Facile One Pot Synthesis of Thiocarbamoyl Chitosan for
the Adsorptive Elimination of Hexavalent Cr (VI) Ions

Choudhary Anurag\textsuperscript{a}, Kumar Praveen, Kadwasara Anurag and Poonia Sardaar Singh
Department of Chemistry, JNV University, Jodhpur, INDIA
\textsuperscript{a}anurag051981@gmail.com

Abstract
The industrial effluents include heavy metals such as Cr, Pb, Hg, Cu, Ni etc. which are affecting ecosystem and have harmful effects on mankind. Biopolymers like chitosan have been extensively applied for waste water treatment. Use of thiourea and glutaraldehyde to make thiocarbamoyl chitosan was investigated for removal of chromium ion from aqueous solution. TC-CS was characterized by various spectrometric techniques such as FTIR, SEM, EDX, BET and pH\textsubscript{pzc}. It was observed that 94% of metal ions have been removed within the first 2 hrs after contact with bio-sorbet. The adsorption study indicates that the removal rate of Cr (VI) ions from aqueous solution by TC-CS sorbent was excellent and up to 1.06 mmol/gm (56.18 mg/gm).

The removal efficiency was dependent on solution-pH, contact time, adsorbent dose and initial metal concentration. The highest adsorption was found at pH 6 at 100 mg of adsorbent. Adsorption kinetics data followed pseudo second order kinetic model with linear coefficient of 0.9997. The adsorption process could be described well by Langmuir isotherm ($R^2=0.9860$) suggesting favourable adsorption through homogeneous monolayer adsorption.

Keywords: Industrial effluents, chitosan, bio-sorption.

Introduction
In recent decades, industrialization and modernization introduced irrecoverable and grave harm to the earth’s environment\textsuperscript{16}. These effluents are persistent in the ecosystem and have reached an alarming level in aquatic and terrestrial environments\textsuperscript{15}.

Among these, heavy metals are highly significant pollutants and therefore, are concerned as contemplation to many research studies worldwide level owing to their adverse influence on human health and animal life. Heavy metals are extensively utilized in the industries like paper, textiles, leather, electroplating, plastics, cement, metal processing, wood preservatives, paints, pigments and steel fabricating industries. Wastewater discharge from these industries normally encompasses metal ions such as Cr (VI), Pb (II), Hg (II), Cu (II), Ni (II) etc. and plays a vital role in contaminating the environment.

The contamination of water by waste disposal from industries leads to an increase in the considerable amount of heavy metals. These heavy metals have a lethal effect on aquatic as well as terrestrial life even at very low concentrations and have tendency to bioaccumulate. The improper disposal of these toxic elements can pose serious environmental problems.

Contamination of water sources is hazardous to plants, animals and microorganisms and can be carcinogenic to mankind\textsuperscript{8}. Many developed countries have achieved advanced technologies such as ion exchange, vacuum evaporation, crystallization, membrane process and solvent extraction technologies for removing these heavy metal ions from industrial effluents\textsuperscript{22,30}.

Chromium pollution in aqueous media is of considerable concern as the metal has found widespread adoption in electroplating, leather tanning, metal finishing, nuclear power plants, the textile industry and chromate manufacturing. The National Institute for Occupational Safety and Health (NIOSH) recommends reducing the chromium content in water to $10^3$ mg / L. The metal is reported to bioaccumulate in flora and fauna causing ecological problems\textsuperscript{16}.

Wide range of physical and chemical processes is presently available and is adopted for the elimination of these toxicants from wastewater such as precipitation, ultrafiltration, adsorption, ion exchange, reverse osmosis, ozonation, coagulation and membrane filtration process. Among these, adsorption techniques have proved to be most versatile due to its simple mechanism, low cost, high efficiency and easy availability of various adsorbents\textsuperscript{21}.

