Adsorption of hexavalent chromium (Cr(VI)) from wastewater using novel chitosan/halloysite clay nanocomposite films

Padmavathy K S1, Amith Murali1, G Madhu*2 & Deepak Kumar Sahoo2

1Department of Chemical Engineering, Government Engineering College, Thrissur 680 009, Kerala, India.
2School of Engineering, Cochin University of Science and Technology, Cusat 682 022, Cochin, Kerala, India.

E-mail: padma426@gmail.com

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Nano composite films have been prepared in the laboratory by impregnating halloysite nanoclay on chitosan matrix. The functional groups present in the composite films have been investigated using Fourier transform infrared spectroscopy (FTIR) and morphological structure of the synthesized films are analysed using scanning electron microscopy (SEM). Thermo gravimetric analyser (TGA) is used for investigating the thermal stability of the composite. The films are used for adsorption of hexavalent chromium from wastewater. Optimum $pH$ for adsorption is 3.0 and all other experiments are conducted at $pH$ 3.0. It has been observed that adsorbent dosage required is very less when compared to pure chitosan as adsorbent. The adsorption capacity is also very high when compared with pure chitosan for removal of Cr (VI) under the same conditions. The equilibrium studies have been conducted and data is fitted to the Langmuir equation. The kinetic studies reveal that the adsorption mechanism is pseudo second order. The study shows that the chitosan/halloysite clay can be used as a promising adsorbent for hexavalent chromium uptake from wastewater.

**Keywords:** Adsorption, Chitosan, Halloysite nanoclay, Hexavalent chromium, Wastewater

Chromium has got wide applications in textile, metallurgical, tanning and electroplating industries. The wastewaters generated from these industries are rich in hexavalent chromium. This poses a serious and complex problem as it accumulates in the biosphere1,2. Chromium exists in two states Cr (III) and Cr (VI). Cr (III) is non toxic and immobile. Cr (III) is naturally occurring and is a micronutrient for metabolizing sugar, protein and fat3. Cr (VI) is toxic and causes skin ulceration, damage of the liver and is highly carcinogenic4. Treating wastewater containing chromium is a prerequisite in the preparation of potable water supplies due to lack of the fresh water available.

Wastewater should be treated effectively so that the toxic contaminants are removed. Heavy metals from wastewater can be removed by various methods like coagulation, precipitation, ion exchange, adsorption, reverse osmosis and solvent extraction5. Adsorption is a flexible operation and produces higher quality of water when compared to other technique. It is also low cost process and can effectively remove at very low concentrations of contaminants6. Adsorption using activated carbon as adsorbent is one of the efficient techniques for removal of heavy metals from wastewater. The high cost of activated carbon limits its use7. Various natural materials are also available as adsorbent for removal of chromium from wastewater. Now-a-days nanomaterials are used as adsorbents due to their very high surface area and active sites. A long list of nanoparticles is available in the market or is now going under final research steps. The application of nanoparticles for treatment of wastewater is recognized now as a reality. When nanoparticles are used as adsorbents, a low weight of adsorbent is required when compared to conventional adsorbents. Clay minerals are used in pollution control and have captured wide attention now a days8,9. Clay minerals like montmorillonite, kaolinite, bentonite and illite have been used for adsorptive removal of heavy metal ions. They are naturally available adsorbents10.

To improve the sensitivity and precision of adsorptive removal, the search for new adsorbents is an important factor. The poor recovery of target metal ions from solution by traditional adsorbents is due to several factors such as diffusion limitations, lack of active sites and low binding capacity. Hence, a novel adsorbent has to be developed which has large adsorptive surface area, low resistance to diffusion, fast separation of adsorbent after removal and high adsorption capacity11.
Halloysite nanoclay is naturally occurring clay mineral and has similar composition as kaolin. It is a two layered aluminosilicate with a predominantly hollow nontubular structure and is a naturally available clay mineral. Halloysite nanoclay is cheap and abundantly available and as a result they have got wide applications in wastewater treatment. Due to their size, they will not form stable suspensions in water even though they are hydrophilic. The outer surface of halloysite nanoclay has a structure similar to silicon dioxide while the inner surface is similar to that of aluminium oxide. The chemical formula of Halloysite nanoclay is Al₂Si₂O₅(OH)₄2 H₂O and it has a 1:1 Al: Si ratio.

