Trimesic acid in CD and CTMA respectively and presence of chromium after equilibration with chromium containing solutions.

Figure 2.6 SEM/EDAX a) CD and $CDCr^{6+}$

Figure 2.7 SEM/EDAX b) CTMA and $CTMACr^{6+}$

2.3.6 XRD analysis

The X-ray diffraction spectra of CD (Figure 2.8) show crystalline areas 2 theta = 10°, 20°, 26° and 73° (due to grafting of DTPA at the CH backbone). The peaks at 10° and 20°(indexed to 110 plane) are characteristic of chitosan (X. Wang, Du, Fan, Liu, & Hu, 2005). while additional peaks appeared after ionic interaction, It is observed that the adsorbent has become amorphous after adsorption of chromium with a weak broad peak at 34.5° (Kalidhasan, Santhana KrishnaKumar, Rajesh, & Rajesh, 2012; Lin, Chen, & Lin, 1997).

Figure 2.8 XRD a) CH, CD and $CDCr^{6+}$ b) CTMA and $CTMACr^{6+}$

CTMA shows two crystalline peaks at 2θ of 10° and 21° with a small peak at 2θ 73°.The structure has become amorphous after adsorption of chromium with a less intense peak at 2θ of 21°. These phenomena might be due to a induced by ionic interactions (X. Wang et al., 2005).The ionic interactions cause modifications in the arrangement of molecules in the crystal lattice and may as well as destroy the intra- and intermolecular

hydrogen bonding. As a result, the crystal structure partially transforms into an amorphous one in CTMA and further becomes amorphous after adsorption of chromium.

2.3.7 ESR analysis

ESR spectra of CD, CTMA and Cr^{6+} loaded CD and CTMA are shown in Figure 2.9. ESR spectra of Cr^{6+} loaded adsorbent showed a signal with g value of 1.9839 which could be attributed to the exchange coupling between Cr^{3+}-Cr^{3+} ion pairs or large clusters of Cr^{3+} suggesting that adsorption of Cr^{6+} onto CD has resulted in its reduction to Cr^{3+} (Ahmad, 2014). Reduction of Cr^{6+} to Cr^{3+} was also reported by Nakajima and Baba (Nakajima & Baba, 2004) on the surface of persimmon tannin gel and Araujo et al. (Araújo et al., 2013) on termite's nest. The g-value for the Cr^{3+} ion is 1.9765 and is isotropic in CTMA (Nakajima & Baba, 2004). CD and CTMA exhibit an ESR signal with a g value 2.128 and 2.179 respectively which can be ascribed to chitosan. There are several ESR studies on chitosan and g values in the range 1.99 to 2.2 are observed (Dreve et al., 2011).

Figure 2.9 a) CD and $CDCr^{6+}$ b) CTMA and $CTMACr^{6+}$

2.3.8. XPS analysis

Figure 2.10 and Table 2.5 summarize the binding energies and percentage atomic concentration of CH, CD and chromium-loaded CD. It is observed that the deconvoluted C 1s spectrum of CH and CD comprised of two peaks with BEs 284.6 and 287.7 eV. These peak scan be assigned to C-C, and O-C-O bonds of alcoholic and ether groups. The carbon atoms of these respective organic functional groups of the adsorbents have different electron densities. Results indicate that the atomic concentration (%) of C-C groups (286.5 eV) increases after complexation with DTPA due to addition of alkyl groups induced by DTPA. However, in CD loaded with chromium there is an additional peak at binding energy 288.2 eV which can be attributed to carbonyl groups bound with chromium.

There are two peaks in the N 1s spectrum of CH and CD at BEs of about 398.7 and 400.6 eV which could be attributed to the N atom in the R-NH_2 group and protonated R-NH_2. The NH_3^+ moieties present in the CH were reported to react with COO- moieties to form ionic complex (Singh et al., 2013). The N peaks at 398 and 400 eV were slightly shifted to lower binding energies (0.1 and 0.7 eV, respectively) after adsorption of chromium suggesting the interaction between chromium and amino group to be predominantly non-specific electrostatic interaction. However, a peak of low intensity is observed at a BE 401.7 eV which could be attributed to the formation of metal-NH_2 complex but of low predominance. The appearance of this N peak at higher binding energy is indicative of ion pair formation between NH_3^+ and hexavalent chromate.