Over the last decade, several studies have been reported globally on natural polymers and various methods have been developed for enhancing their metal-binding abilities. Some of the well-known natural polymers such as chitosan\textsuperscript{1}, alginate\textsuperscript{4}, cellulose\textsuperscript{11} lignin\textsuperscript{12} and starch\textsuperscript{17} have received considerable attention for this purpose. Characteristics of various biopolymers and their sources are tabulated in table 1.

Polysaccharides from plants such as PCL leaves\textsuperscript{23} have been extensively used for eliminating ground water toxicants such as fluoride and nitrate. Biopolymers like chitosan have been extensively explored due to their interaction with metal cations.

These bio sorbents in native and chemically modified forms have been effectively applied for the separation of heavy metals from industrial wastewater\textsuperscript{2}. 

---

\textsuperscript{1}\textsuperscript{1}\textsuperscript{1}Vol. 26 (5) May (2022) 
Chitosan is a natural polycationic polymer obtained by alkaline N-deacetylation of chitin, having the property of being biocompatible, biodegradable and having excellent metal-binding capabilities. Chitosan is a poly(aminosaccharide) containing poly(1-4)-2-amino-2-deoxy-D-glucose units. It possesses a high ratio of hydroxyl group and amine group, making it conducive to the introduction of new functional groups. Both hydroxyl and amino groups are often used for chemical modification for enhancing stability and improving its heavy metal ion chelating properties.\(^{25}\)

The free amino function of chitosan gives it a better ability to chelate ions of transition metals than other natural polymers such as cellulose and its derivatives. The chelating properties are utilized for water treatment and to recover metals.\(^{27}\) It has been shown that the cross linking reduces the adsorption capacity of the chitosan. The main reason for the loss of adsorption capacity is the involvement of amino groups in the cross-linking reaction.\(^{29}\) The ability of chitosan to capture metal ions can be enhanced by suitable modification of the molecule. The amino and two hydroxyl groups on each glucosamine in the repeating unit of chitosan can act as reactive sites for chemical modification. Several such studies have been reported in the literature on the enhancement of adsorption ability of chitosan and adsorption selectivity.\(^{10,29,33}\)

According to HSAB (hard and soft acids and bases) principle used for the prediction of complexation reactions, sulphur serving as a soft legend group has a very strong affinity for a large number of heavy metals which are considered to be soft acids and can form a stable metal–sulphur complex.\(^{31}\) Increasing attention has been paid towards thiourea (TH) which offers more amino groups. Thiourea is known for its sequestering properties due to its high binding ability for metal ions. Several sorbents were prepared by blending chitosan with TH which has been used for the removal of metal ions from an aqueous solution. However, Huahua et al.\(^{20}\) found slow sorption kinetics and achieved sorption equilibrium in more than 6 h. Moreover, some of these exhibited lower efficiencies under pH value less than 4.0 and low sorption capacity.\(^{6,12}\) In these circumstances it becomes important to design some new and more desirable sorbents to increase removal efficiency.

The major objective of the existing work was to the development of simple one pot synthetic approach for chemically modified chitosan derivative with thiourea using cross linking agent glutaraldehyde at room temperature and to characterize the prepared material and to project for an exhaustive investigation of sorption properties for adsorption of Cr(VI) ions from a standard solution of chromium. The obtained experimental results were assessed with mathematical models of Langmuir and Freundlich isotherms. Batch adsorption studies were conducted to evaluate the adsorption capability of modified chitosan.

### Material and Methods

**Reagents:** Chitosan powder was purchased from Alfa Aesar, USA (Batch No A2041604). The degree of deacetylation (DA) was reported as 85 % by the manufacturer. Analytical grade thio urea, glutaraldehyde (25% w/v) and potassium dichromate were purchased from Fisher Scientific, India and were used without any further purifications. Cr (VI)
standard stock solution (100 ppm) was prepared by dissolving 0.141 gm of potassium dichromate in 500 ml double distilled water and then a range of solutions with desirable concentrations was prepared by diluting stock solution.