Chitosan is a highly basic polysaccharide and is naturally occurring. Chitosan is a low cost material when compared to conventional adsorbents. Chitosan is a derivative of chitin and has got a wide number of applications in water and wastewater treatment. It is having a molecular weight 100,000-300,000. Crab and shrimp shells are the main sources of chitosan. Chitosan is soluble in acidic media while in alkaline media, it gets solidified. It is highly compatible with supporting materials like clay minerals, sand and activated carbon. Chitosan is used as a flocculating agent, for heavy metal removal, coatings to improve dyeing characteristics of glass fibre, wet strength additives for paper. Chitosan is the second abundantly occurring natural biopolymer next to cellulose. It is a non toxic and non allergic material. Other characteristics of this naturally occurring biopolymer are biodegradability, biocompatibility, inexpensiveness and hydrophilicity. It is capable of undergoing deacetylation which controls the fraction of amine groups that will be available for interaction with metal ions. The functional groups present in chitosan are hydroxyl (-OH) and amino (-NH₂). As a result, chitosan is extremely reactive. It has got a powerful absorptive capacity and is used as a natural adsorbent for removal of heavy metals in wastewater. Chitosan can be transformed into a number of shapes such as beads, membranes, films etc. This transformation capacity helps in the ease of continuous operations.

The two materials having different physical and chemical properties are combined to ensure that each material remains distinct in the composite. The combination of desirable properties of the materials used, is utilized in the composite. The selectivity, surface area, regeneration, mechanical strength etc are observed to improve for composite adsorbents. Polymer-clay composites undergo interface reactions and are observed to have better mechanical, thermal, biodegradable and physiochemical properties more than that of conventional composites. The structural, absorptive and mechanical properties of chitosan and nanoclay are improved on forming polymer-nanoclay composite films. In the present study, Halloysite nanoclay- chitosan biopolymer films are firstly prepared for the absorptive removal of Chromium (VI) from wastewater. The effect of various parameters such as pH, temperature, film weight, initial concentration and time of adsorption has been studied. Adsorption isotherms and kinetics for Cr (VI) removal from water have been investigated.

**Experimental Section**

**Materials**

Halloysite nanoclay, chitosan with deacetylation degree of 85.0% and potassium dichromate for Cr (VI) stock solution were purchased from Sigma-Aldrich Chemicals. 1, 5 Diphenyl carbazide, acetone used in the preparation of 1, 5 diphenyl carbazide solution. Lactic acid (1%), sulphuric acid (5%), hydrochloric acid (0.1 N) and sodium hydroxide (0.1 N) were purchased from Merck chemical company. Water used for preparation of various solutions and rinsing was HPLC grade water, obtained from the Millipore water purification system.

**Preparation of chitosan / halloysite nanoclay films**

2.0 g chitosan was dissolved in 100 mL of 1% lactic acid and stirred for 10 h at 500 rpm. 0.5 g halloysite nanoclay was added to the above mixture. The resulting solution was magnetically stirred for 8 h at 1000 rpm. After stirring, the solution was sonicated for 4 h. After sonication, 40 mL of the above solution was poured into a glass petridish. The films were dried in an oven at 80°C for 24 h. After drying, the films were washed with distilled water to remove sodium hydroxide. The films were then peeled off. The film was cut into equal diameter particles for performing the adsorption experiments. Thickness of the film was 0.2 mm, diameter of adsorbent particles was 6.5 mm and average weight of particles was 0.004 g. The synthesized nanofilm is shown in Fig. 1.
Characterization of chitosan/halloysite film

The surface morphology of nanoclay dispersed chitosan was analysed using scanning electron microscope JEOL-JSM-6390. Fourier transform infrared spectroscopy was used to analyse the structure of chitosan nanocomposite film. Perkin Elmer FTIR spectrophotometer with 20 scans and resolution 4 was used for analysing the composite film. Thermo gravimetric analysis was performed to analyse the thermal stability of nanofilm. STA 6000 Perkin-Elmer was used for thermal analysis in the present study. Nitrogen gas was used to maintain the inert atmosphere. At the rate of 5° per minute the film was heated from room temperature to 895°C and the weight loss was noted. If there is no weight loss, the material will be thermally stable in that temperature range. The film thickness was measured using a hand held digital micrometer.