The O spectrum was deconvoluted into two peaks for CD loaded with Cr^{6+} while a single peak was present in CH and CD. The peak at 532.2 eV can be attributed to C-O (acetate) in C and CD while in Cr^{6+} loaded CD the peak at 531.8 eV can be attributed to carbonyl group and the peak at 533.1 eV can be attributed to the interaction of chromium ions with carbonyl groups of CD. A peak for oxygen attributed to dichromate or chromate (530 eV) could not be found (Biesinger, Brown, Mycroft, Davidson, & McIntyre, 2004). This suggests that all of the chromium is present in +3 oxidation state in different forms, as $Cr(OH)_3$ and as Cr^{3+} stabilized by binding to carboxylate groups from DTPA. These results along with FT-IR spectral analyses imply that Cr^{3+} co-ordinations were formed with carbonyl groups.

High-resolution spectra collected from the Cr 2p core region indicated that there was no Cr^{6+} on the adsorbent surface. However, it is evident from the spectra that there are two different species of Cr^{3+} present on the adsorbent with peaks at binding energies 577.0, 586.0, 579.1 and 588.5 eV. The positions of the peaks at 579.1 and 588.5 eV fall at the lower edge of the Cr^{6+} binding energies (Allen, Curtis, Hooper, & Tucker, 1973). However, the spin orbit splitting values as well as FWHM values are quite low suggesting that the binding energies at 579.1 and 588.5 eV can also be attributed to Cr^{3+}. The high binding energies of 579.1 and 588.5 eV could be indicative of stabilization of Cr^{3+} by binding (Groppo, Lamberti, Bordiga, Spoto, & Zecchina, 2005). Therefore, it can be concluded that the Cr^{6+} was removed from aqueous phase and finally reduced to Cr^{3+}.

Figure 2.10 XPS of CH, CD and $CDCr^{6+}$

Figure 2.11 XPS of CTMA and $CTMACr^{6+}$

Table 2.5 Binding energies of CH, CD, $CDCr^{6+}$, CTMA and $CTMACr^{6+}$

Sample Name		Binding Energy (eV)	FWHM eV	Area	%	
CH	C 1s	284.6	2.786	25638.3	81.5	C=O or O-C-O
	C 1s	287.1	2.833	5826.9	18.5	$C\text{-}N^+$ or C-O
	O 1s	532.2	2.778	38366.7	100	C=O
	N 1s	398.7	2.478	1919.4	67	NH_2/NH_3^+
	N 1s	400.6	2.81	947	33	C-N
CD	C 1s	287.6	2.521	21542.9	73	C=O or O-C-O
	C 1s	286.5	2.788	7986.1	27	$C\text{-}N^+$ or C-O
	O 1s	532.3	2.709	26897.4	100	C-O C=O
	N 1s	397.7	2.654	3597	70.6	NH_2/NH_3^+
	N 1s	400.9	3.175	1496.3	29.4	C-N
$CDCr^{6+}$	C 1s	284.6	2.062	11380	60.6	C-C, $C\text{-}N^+$
	C 1s	286.3	2.154	5756.9	30.7	C−O or C−OH
	C 1s	288.2	1.957	1629.8	8.7	C=O, O-C-O
	O 1s	531.8	3.167	15671.9	65.8	COO^-
	O 1s	533.1	2.832	8154.6	34.2	C-O
	N 1s	398.7	1.781	723.7	34.3	Protonated NH_2
	N 1s	400.2	1.813	1068.5	50.6	C-N
	N 1s	401.7	1.652	318.6	15.1	Protonated nitrogen of DTPA
	Cr 2p3/2	577.0	2.477	3670.3	38.7	Cr(III)
	Cr 2p1/2	586.0	3.765	2418.9	25.5	Cr(III)
	Cr 2p	579.1	2.23	1911.2	20.2	Cr(III)
	Cr 2p1/2	588.5	2.62	1480.7	15.6	Cr(III)
CTMA	C1s	284.6	2.03	27376.1	56.5	C-C, $C\text{-}N^+$
	C1s	285.9	1.792	15735.3	32.5	phenylic carbon C−O−C or C−OH
	C1s	287.8	1.925	5319.7	11	C=O
	O1s	532.6	2.6	16945.6	58	C=O
	O1s	534.0	3.164	12279.9	42	C-O of COO group
	N1s	399.5	2.014	802.7	37.3	protonated NH_2
	N1s	400.9	2.097	1026.7	47.6	C-N
	N1s	402.9	1.486	325.3	15.1	N+---O- Oxidised nitrogen
$CTMA\text{-}Cr^{6+}$	C1s	284.7	1.866	19302.1	53.3	C-C
	C1s	286.0	1.93	14095.2	38.9	C−O−C or C−OH
	C1s	288.2	1.837	2833.3	7.8	C=O
	O1s	532.6	2.392	16669.3	66.4	C=O Oxygen connected with hydroxide groups
	O1s	534.3	2.47	8451.9	33.6	C-O
	N1s	399.3	2.145	555.2	35.3	Protonated $NH_2/-NH_3^+$
	N1s	402.7	2.262	363.9	23.1	Oxidised nitrogen
	N1s	400.7	1.803	652.8	41.5	C-N
	Cr 2p3/2	578.9	1.974	382.5	27.4	Cr(VI)
	Cr 2p3/2	577.0	1.722	219.3	15.7	Cr(III) CrOOH
	Cr 2p1/2	585.1	1.608	93	6.7	Cr(III)
	Cr 2p1/2	586.8	1.547	137.1	9.8	Cr(III) CrOOH
	Cr 2p	582.6	1.912	217.9	15.6	Cr(III)
	Cr 2p3/2	580.7	1.686	166.4	11.9	Cr(VI)Cr 2p3/2
	Cr 2p1/2	588.4	1.541	97.9	7	Cr VI 2p1/2
	Cr 2p1/2	589.9	2.184	80.5	5.8	Cr(VI)Cr 2p1/2