**Preparation of Thiocarbamoyl Chitosan (TC-CS):** TC-CS was prepared with an interaction of 4.0 g of thiourea (TH) and 8 ml glutaraldehyde in 50 ml of double demineralized water in a single neck reaction flask overnight at room temperature in a nitrogen environment. After the reaction between thiourea and glutaraldehyde, 3.5 g of chitosan was added to the solution and then placed under agitation for another 72 h. Finally, the functionalized chitosan sorbent (TC-CS) was separated by filtration using a vacuum filter and rinsed several times with deionised water and dried at room temperature overnight. The yield was found to >85%. EDAX plots (figure 3) have been shown for the elemental composition of modified sorbent.

**Metal concentration and Characterization analysis:** Chromium ions were determined by spectrophotometer (Systronic 106) using di-phenyl-carbazide method. Characterization of thiocarbamoyl chitosan and metal loaded chitosan was investigated using FTIR, SEM analysis and EDX analysis. Surface area, pore volume and pore volume were determined by BET analysis (Table 3). pH of the adsorbent was determined for finding optimum pH range and nature of charge on the adsorbent surface.

**Batch adsorption studies:** For each batch experiment, known concentration of 100 ml of synthetic solutions of chromium (VI) ion solution was taken in 250 ml Erlenmeyer flask with glass stopper with known amount of adsorbent and assessed for adsorption process at room temperature. The adsorbent used was sieved through a sieve shaker to obtain particle size in the range of 0.5 -0.6 mm. This solution was then stirred continuously using a rotator shaker at 150 RPM to achieve adsorption equilibrium. After achieving the equilibrium, all the solution was taken out from the flask and filtered through Whatmann filter paper no. 42 and supernatant liquid was analyzed for residual metal ion concentration with spectrophotometer.

The extent of adsorption was investigated by varying adsorbent dose, time, pH of medium and initial metal concentrations. Effect of the adsorbent dose was carried out using varying amounts of adsorbent from 10 to 100 mg for a fixed concentration of chromium ion at room temperature for 6 hrs shaking. The entire assay was run for triplicate for each experiment differing with less than 1% and only means values are presented. The entire process is illustrated in figure 1.

The removal efficiency (%) and adsorption capacity (mmol/g) for a particular experiment were determined using the following equations 1 and 2:

Removal efficiency (%) = \( \frac{|C_i - C_t|}{C_i} \times 100 \)  \( \text{(1)} \)

Adsorption capacity (mmol/g) = \( \frac{|C_i - C_t|}{m} \times \frac{V}{m} \)  \( \text{(2)} \)

where \( C_i \) is initial metal ion concentration (mmol/L), \( C_t \) is the residual concentration (mmol/L) at time t (min), m is mass (gm) of adsorbent and V is the volume of solution (L) used in the batch.

**Figure 1: Process of preparation and adsorption**
Results and Discussion
Characterization of chemically modified adsorbent
FTIR analysis of prepared adsorbent: Fourier Transformed Infrared spectroscopy (FT-IR) was used to confirm structural changes in the polymer backbone of chitosan matrix during the preparation of thiocarbamoyl chitosan. The measurement was carried out by Agilent carry 630 FTIR spectrophotometer in the attenuated total reflectance (ATR) mode in the range of 4000-650 cm\(^{-1}\) with a resolution of 8 cm\(^{-1}\) at room temperature.

The FTIR spectra of metal-loaded and unloaded adsorbent were analysed. As shown in figure 2 (a), the infrared spectrum of thiocarbamoyl chitosan showed that the absence of a peak at 1720 cm\(^{-1}\) indicates that no free aldehydic group for glutaraldehyde remains free which indicates the involvement of these groups in cross-linking. The band at 3420 cm\(^{-1}\) is due to the elongation of N-H and O-H bonds. The original signal at 1580 cm\(^{-1}\) in untreated chitosan due to \(-\text{N-H} \) deformation vibration disappears as a result of the amino group of chitosan being substituted and a weak band at 1656 cm\(^{-1}\) is an indication of C=N bond starching vibration. The bands at 2875 and 2920 cm\(^{-1}\) could be attributed to the C-H (CH\(_3\), CH\(_2\)) stretching vibration and are characteristics of saturated carbon. The sharp peak at 1075 cm\(^{-1}\) is due to the asymmetric stretching of S-C-S groups which has been shifted to 1041 cm\(^{-1}\) after treatment with chromium solution.