Analysis method

Cr (VI) solution was analysed using UV-VIS spectrophotometer (Hitachi U-2900). 1, 5 Diphenyl carbazide was used for spectrophotometric determination of Cr (VI) at \( \lambda_{\text{max}} = 540 \) nm. 1, 5 diphenyl carbazide was dissolved in 250 mg acetone and stored in a brown bottle. 4 mL of diphenyl carbazide solution was mixed with required concentration of Cr (VI) solution and made up to 50 mL. This solution was analysed in spectrophotometer. A blank solution containing diphenyl carbazide made up to 50 mL was used as the blank for analysis. Spectrophotometer was first calibrated using Cr (VI).

Experimental procedure

Potassium dichromate (2.835 g of 99%) was dissolved in deionised HPLC grade water to prepare 1000 ppm Cr (VI) stock solution. Cr (VI) solution for batch tests was prepared by dilution of the stock solution. Chitosan/clay composite film was used as the adsorbent for the batch tests done in a temperature controlled incubated shaker at 120 rpm. Experiments were carried out at varying pH values, time intervals, initial concentration values, adsorbent weight values and different temperatures. A definite amount of adsorbent was added to 100 mL Cr (VI) solution of known initial concentration at a constant pH. This was shaken in an incubated shaker at constant temperature for a specified time and the solution was filtered in whatman 40 filter paper and the filtrates were diluted using diphenyl carbazide and analysed using UV-vis spectrophotometer. The pH of the solution was adjusted using either hydrochloric acid or sodium hydroxide (0.1 N). All the experiments were done in duplicate and the average values were noted. All parameters except one parameter were fixed keeping the others constant for optimization studies. For pH study, 25 mg/L of constant initial concentration was taken and 0.06 g adsorbent was added to 100 mL of solution taken in stoppered flasks. The pH was varied from 2-10.8 and shaken for 60 min at 50°C in temperature controlled incubated shaker. The pH at which maximum removal takes place was 3 which was set as the optimum pH for performing further experiments. For adsorbent dose, study weight of composite film was varied from 0.02 to 0.2 g/100 mL, keeping temperature at 50°C, time of shaking at 60 min and initial concentration 25 ppm. Temperature of adsorption was varied from 30-110°C for studying the effect of temperature. Time for the study was fixed at 60 min, adsorbent dose was 0.06 g and initial concentration was 25 ppm. To study the effect of initial concentration, shaking was performed at 50°C until equilibrium was reached, where adsorbent dose was fixed at 0.06 g and time maintained at 60 min. Initial concentration was varied from 5 to 90 ppm for the study. Kinetic studies were performed varying time from 15 -75 min at 50°C and adsorbent dose of 0.06 g/100 mL. For kinetic study, initial concentration was fixed at 25 ppm at pH 3.0 and batch tests were performed until equilibrium was reached. Isotherm studies were carried out varying the initial concentration at pH 3.0 and temperature 30°C. Adsorbent dose was taken as 0.06 g/L. Shaking was performed at 120 rpm and 60 min. For each initial concentration, the batch experiment was carried until equilibrium was reached. The amount of Cr (VI) adsorbed per unit adsorbent, \( q \) (mg/g) was calculated according to the equation

\[
q = \frac{(C_0 - C_f)}{m} \quad \ldots (1)
\]
and $C_t$ are the concentrations (mg/L) of Cr (VI) before adsorption and after adsorption respectively. $m$ is the amount of adsorbent (g) in one litre of the solution. Efficiency (%) of adsorption was calculated using the equation:

$$E = \frac{(C_0 - C_t)}{C_0} \times 100$$  \tag{2}

Equilibrium models

Equilibrium between adsorbed metal ion concentration and concentration of solution at equilibrium is explained by Langmuir and Freundlich models. Langmuir model represents monolayer adsorption where the adsorbed molecules are not interactive and adsorption takes place on a surface having finite number of identical sites. The Langmuir equation is given by equation (3) and the linearized form of equation (3) is given by equation (4).

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$  \tag{3}

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m C_e}$$  \tag{4}

$C_e$ represents the equilibrium concentration of the solution in ppm, $q_e$ is the adsorption capacity in mg/g at equilibrium, $q_m$ is related to the maximum adsorption capacity (mg/g), and $b$ is related to the energy of adsorption (l/mg)$^3$. $q_m$ and $b$ are called Langmuir constants which are respectively the intercepts and slope of the plot between $\frac{1}{q_e}$ vs $\frac{1}{C_e}$.