For CTMA the C1s region (Figure 2.11) fitted with three peaks (eV) at 284.6 (C–C), 285.9 (C–N, C–O) and 287.8 (C-C, C–O). The assignments of other peaks in CTMA and CTMA-Cr are given in Table 2.5.

It was observed that XPS peaks characteristic of chromium are broad with high FWHM. It is possible that when Cr is paramagnetic the peaks are broadened because of the effect of the multiplet splitting due to the interaction with 3d electrons. FWHM of 1.3–1.4 eV is complicated by the overlap with the multiplet splitting of Cr^{3+} species. Both of the effects from electrostatic attraction and the coordination interaction would reduce the outer-shell electron density of N atoms, which caused the nuclear charge on the inner electron shielding effect to be weakened. The inner electron binding energy of N1s increased, so the peaks of N1s in XPS spectra shifted to higher binding energies (Shen et al., 2013). The different Cr^{6+} 2p(3/2) BE in CTMA demonstrated that this surface Cr is surface-stabilized chromate species (including monochromate, dichromate and sometimes even polychromate expressed as $Cr^{6+}O_{x,\ surf}$) (Liu & Terano, 2001).

2.4. Adsorption-Desorption studies

2.4.1 Effect of pH

Hexavalent chromium exists in aqueous solution in the form of oxyanions such as $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} depending on pH of the aqueous solution. In the pH ranging from 2.0 to 6.0, $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions mainly exist in equilibrium and the predominant species shifts to chromate ion (CrO_4^{2-}) as pH increases. A chromate ion (CrO_4^{2-}) needs two adsorption sites due to its charge of -2, whereas a $HCrO_4^-$ needs only one active adsorption site. Hence, an increase in the adsorption capacity of Cr^{6+} is observed due to the formation of more $HCrO_4^-$ ions with decreasing pH value. However, the situation only persists down to a pH value 2.0 to 3.0, and a further decrease in the pH value causes a sharp decrease in the adsorption capacity of Cr^{6+}. The free amino groups (NH_3^+) and hydroxy groups of chitosan in CD and CTMA as well as tertiary amine groups of DTPA in CD were protonated at low pH values. The positively charged functional groups of the adsorbents bound the anions $HCrO_4^-$, CrO_4^{2-}, or $Cr_2O_7^{2-}$ via electrostatic attraction as well as by hydrogen bonding depending on the pH. As the pH increased, the protonation gradually weakened and in alkaline conditions the OH^- ions competed with these Cr^{6+} anionic species (Sharma & Kothiyal, 2013). As a result, low Cr^{6+} adsorption capacity was observed at high pH values. Maximum removal occurs at pH 3 (CD) and 2 (CTMA) as seen from Figure 2.12

Figure 2.12 Effect of pH a) CD and b) CTMA

Volume = 25 ml, adsorbent dose = 0.05 g, [Cr^{6+}] = 50 ppm: pH = 1 to 11, contact time = 5h, Temp= 30°C.