Scanning Electron Microscope (SEM) analysis: The field emission scanning microscopy (FE-SEM, nova nano SEM 450) was used to study for surface morphology of TC-CS before and after loading by chromium ions. The samples were gold coated to improve their conductivity for obtaining a better image. The representative micrograph has been presented in figure 3(a) and 3(b). The surface of TC-CS has been found to be rough and crusted-like structure with holes and tiny interspaces providing easy site availability and increased contact area for improved adsorption of metal cations from aqueous solution. After adsorption of chromium, there is marked change in surface morphology (fig. 3b). The energy dispersive X-ray (EDX plot) analysis spectrum of the prepared sorbent further confirmed for the presence of sulphur on to chitosan framework and the weight percentage of sulphur was found to be 2.73% (Table 2).

EDX analysis: Table 2 shows the elemental composition of prepared material before and after adsorption identified by EDX plots (fig. 3c and 3d).

![Figure 2: FTIR spectra of (a) plain TC-CS and (b) Cr (VI) treated TC-CS](image-url)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight (%)</th>
<th>Atomic (%)</th>
<th>Error (%)</th>
<th>Weight (%)</th>
<th>Atomic (%)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-K</td>
<td>59.07</td>
<td>65.37</td>
<td>7.76</td>
<td>41.89</td>
<td>52.74</td>
<td>9.12</td>
</tr>
<tr>
<td>O-K</td>
<td>23.31</td>
<td>19.37</td>
<td>3.77</td>
<td>04.38</td>
<td>04.73</td>
<td>6.29</td>
</tr>
<tr>
<td>N-K</td>
<td>14.89</td>
<td>14.13</td>
<td>3.24</td>
<td>40.64</td>
<td>38.42</td>
<td>5.40</td>
</tr>
<tr>
<td>S-K</td>
<td>2.73</td>
<td>1.13</td>
<td>0.14</td>
<td>01.69</td>
<td>00.80</td>
<td>0.20</td>
</tr>
<tr>
<td>Cr-K</td>
<td>11.40</td>
<td>03.32</td>
<td>3.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
<td>100.00</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>
Point of zero charge ($pH_{pzc}$): Point of zero charge for modified chitosan was found at 7.6 (Figure 4). That means the surface of modified chitosan has positive charge below pH of 7.6 which is created by the protonation of amine group in the chitosan, this favors for adsorption of negatively species at pH below 7.6 and species like heavy metals which have positive charge interacted and adsorbed easily on were adsorbent at pH above 7.6.

Adsorption Studies

Effect of adsorbent dose: The effect of adsorbent dose was investigated using varying amount of TC-CS. The adsorption results have shown that sorption of metal had increased from up to 98 % as the adsorbent dose increased from 10 mg to 100 mg keeping constant metal ion concentration of 10 ppm chromium (28.2 mg/L) at 6.0 ± 0.02 pH and the temperature was kept at room temperature with shaking time of 6 hrs at 150 RPM on a rotatory shaker. The results are shown in figure 5. It is observed that adsorbent dose increase from 10 to 100 mg, adsorption increases from 63.1 to 97.6 %.

However, there are no significant increases in sorption after reaching an adsorbent dose more than 100 mg. Due to its high adsorption efficiency, a small dosage of TC-CS was sufficient to extract the targeted ions. The highest adsorption efficiency is found around 100±10 mg of dose. Therefore, 100 mg of the adsorbent dose was used for subsequent studies.

Effect of initial metal ion concentration: The effect of initial chromium concentration on adsorption capacity was investigated by using different ranges of chromium solution from 1 ppm to 10 ppm keeping adsorbent dose at 100 mg at
pH 6 at room temperature. Varying concentration leads to affect driving forces for adsorption and consequently affects the adsorption behaviour of metal ions. The results are illustrated in figure 6. Cr(VI) ion removal significantly increased from 61.3 % to 97.9 % when initially chromium concentration increases from 1 to 10 ppm. This is because a high initial concentration gradient between bulk solution and TC-CS overcomes the mass transfer resistance of Cr(VI) ions. The results show that the adsorption process is fast and affected significantly by initial metal ions concentration.