Freundlich isotherm represents adsorption on a heterogeneous surface and binding sites are not identical. Here monomolecular layer coverage of solute by the adsorbent is considered and adsorbed molecules are interactive. Freundlich model is given by equation (5) and in linearized form is given by equation (6).

$$q_e = K_f C_e^n$$  \tag{5}

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$  \tag{6}

$K_f$ indicates adsorption capacity in mg/g and $n$ is the intensity of adsorbent and are called Freundlich constants.

Kinetic study

To determine the rate of adsorption, the data was fitted with Lagergren equation, the pseudo second order equation, the second order rate equation and intraparticle diffusion model as given below. Lagergren equation is given by equation (7) pseudo second order equation is represented by equation (8), the second order equation by equation (9) and intraparticle equation by (10).

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$$  \tag{7}

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$  \tag{8}

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t$$  \tag{9}

$$q_t = K d t^{1/2}$$  \tag{10}

$K$ is the Lagergren constant (min$^{-1}$), $K_1$ is the pseudo second order rate constant for adsorption in gmg$^{-1}$min$^{-1}$, $K_2$ is the second order rate constant (g mg$^{-1}$min$^{-1}$) and $K_d$(mgl$^{-1}$min$^{-1/2}$) is the rate constant for intraparticle diffusion. $q_e$ is the amount of metal ion adsorbed at equilibrium and $q_t$ is the amount of metal ion adsorbed at time t in mg/g.

Results and Discussion

Effect of pH on adsorption of Cr (VI)

The quality of the adsorbent is dependent on solution pH. The surface charge of the adsorbent is controlled by solution pH. The removal efficiency and adsorption capacity versus pH is shown in Fig. 2. Maximum removal of hexavalent chromium was observed at pH 3. Below pH 3, removal efficiency and adsorption capacity increases with increase in pH. Adsorption capacity and efficiency decreases with increase in pH above 3.

Efficiency of Cr (VI) removal reached 14 % at pH 10.8. Cr (VI) exists in various forms such as $CrO_4^{2-}$, $HCrO_4^-$, $Cr_2O_7^{2-}$. At pH below 2, Cr (VI) takes the form $H_2CrO_4$. As a result at low pH interaction
between Cr (VI) and –NH$_2$ is much less. Therefore adsorption efficiency is less at pH<2. At acidic pH around 3.0, Cr (VI) exists as CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$.

At such pH values, adsorption of negatively charged chromate ion onto positively charged amino group are very efficient. Adsorption mechanism is by ion exchange in this pH range. As pH increases, formation of OH$^-$ takes place and adsorption chromate ions become competitive. As a result, % removal of Cr (VI) decreases at higher pH. Previous works similar to the present work also report higher removal at low pH. Previous work$^7$ showed that above 90% removal efficiency of Cr (VI) was obtained using chitosan flakes as adsorbent. Adsorbent dose for the above study was 13 g/L under almost similar conditions. In the present study, 90% removal was obtained with an adsorbent dose of 0.6 g/L. Quantity of Chitosan/halloysite nanoclay required is much less when compared to previous studies.

**Effect of adsorbent dose on adsorption of Cr (VI)**

The effect of chitosan/halloysite nanoclay film on efficiency of adsorption and adsorption capacity is shown in Fig. 3. At pH held at 3.0 and initial concentration 25 ppm, removal of Cr(VI) increases with increase in adsorbent dose and at an adsorbent weight of 1.7 g/L, maximum removal of 92% is observed. Further increase in adsorbent weight causes decrease in removal of Cr (VI). After 2 g/L of adsorbent removal adsorption reached saturation level and no further removal is observed. Increase in efficiency with increase in adsorbent dose indicates that more active sites are available for adsorption of Cr (VI). At high adsorbent dosage, there may be some aggregation of particles since the agitation speed is maintained at constant value of 120 rpm. So at higher dosages, active site is less and hence efficiency decreases. With further increase in weight of chitosan/clay film equilibrium is reached and no further removal is observed. The adsorbent is saturated at this condition. This result shows similarity with those reported in previous literature.

**Effect of time**

Adsorption capacity varies from 17 mg/g to 37.5 mg/g when the contact time is varied between 15 to 70 min. Adsorption capacity increases rapidly with time up to 70 min and thereafter it remains constant. Also 90% removal efficiency is achieved in 70 min time and after 70 min equilibrium is reached. As time progresses, adsorption of Cr (VI) onto chitosan/clay film increases and after 70 min, no further adsorption takes place.