2.4.2 Effect of Adsorbent Dose

The Effect of Dose of adsorbents under study on the removal of Cr^{6+} is shown in Figure 2.13. Which show the percent adsorption of Cr^{6+} increased with change of dose of adsorbent from 0.01g to 0.10 g. 0.06 g and 0.04 g for CD and CTMA respectively. This could be due to greater surface area and more active sites with increase in adsorbent dose. However, if the adsorption capacity is expressed in mg adsorbed per gram of adsorbent, the capacity decreased with increasing adsorbent dose. This may be attributed to aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to the adsorbate and also an increase in diffusion path length (N. Zhang et al., 2014).

Figure 2.13 Effect of Dose a) CD and b) CTMA

Volume = 25 ml, Amount adsorbent = 0.01 g to 0.1g, [Cr^{6+}] = 50ppm pH = 3 (CD) & 2 (CTMA), contact time =5h, Temp. = 30°C

2.4.3 Effect of Concentration Variation

The effectiveness of CD and CTMA for the uptake of chromium over a wide range of concentration (30-1000 ppm) was investigated (Figure 2.14). It was observed that removal was higher at lower initial concentration of chromium and decreased from 85 to 75% and 90 to 65% with the increase of initial concentration from 50 to 100 ppm for CD and CTMA respectively. Due to the availability of large amount of free adsorption sites at initial stages, removal of Cr^{6+} ions was quite high but these available adsorption sites got occupied with the progress of adsorption at later stages resulting in decreased removal. At a fixed adsorbent dosage, the finite number of available binding sites leads to a decrease in the removal percentage of Cr^{6+} ions with increasing initial concentration of Cr^{6+} ions (Nematollahzadeh, Seraj, & Mirzayi, 2015).

Figure 2.14 concentration study

Volume = 25 ml, Amount adsorbent = 0.05g, [Cr^{6+}] = 30ppm to 1000ppm pH = 3 (CD) & 2 (CTMA), contact time=5 h, Temp. = 30°C.

The Cr^{6+} adsorption isotherms for CD and CTMA were investigated and the calculated isotherm constants from the fitting plots (Figure 2.15 and 2.16) for the models investigated are presented in Table 2.6. The adsorption data for CD gave reasonably high correlation coefficient values for all the models studied. The well fit data of Freundlich model and the fact that Freundlich constant, n was greater than unity (CD=1.8423, CTMA=2.2755) implied that the adsorption intensity was favourable over the entire range of concentrations studied. However the correlation coefficients of Langmuir model are slightly higher for CTMA while for CD the correlation coefficients of Freundlich and Langmuir isotherm models are comparable. The Langmuir model suggests homogeneous surface and monolayer adsorption process which indicates active sites are well distributed throughout CD and also to a reasonable extent in CTMA. The Parameters K_L and qmax were calculated from the intercept and slope of the plot of Ce/qe versus Ce of Langmuir

isotherm model. The standard deviations for Langmuir model were slightly higher. The maximum Langmuir monolayer adsorption capacity for Cr^{6+} using CD was found to be 192.3 mg/g and for CTMA 129.53 mg/g.. Fitting of Langmuir isotherm model suggested the presence of homogeneous adsorption sites. The adsorption capacity was found to be greater for CD than for CTMA.