Effect of pH: Solution pH is of great importance owing to its influence on adsorption performance. For this purpose, modified chitosan was investigated towards chromium adsorption at different pH range. Figure 7 shows the effect of solution pH on the adsorption of chromium ions. These results show that initial adsorption of chromium was raised from 68.9 % at pH 2 to 95.3 % at pH 6 and then was raised down to less than 5% at pH 9 and more. Therefore, pH 6 was chosen as the optimal pH for further experiment.

The amount of Cr (VI) adsorbed increases when the pH of the solution changes from 1 to 6 and further increases in pH result in decreased adsorption capacity. This is because pH_{zpc} is given as 7.6 (ongoing work) for prepared TC-CS show that below pH_{zpc} of the solution pH, the surface of the adsorbent is positively charged due to the protonation of the amino group and the sorbate in the acidic medium is negatively charged, since Cr (VI) exists as $HCrO_4^-$. Therefore, there is an electrostatic interaction between sorbent and sorbate which leads to the reduction of Cr (VI) to Cr (III) by the thiocarbamoyl group and promotes the adsorption.
Effect of time: Effect of contact time on adsorption was studied and the results are shown in figure 8. An increase in removal capacity with increase in time from 10 min to 12 hrs of contact can be attributed to the fact that more time becomes available for metal ions to make an attractive complex with TC-CS. It was found that the removal of metal ions increased rapidly with increase in contact time initially and reached a plateau after the first 2 hrs. The fast adsorption might be due to the highly porous surface of the sorbent material. This trend was similar to prior studies²¹. Further
increase in contact time did not increase the uptake due to deposition of metal ions on the available adsorption sites on the adsorbent materials. Preliminary investigations into the uptake of Cr (VI) ions on the adsorbent materials at their optimum pH values indicate that the process is rapid. Typically, 50-80% of the ultimate adsorption efficiency occurs within the first two hours of contact. This initial rapid adsorption subsequently gives way to a very slow approach to attain equilibrium and saturation is reached in 5-6 hr.

Adsorption kinetics: The adsorption kinetics for Cr(VI) adsorption onto TC-CS was determined by carrying out measurements after different contact times (0.5,10,20,30,60,120 min) at room temperature on solution-pH of 6 and an initial metal concentration was 3000 mg/L. To explore adsorption behavior, pseudo-second-order models were used to fit adsorption data as shown in figure 9. Generally, the linear pseudo-second-order model\(^9\) is expressed by equations 3:

\[
\frac{t}{q_t} = \frac{1}{K_f q_e^2} + \frac{t}{q_e}
\]

where \(K_f\) is the rate constant of the adsorption (L/mg/min). \(q_t\) and \(q_e\) are amounts adsorbed (mg/gm) at equilibrium and time \(t\) respectively. The linear plot between time and \(t/q_t\) is shown in figure 9. From the graph, it is evident that the adsorption is followed by pseudo-second order kinetics. The rate constant is found to be 0.24 L/mg/min.

Adsorption isotherms: The distribution of sorbate between solid and solution interface at equilibrium has been described by adsorption isotherms which demonstrates mathematical expression of adsorption behaviour of a given adsorbate species based on surface activity of adsorbent and possible interaction between species. Adsorption experimental data are usually subjected to both the adsorption isotherms such as Langmuir and Freundlich isotherms. The results of the adsorption experiment data were fitted to Freundlich and Langmuir isotherm models for the description of the adsorption process and to determine the relationship between the adsorption isotherm parameters and to shed light on how the heavy metals interact with the adsorbent surface.