**Effect of initial concentration**

Increase in initial concentration of Cr (VI) solution from 5 ppm to 90 ppm showed an increase in % removal from 54% to 88%. Initially the increase in removal efficiency is much less and no steady increase is observed but after 60 ppm, removal of Cr (VI) shows a steady increase and the removal efficiency reached 88% and then after 70 ppm, no change in removal is observed and equilibrium is reached at 70 ppm. This shows that initial concentration has important effect in the adsorption of Cr (VI) using chitosan/clay composite film. Adsorption capacity also increases from 5 to 133 mg/g with increase in initial concentration. With increase in initial concentration, concentration gradient in the system also increases. Hence removal
increases. At high concentration the active sites of adsorbent are saturated and adsorption ceases. Previous work reported similar result.

**Effect of temperature**

Initially the removal of Cr (VI) is less but with increase in temperature, the adsorption efficiency increases up to 60°C and afterwards, efficiency decreases. This shows that adsorption is endothermic initially and after 60°C, desorption takes place and as a result, efficiency of Cr (VI) removal decreases. Chromium uptake (mg/g) also increases with temperature and then decreases. The effect of temperature is shown in Fig. 4.

**Kinetic study of adsorption of Cr (VI)**

For modelling and design, kinetic analysis is required to find the rate of adsorption and rate limiting step. At 70 min, equilibrium was reached and adsorption capacity at equilibrium is 37.5 mg/g. The kinetic constants and correlation coefficients are given in Table 1. The linear regression coefficients for pseudo first order, second order and intraparticle diffusion model are much less. Also these models, show much deviation from experimental and calculated values of adsorption capacities. Kinetic data is best fitted by pseudo second order model with correlation coefficient is approximately 0.9. The experimental and calculated values of adsorption capacity are 37.5 and 34.48 mg/g which do not show so much deviation when compared to other models. Rate constant for pseudo second order kinetic model is obtained as 0.001483 g mg\(^{-1}\) min\(^{-1}\). Hence the adsorption mechanism of Cr(VI) on chitosan/ halloysite nanoclay obtained is pseudo second order.

**Adsorption isotherm**

The Langmuir and Freundlich plots for adsorption of Cr (VI) on nanocomposite films are shown in Fig. 5. The initial concentration for isotherm study was varied from 5 ppm to 15 ppm at temperature 30°C. The values of Langmuir and Freundlich constants are given in Table 2. The equilibrium data fitted more to Langmuir model than to the Freundlich model indicating unilayer adsorption. Freundlich model, while having \(R^2\) value 0.996, the adsorption capacity is observed to be much less when compared to Langmuir model. Langmuir isotherm gives an adsorption capacity of 142.85 mg/g which is very high when compared with conventional adsorbents.
reported in the literatures. The adsorption capacity of chitosan for Cr (VI) adsorption is only 7.943 mg/g at room temperature as reported in previous literature. When compared to chitosan, nanocomposite film of chitosan/halloysite nanoclay possesses high adsorption capacity for Cr (VI) removal. Impregnation of halloysite nanoclay is an advantage for adsorption of Cr (VI) from wastewater. A dimensionless separation factor \( R_L \) was determined. It indicates whether the adsorption is favourable or not. Value of \( R_L < 1 \) indicates that adsorption is favourable and \( R_L > 1 \) indicates unfavourable adsorption. It is calculated using equation 11.

\[
R_L = \frac{1}{1 + bC_0} \quad \ldots (11)
\]

where \( b \) is the Langmuir constant in l/mg and \( C_0 \) is the initial adsorbate concentration in mg/L. In the present case \( C_0 \), taken as 5 ppm which is the lowest initial concentration taken for isotherm study, \( R_L \) is 0.94 which indicates that adsorption is favourable. The value of \( R_L \) between 0 and 1 for all initial concentrations in the adsorption study which shows that adsorption is favourable.

**Characterization of synthesized chitosan/halloysite nanoclay films**

**Scanning electron microscopy (SEM)**

The morphological structure of halloysite nanoclay and chitosan/nanoclay films were analysed using SEM. SEM images are shown in Fig. 6. The SEM analysis gives a clear cut idea regarding the aggregation of clay in chitosan matrix. From the SEM image, it is seen that the clay particles are amorphous in nature. The SEM image of chitosan-halloysite nanoclay composite film indicates that the nano clay particles are dispersed well in the chitosan matrix. When nanoclay is added to chitosan matrix, the structure of chitosan is altered considerably.