The Correlation coefficients of Temkin Model (CD=0.9984 and CTMA=0.9827) indicate a satisfactory fit of the model to the experimental data. The equilibrium binding constant (K_T) related to the maximum binding energy in the Temkin isotherm was 0.1352 and 0.1282 L/mmol for CD and CTMA respectively. which is a constant related to the heat of adsorption, was 30 and 25 J/mol, values which are higher than 20 J/mol. This result means that the adsorption is chemisorption process (Shin & Kim, 2016). The linear fitting of Temkin model indicated that the adsorption process is chemisorption. However, the Temkin isotherm model mainly describes the chemical adsorption process as electrostatic interaction. Hence, electrostatic interaction is an important mechanism affecting the interaction between the adsorbents under study and chromium (Fan et al., 2016). The high regression values (>0.99) for Halsey model affirmed the heteroporous nature of the adsorbent and suggested multilayer adsorption, while the low values of K_H (CD=4.4043 and CTMA=6.9) suggest that multilayer adsorption might be playing only a small role (Rao & Khatoon, 2016). The Flory-Huggins (F-H) isotherm used to assess the isotherm data. From the linear plots for chromium adsorption on the adsorbents and r^2>0.99 is shows that the model is good fits for all adsorbent. But negative values of n and low values of K_{FH} suggest that the model cannot be used to describe the adsorption data.

Figure 2.15 Linear fit of Isotherm models for CD

Figure 2.16 Linear fit of Isotherm models for CTMA

Table 2.6 Isotherm model constants

Model	Constants				
Freundlich	K_f (L.g^{-1})	N	r^2	SD	
CD	5.7521	1.8423	0.9889	0.0400	
CTMA	6.8478	2.2755	0.9853	0.0381	
Langmuir	K_L(L.mmol^{-})	qm (mg.g-1)	ΔG(kJ.mol^{-1})	r^2	SD
CD	0.0098	192.3077	-12.0326	0.9830	0.1985
CTMA	0.0217	129.5337	-9.9520	0.9974	0.1118
Halsey	k_H (L.g-1)	nH	r2	SD	
CD	4.4043	-1.5694	0.9919	0.0468	
CTMA	6.9000	-2.26280	0.9992	0.0756	
Temkin	BT (J/mol)	-ΔH (kJ.mol^{-1})	K_T (L.mmol^{-1})	r^2	SD
CD	30.2305	16.0252	0.1352	0.9984	0.9483
CTMA	25.2173	12.9401	0.1292	0.9827	5.9214
F-H	nfh	Kfh	r2	SD	
CD	-3.2584	0.0001	0.9955	0.0419	
CTMA	-2.9203	0.0001	0.9968	0.0672	
Elovich	qm (mg.g-1)	Lnqm	K_E (L.mmol^{-1})	r^2	SD
CD	77.4593	4.3498	0.0294	0.9977	0.0341
CTMA	43.9174	3.7823	0.0525	0.9832	0.1341

Figure 2.27 Back Calculation Isotherms for CD and CTMA

2.4.4. Sorption kinetics

The time dependent Cr^{6+} adsorption was studied on CD and CTMA. The experimental results show increase in the Cr^{6+} removal with time (Figure 2.18). The adsorption kinetics is faster on CTMA wherein 72% Cr^{6+} removal is completed within 40 min of equilibration while in CD 73% Cr^{6+} removal is completed within 45 min of equilibration. The equilibrium condition has been achieved within 5 hours for CD and CTMA. The higher and rapid uptake in the initial time period is also due to the high driving

force exerted by the large concentration gradient between the bulk solution and adsorbent phase.

Figure 2.38 Effect of Time a) CD and b) CTMA

Volume = 25 ml, Amount adsorbent = 0.05 g, [Cr^{6+}] = 50 ppm pH =3 (CD) & 2 (CTMA), Temp. = 30°C

Kinetic models were studied and the fitting of all the models with experimental data are shown in Figure 2.19 and 2.20 and the rate constants for the adsorption of Cr^{6+} by CD and CTMA are presented in Table 2.7.

The pseudo second order kinetics provided the best fit for the kinetic data at optimum pH. The correlation coefficients for pseudo-second-order model were found to be greater than the other kinetic models for CD (0.9999) and CTMA (0.9997). The calculated equilibrium adsorption capacity values were closer to those obtained experimentally for pseudo second order.

This supported the assumption behind the model that the surface complexation may be the rate limiting step involving valence forces through sharing or exchanging of electrons between adsorbent and adsorbate (Zimmermann, Mecab0, Fagundes, & Rodrigues, 2010).

However, rapid adsorption during the first 40-50 min of adsorption may be mainly due to physical adsorption or ion exchange at adsorbent surface (L. Zhang & Zhang, 2014). Thus there may be more than one mechanism participating in the actual adsorption process.