Adsorption equilibrium was studied at different initial Cr(VI) concentrations, at 0.95, 1.90, 3.8, 7.6 and 15.1 mmol/L. Adsorption experiments were carried out at room temperature at optimum pH at 6 for 240 min taking the adsorbent amount of 1gm.

The Langmuir isotherm model is based on monolayer adsorption onto an adsorbent surface containing a limited number of adsorptive sites with uniform energies. The Freundlich isotherm model can be used for the adsorption onto heterogeneous surfaces and multilayer adsorption with different energies\(^5\).

Freundlich isotherm: Freundlich isotherm model applies to adsorption processes on heterogeneous surfaces with the interaction between the adsorbed molecules and formation of a multilayer adsorption with different energies\(^5\).

This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and correspondingly, the sorption energy exponentially decreases on completion of the sorption centres of the adsorbent\(^18\). Linear forms of Freundlich equation is followed as eq. 4:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

where \(q_e\) is the amount of chromium (VI) adsorbed by per unit mass of adsorbent (mmol/g). \(C_e\) is residual adsorbate concentration (mmol/L) at equilibrium in solution after adsorption and \(K_f\) and \(n\) are Freundlich constants which indicate the adsorption capacity (mmol/g) and adsorption intensity respectively. The value of adsorption intensity (n) more than 1 (n > 1) indicates about favourable condition for adsorption\(^7\). Figure 10 shows the experimental equilibrium isotherm through a linear graph plotted between log \(q_e\) against log \(C_e\) which demonstrates that adsorption behaviour is obeying Freundlich model.

<table>
<thead>
<tr>
<th>Table 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical and chemical properties of TC-CS</td>
</tr>
<tr>
<td>Parameters</td>
</tr>
<tr>
<td>----------------------------</td>
</tr>
<tr>
<td>Physical nature</td>
</tr>
<tr>
<td>Surface area</td>
</tr>
<tr>
<td>Pore size (mm)(^*)</td>
</tr>
<tr>
<td>Pore volume (m(^3)/g)(^*)</td>
</tr>
<tr>
<td>pH at point of zero charges</td>
</tr>
<tr>
<td>Compositions</td>
</tr>
<tr>
<td>Carbon content (wt %)</td>
</tr>
<tr>
<td>Oxygen content (wt %)</td>
</tr>
<tr>
<td>Nitrogen Content (wt%)</td>
</tr>
<tr>
<td>Sulphur content (wt %)</td>
</tr>
</tbody>
</table>

* Determined by Brunauer–Emmett–Teller (BET) measurement.
** Determined by Energy dispersive X-ray spectroscopy (EDX).
The values of Freundlich constants $K_f$ and $1/n$ are determined by intercept and slope respectively and are depicted in Table 4. The values of $n$ (6.64) were found to be more than one indicating for physical adsorption process. The situation of $n > 1$ is most common and may be due to distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction due to decrease in bond energy with increase in surface density.26

**Langmuir isotherm:** The Langmuir isotherm model is based on the assumption that there are finite numbers of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a monomolecular layer and there is no interaction between adsorbed molecules. Langmuir adsorption which was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the adsorptive capacity of various adsorbents.24

Langmuir isotherm can be represented as following linear form by eq. 5:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_0}$$

where $q_m$ and $K_L$ are Langmuir constants which represent maximum adsorption capacity (mmol/gm) and binding affinity of adsorbent (mmol/L) respectively. A plot of $1/C_e$ verses $1/q_e$ should be obtained as a straight line with a slope of $1/q_m K_L$ and intercept equal to $1/q_m$.

The linear plot of $1/q_e$ against unadsorbed metal ion concentration $1/C_e$ (Figure 11) demonstrates that the adsorption is obeying the Langmuir isotherm model. The Langmuir constants $q_m$ (mmol/g) and $K_L$ were determined from the intercept and slope respectively from the graph and represented in Table 5.