**Fourier Transform Infrared (FTIR) spectroscopy**

Spectra of chitosan/halloysite clay bio composite film before and after adsorption were analysed using FTIR spectroscopy. FTIR spectra of bio composite film is shown in Fig. 7. FTIR spectra give the functional groups present in the composite material.

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**Table 2 — Equilibrium parameters for adsorption of Cr (VI) on nano composite film**

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_m, \text{mg/g} )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>142.85</td>
<td>0.0125</td>
</tr>
</tbody>
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Fig. 6 — SEM micrographs of nano composite film

Fig. 7 — FTIR spectra of nano composite film before adsorption

The characteristic bands present in the film are 3252.36 cm\(^{-1}\) due to O-H stretching, 2927.7 and 2925 cm\(^{-1}\) due to C-H stretch, 2103.31 cm\(^{-1}\) due to C=C stretch and 1719.91 cm\(^{-1}\) due to C=O stretch. -H bending causes band at 1454.86 cm\(^{-1}\). Peaks at 1029.72 cm\(^{-1}\) and 1067.65 cm\(^{-1}\) are due to C-N stretching. The band at 926.72 cm\(^{-1}\) in the film corresponds to \( \equiv \text{C-H} \) bend. The bands at 1119.06 and 1151.25 cm\(^{-1}\) corresponds to Si-O stretching. Peak at 897.17 cm\(^{-1}\) corresponds to Al-OH vibrations and at 926.72 cm\(^{-1}\) is due to Al-OH. The characteristic bands present in the spectrum of pure chitosan are also present in the chitosan/halloysite nanocomposite film. Pure chitosan shows IR bands at 2880 cm\(^{-1}\) due to C-H stretching, 1375.95 cm\(^{-1}\) due to C-H bending,
1590 cm\(^{-1}\) due to N-H bending, 1150 and 1025.51 cm\(^{-1}\) due to C—O stretching. Additional peaks in the FTIR spectrum of composite film is due the presence of halloysite nanoclay in the chitosan matrix. After adsorption, there is considerable change in the spectrum of nanocomposite membrane. The peak corresponding to O-H stretching is shifted to 3333.76 cm\(^{-1}\) after adsorption. The band at 1600 cm\(^{-1}\) corresponds to C=C stretching. The bands at 673.00 cm\(^{-1}\) and 666.21 cm\(^{-1}\) corresponds to Al-OH. Intensity of Si-O stretching is reduced and C-O stretching vibration is reduced significantly. The disappearance of various bands after binding of Cr (VI) is attributed to interaction of Cr (VI) with the film. The FTIR spectrum before adsorption indicates the image shows that nanoclay is dispersed in chitosan for adsorption of Cr (VI) from wastewater. The SEM images of nanoclay are successfully prepared and used for TGA study, a non oxidative degradation occurs. Initially the weight loss is much less and weight loss shows rapid increase after 200°C. Initially weight losses are due to loss of moisture. After 200°C, weight loss is due to degradation of nanofilm and at 450°C, only 5% of the material is remaining. It was reported that thermo gravimetric degradation of chitosan starts at 60°C where moisture removal takes place. Around 220°C, rapid degradation of chitosan takes place and reaches maximum at 240°C\(^{22}\). From the comparison of TGA curve for standard chitosan, it is clear that the addition of halloysitenanoclay decreases the thermal stability of chitosan.

**Conclusion**

Surface modified chitosan films using halloysitenanoclay are successfully prepared and used for adsorption of Cr (VI) from wastewater. The SEM image shows that nanoclay is dispersed in chitosan matrix. FTIR spectrum before adsorption indicates the presence of halloysite clay in the nanocomposite film and after adsorption shows a significant change in the structure of nanocomposite film due to adsorption of chromium. The quantity of adsorbent required is much less for hexavalent chromium uptake from wastewater. The equilibrium data fits more to the Langmuir isotherm and kinetic data better fitted by the pseudo second order model. The maximum adsorption capacity from Langmuir isotherm is 142 mg/g. Optimum pH for adsorption is 3.0 and equilibrium time is 70 min. Chitosan/halloysitenanoclay provides very high adsorption capacity when compared to pure chitosan. Altogether, this novel nanocomposite film is an excellent adsorbent for uptake of Cr (VI) from wastewater.

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**References**