In Pseudo first order model the qt (exp) values were much higher than Calculated qt for CD and CTMA. The large differences show that the adsorption kinetics cannot be classified as pseudo first order though good correlation coefficients were obtained for both CD and CTMA.

The adsorption process of the adsorbates onto adsorbents may involve the following steps : (1) solute transfers to the sorbent particle surface (film diffusion); (2) transfer from the sorbent surface to the intraparticle active sites (intraparticle diffusion); and (3) retention

on the active sites. The third step is very rapid and can be considered negligible, while either first or second steps may be the slowest step to be considered as the rate-limiting step for the sorption process (Choy, Porter, & Mckay, 2004). The first and second steps can be modeled by the liquid film diffusion model and intraparticle diffusion model, respectively. The plot of q_t versus $t^{1/2}$ as well as LFD plots for CD and CTMA did not pass through origin suggesting that intraparticle diffusion was not the only rate controlling step but some degree of the boundary layer diffusion also controlled the adsorption process and that the overall rate of the metal adsorption process appeared to be controlled by more than one step. However, the low correlation coefficient for the IP model as compared to that of the LFD model suggested that LFD mainly controlled the adsorption process of chromium onto CD and CTMA along with a significant contribution of intra particle diffusion. The multilinear profile obtained for intraparticle diffusion model plot and that the plot did not pass through the origin suggested that boundary layer diffusion also occurred in the uptake of chromium onto CD and CTMA.

Elovich kinetic relationship is suitable to describe second order kinetics assuming that the actual solid surfaces are energetically heterogeneous. The initial adsorption rate, α, and the desorption constant, β, were calculated from slope and intercept of straight line plot between Qt and ln(t) for CD and CTMA (Figure 18 and 19).β a constant related to the extension of surface coverage was found to be very low for both CD and CTMA indicating that uptake of chromium onto CD and CTMA may have been more through functional groups. However, the constant α that is related to chemisorption rate was high suggesting that more than one mechanism governs the uptake of chromium. The large α values as compared to β suggested that the rate of adsorption was much higher than the rate of desorption, indicating the viability of adsorption process. High regression coefficients (~0.99) for both CD and CTMA indicated well-fitting of adsorption data to Elovich kinetic model (Y. S. Ho & McKay, 2009). The reasonably good correlation coefficient for Bangham equation indicated that the diffusion of Cr^{6+} into the pores of the adsorbent under study also controlled the adsorption process.

Adsorption capacity of adsorbents was initially high due to binding of adsorbate ions on the surface of adsorbents through proton exchange and later on slower due to inter particle diffusion and diffusion of chromium from the aqueous phase to the adsorbent. Furthermore the metal adsorption process was controlled by more than one step.

Figure 2.49 Linear fit of Kinetics for $CDCr^{6+}$

Figure 2.20 Linear fit of Kinetics for $CTMACr^{6+}$

Table 2.7 Kinetic model constants for CD and CTMA

Model	**Constants**				
Experiment	$CDCr^{6+}$	20.631			
q_t (mg/g)	$CTMACr^{6+}$	20.145			
Pseudo second order	q_e (mg/g)	K	r^2	H	SD
$CDCr^{6+}$	21.5332	0.0042	0.9999	4.7250	0.0387
$CTMACr^{6+}$	20.2963	0.0115	0.9997	1.9507	0.0680
Lagergren	q_e (mg/g)	K	r^2	SD	
$CDCr^{6+}$	5.6799	0.0148	0.9972	0.0283	
$CTMACr^{6+}$	3.2151	0.0158	0.9743	0.0528	
IP	K	I	r^2	SD	
$CDCr^{6+}$	0.2956	16.190	0.9741	0.0061	
$CTMACr^{6+}$	0.3711	15.989	0.9738	0.1730	
Elovich	B	Alpha	r^2	SD	
$CDCr^{6+}$	0.6031	1817.3	0.9962	0.0163	
$CTMACr^{6+}$	1.2403	2.4E+08	0.9918	0.0524	
Liquid film diffusion model	K_{FD}	r^2	SD		
$CDCr^{6+}$	0.0148	0.9973	0.0652		
$CTMACr^{6+}$	0.0048	0.9998	0.0063		
Bangham	K_m	Alpha	r^2	SD	
$CDCr^{6+}$	-34.2082	0.1999	0.9992	0.0026	
$CTMACr^{6+}$	-26.7367	0.1412	0.9809	0.0063	