**Table 4**

<table>
<thead>
<tr>
<th>$Q_e$ (mg/gm)</th>
<th>$K_2$ (L/mg/min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.66</td>
<td>0.24</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

Figure 10: Freundlich isotherm plot for Cr ion adsorption

Figure 11: Langmuir isotherm for Cr adsorption
Characteristics of Langmuir isotherm can be expressed in term of a dimensionless constant known as separation factor or equilibrium parameter $R_L$, which can be represented in eq. 6.

$$R_L = \frac{1}{1+K_CL_0}$$  \hspace{1cm} (6)

where $C_0$ is initial metal concentration (mmol/L) and $K_C$ (L/mg) is Langmuir constant. The $R_L$ value indicates the type of isotherm to be irreversible ($R_L=0$), favourable ($0<R_L<1$), linear ($R_L=1$) and unfavourable ($R_L>1$). The value of $R_L<0$ (table 2) indicates favourable sorption.

The linear equations for both isotherms were applied to correlate the amount of chromium adsorbed per unit mass of the adsorbent. All the adsorption isotherm parameters obtained from these models and the values of the correlation coefficient ($R^2$) are depicted in table 5.

The Langmuir constants $q_m$ and $K_L$ were determined from a linear curve plotted between $1/q_e$ verses $1/C_e$. The $R_L$ values (0.414) for the adsorbents imply favourable conditions for adsorption. For both the isotherms, linear plots were obtained and the degree of linearity for Langmuir isotherm plots is higher (0.9860) than that of Freundlich isotherm plots (0.8695) indicating that the data were more in favour of Langmuir isotherm as compared to Freundlich isotherm and Langmuir isotherm model could well interpret the adsorption procedure, which indicates that the adsorption process of both metals on the chitosan beads is driven by the formation of a heavy metal monolayer on the adsorbent surfaces. However, both the isotherms are applicable for the presented adsorption process.

**Conclusion**

The present modification by introducing sulphur content to cross-linked chitosan results in higher adsorption efficiency for metal cations. More than 94% of metal ions have been removed within the first 2 hrs after contact with bio-sorbent. The adsorption study indicates that the removal rate of Cr (VI) ions from aqueous solution by TC-CS sorbent was excellent and up to 1.06 mmol/gm (56.18 mg/gm). The prepared bio-sorbent was found to be a promising agent for eliminating toxic agents from industrial wastewater. The removal efficiency was dependent on solution-pH, contact time, adsorbent dose and initial metal concentration. The highest adsorption was found at pH 6 at 100 mg of adsorbent. Adsorption kinetics data followed pseudo second order kinetic model with linear coefficient 0.9997. The adsorption process could be described well by Langmuir isotherm ($R^2=0.9860$) suggesting favourable adsorption through homogeneous monolayer adsorption. The interaction between divalent metal cations and added sulphur elements onto bio polymer appears to be a major contributing factor governing adsorption.

**Acknowledgement**

Thanks go to CSIR, New Delhi for providing NET-JRF to Sardar Singh Poonia and to Department of Chemistry, JNV University for providing necessary instrumentation and laboratory facilities.

**References**


12. Dai J., Tao C. and Ren F., Adsorption Behavior of Fe(II) and Fe(III) Ions on Thiourea Cross-Linked Chitosan with Fe(III) as Template, Molecules, 17, 4388-4399 (2012)


15. Freundlich H., Colloidal and Capillary Chemistry, Methuen, London (1928)


20. Huahua Yu, Lin Wang, Kecheng Li, Pengcheng Li, Rongfeng Li, Song Liu and Yukun Qin, Studies on adsorption behaviour of Pb(II) onto a thiourea-modified chitosan resin with Pb(II) as template, Carbohydrate Polymer, 81, 305 (2010)

21. Huang Li, Huang wan, Shen Ru and Shuai Qin, Chitosan/thiol functionalized metal–organic framework composite for the simultaneous determination of lead and cadmium ions in food samples, Food Chemistry, 330, 127212 (2020)


33. Salih Suhaib S. and Ghosh Tushar K., Preparation and characterization of bioadsorbent beads for chromium and zinc ions adsorption, Cogent Environmental Science, 3, 1401577 (2017). (Received 12th January 2022, accepted 14th February 2022)