Figure 2.51 Kinetics Back Calculation of CD and CTMA

2.4.5 Effect of Temperature

Effect of temperature on adsorption of Cr(VI) by CD and CTMA was studied in order to obtain relevant thermodynamic parameters at varying temperatures. The uptake of chromium by CH, CD and CTMA were found to be almost same trend for all adsorbents under study at period of time for each temperature. From the figure it can be seen that uptake decreased with increase in temperature (Figure 2.22) indicating the adsorption process to be exothermic and that some desorption is happening at high temperatures.

Figure 2.62 Temperature Variation a) CD and b) CTMA

Volume = 25 ml, Amount adsorbent = 0.05 g, $[Cr^{6+}]$ = 50 ppm effect of temperature: pH = 3 (CD) & 2 (CTMA), contact time =5 h, Temp. = 30-70°C.

The Thermodynamic parameter of the adsorption process could be determined from the experimental data at various temperatures using below equations.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

Figure 2.73 Thermodynamics Plot

ΔH° and ΔS° can be calculated from the slope and intercept of the plots of ΔG° versus 1/T. The calculated thermodynamic parameters are tabulated in Table 2.8 The negative ΔG° values -indicate that the adsorption of Cr^{6+} on CD and CTMA is a spontaneous process, and the increase of ΔG° with increasing temperature indicates that the adsorption process is more favourable at lower temperature (W. Cheng, Ding, Sun, & Wang, 2015). This enhanced adsorption at lower temperature is attributed mainly to the feasibility of electrostatic interactions between −OH, R_3N^+, NH_3^+ and $HCrO_4^-$ which results in high adsorption capacity of CD and CTMA for Cr^{6+}. Generally, the change in free energy for physisorption is between 20 and 0 kJ/mol, but chemisorption is in a range of 80 to 400 kJ/mol (Gerçel, Özcan, Özcan, & Gerçel, 2007). The values of ΔG° obtained in this study are within the ranges of the physisorption mechanism.

Table 2.8 Thermodynamic parameters

	Constants			
	Temp K	ΔG kJ/mole	ΔH kJ/mole	ΔS J/moleK
$CDCr^{6+}$	303	-2.1637	-44.445	-139.542
	313	-0.7683		
	323	0.6271		
	333	2.0226		
	343	3.4180		
$CTMACr^{6+}$	303	-1.8022	-18.9385	-56.5552
	313	-1.2367		
	323	-0.6711		
	333	-0.1056		
	343	0.4600		

The negative ΔH° values for adsorption on CD and CTMA indicate that the process is exothermic (Z. Li et al., 2012). The negative entropy change corresponded to decrease in the degree of freedom of the adsorbed species. The negative value of ΔH° further confirmed the adsorption to be exothermic.

2.4.6. Desorption and reuse of adsorbents

As it was observed that poor adsorption of Cr^{6+} took place on both the adsorbents at high pH (section **2.4.1**), it was felt that the used adsorbents could be regenerated using alkaline desorbents. It is observed from Fig. 2.23 that maximum desorption, (CD=78% and CTMA=75%) occurred in 0.1 N NaOH solution. After desorption CD and CTMA were reused up to three adsorption desorption cycles and the results are presented in Figure 2.24. It was found that the adsorption capacity of the CH decreased by 16% after first cycle and second cycle, while CD decreased by 14% after the first cycle and the second cycle, similarly for CTMA 16% to 8% after first and second cycle. Exposure of the adsorbent to alternate acidic and alkaline conditions during adsorption and desorption did not affect the stability of the adsorbent.

Figure 2.84 Desorption study for CD and CTMA

Figure 2.95 Desorption study for 3 cycles for CD and CTMA

2.5. Environmental significance

In the present study, the use of CD has resulted in complete reduction of Cr^{6+} to Cr^{3+} and the reduced Cr^{3+} remained adsorbed onto adsorbent as Cr^{3+} could form a stable complex unlike other adsorbents reported in literature where in the Cr^{6+} was only partly reduced to Cr^{3+} and the reduced Cr^{3+} was observed to leach into solution. Even when CTM was used though there was partial reduction of Cr^{6+}, no leaching of either Cr^{6+} or Cr^{3+} was observed.

2.6. Mechanism

DTPA has five acid functions and thus five pKa (10.48; 8.60; 4.28; 2.60; 2.00) (Deal, Motekaitis, Martell, & Welch, 1996). Trimesic acid has pKa 3.12. The carboxylic groups can thus exist as COO- in DTPA and TMA at pH 2.0. The acids are expected to form ionic cross links between chitosan polymer chains, because they contain carboxylic groups and chitosan would contain protonated amino groups. The possible ionic crosslinking reactions between amine groups of chitosan and carboxylic groups of DTPA and TMA are schematically showing Figure 2.26 and 2.28. This ionic crosslinking scheme

was based on the scheme suggested by Gümuşoğlu etal.and Fadzallah et al. (Fadzallah, Majid, Careem, & Arof, 2014; Gümüşoğlu, Arı, & Deligöz, 2011).

The removal mechanism of Cr^{6+} from aqueous solution by non-living biomasses has been summarized by Park et al. (Park, Yun, & Park, 2004) as three steps: (1) the binding of anionic Cr^{6+} ions with the positively charged groups on the biomass surface; (2) the reduction of Cr^{6+} to Cr^{3+} by adjacent electron donor groups; (3) the release of Cr^{3+} ions into the aqueous phase due to electronic repulsion between the positively charged groups and the Cr^{3+} ions, or the formation of complexes of the Cr^{3+} with adjacent groups capable of Cr-binding. Furthermore, Park et al. (Park et al., 2004) and Cerqueira et al. (Cerqueira et al., 2012) have shown that the removal of Cr^{6+} is favoured at lower pH as the reduction of Cr^{6+} to Cr^{3+} requires large quantities of protons and electrons in the reaction medium. After adsorption of Cr^{6+} on the adsorbent surface, the reduction of Cr^{6+} to Cr^{3+} is therefore initiated under acidic conditions, due to its high redox potential. Miretzky and Cirelli have identified that hydroxyl (OH), carbonyl (C=O), and methoxy ($O\text{-}CH_3$) groups present on adsorbent surfaces can act as donors of electrons for the reduction reaction (P. Miretzky & Cirelli, 2010). However, with most of the adsorbents only partial reduction of Cr^{6+} to Cr^{3+} has been reported and in some instances reduction of Cr^{6+} to Cr^{3+} in the aqueous phase. The adsorption of chromium onto CD and CTMA may have occurred in three steps: (1) the binding of anionic Cr^{6+} to protonated positively charged functional groups on the adsorbent surface, (2) the reduction of Cr^{6+} to Cr^{3+} by adjacent electron-donor groups and (3) the formation of clusters of Cr^{3+} on the adsorbent in the case of CD as indicated by ESR studies. Carboxyl and amino groups have been reported to be important in the reduction of Cr^{6+} to Cr^{3+} (Murphy, Hughes, & Mcloughlin, 2008). However, in contrast to the observations by Murphy et al., we did not observe any Cr^{3+} in solution. All of the adsorbed chromium was present as clusters of Cr^{3+} (CD) or as both hexavalent and trivalent chromium(CTMA). Reduction of Cr^{6+} to Cr^{3+} on modified chitosan surface has been reported by several researchers (S. S. Kahu, Shekhawat, Saravanan, & Jugade, 2016; S. Kahu, Saravanan, & Jugade, 2014).

Figure 2.26 CD

Figure 2.27 $CDCr^{6+}$

Figure 10 CTMA

Figure 11 CTMACr^{6+}

2.7. Conclusion

Chitosan was modified with DTPA and CTMA by ionic cross linking. The prepared adsorbents CD and CTMA were characterised and their potential as adsorbents for Cr^{6+} was investigated. The optimum pH for removal of Cr^{6+} was found to be 3 for CD and 2 for CTMA. Among the kinetic models tested, the adsorption kinetics was best described by the pseudo-second-order equation. The data fitted well with the Langmuir adsorption isotherm model. Adsorption thermodynamics indicate the adsorption of the metal onto CD and CTMA to be exothermic process. XPS and ESR studies indicated the reduction of Cr^{6+} adsorbed onto adsorbents to Cr^{3+}.

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