Completely bio-based chitosan/carboxymethyl cellulose composites for the removal of Cr (VI) from aqueous solutions

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ABSTRACT
In the present study, completely biobased composites were prepared by reacting chitosan/carboxymethyl cellulose (CMC) with citric acid (CA) and their abilities to remove Cr (VI) from aqueous solutions were investigated. The best removal efficiency of Cr (VI)was noticed for Composite (C11)which was characterized by FT-IR, SEM and TGA.Theeffects of pH, contact time andthe initial concentration of chromium hexavalent ion on adsorption process were studied. The optimum conditions for adsorption of Cr (VI) on chitosan/CMC (C11) were found at pH 2 and a contact time of 7 minutes.
Furthermore, the results have shown that the adsorption process follows a pseudo-second order rate model, while the Langmuir adsorption isotherm provides the best fit.
Keywords: Biobasedcomposites, chitosan/carboxymethylcellulose composites, citric acid, chromium (VI) removal.

I. INTRODUCTION

The removal of the agricultural and industrial pollutants from sewage treatment and the possibility of the re-use of this water for agricultural purposes is the hottest topic for most of the research papers now days. The chemical contaminants are the most harmful types of contaminants found in the water. They are non-biodegradable and highly toxic. The most toxic heavy metals are lead, mercury and chromium. [1] Researchers are concerning on replacing the synthetic polymers by naturally occurring polymer composites for the maximum utilization of biopolymers in different areas of applications for the economical and environmental concerns. The application of biopolymers in water treatment was thoroughly studied. [2] The various adsorbents like Activated carbons, plant or lignocellulosic wastes, clays and biopolymers are among the common adsorbents have been used to remove different types of dyes and heavy metal ions from the wastewater. Chitosan is a good adsorbent biopolymer which is used to remove various kinds of anionic, cationic dyes and heavy metal ions. [3] The cellulose and chitosan being the first two abundant biopolymers in nature offer wide opportunities to be utilized for high–end applications such as water purification.[4] The reason for using polymer based composite is that they have strong chelating property with the metals. Specifically, polymer-based nano composites most of the time have great physical, chemical and mechanical properties, as well as stronger compatibility.[5]for example Alginates and hybrid natural polymers have been used after preparing by sol gel method, or natural polymer based composite due to the presence of a number of free hydroxyl and carboxyl groups.[6] Natural polymers had restriction in term of their fixed structure and few functional groups. This issue has been solved by cross linking of two or more natural polymers for enhancing their physical properties as well as polysaccharide structure stability in aqueous medium. [7] In this article, we cross linked two natural polymers CMC and chitosan with citric acid. The resultant product will have a great potential for the adsorption of heavy metals, based on different functional groups such as hydroxide, carbonyl and amide groups. To the best of our knowledge this article is the first article to report on using chitosan/CMC composites crosslinked with naturally occurring and environmentally friendly citric acid crosslinker for the removal of Cr (VI) from aqueous solutions at ambient conditions.

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II.   MATERIALS AND METHODS

2.1 Chemicals

Chitosanwithdeacetylation of 93% (Moisture ≤ 10%, Faint Beige to Beige powder) was obtained from Oxford Lab Co., Ltd (India) and carboxymethyl cellulose sodium salt(High viscosity)was supplied by Trust Chemical Laboratories (TCL) (India) and they were used as received.Citric acid Monohydrate (2-hydroxy-1,2,3-propanetricarboxylic acid monohydrate, M.W. 210.14)was supplied from CDH Fine Chemicals (India).Acetic acid (99.5%, Extra Pure), was purchased from LOBAChemie LABORATORY REAGENTS & FINE

CHEMICALS(India).Sulfuric acid was obtained from CDH Fine Chemicals(India). 1,5-diphenyl carbazide(m.p. 173-176°C, molecular mass = 242.28 g/mol) LabChem(USA).Acetone,CDH Fine Chemicals(India).Potassium dichromate $(K_2Cr_2O_7)$ was purchased from CDH Fine Chemicals(India).

2.2Preparation of chitosan/CMC composite samples

Stock solution of acetic acid (AA) was prepared using 20ml of the acid and completed to the mark in 1 liter volumetric flask using distilled water.This stock solution was used to dissolve chitosan, CMC and CA.Detailed method of preparation of composite samples is shown in Table 2.1.

In each case, after the materials were mixed according to Table 2.1 the resulting solution was left for 48 hours, centrifuged (for 5 minutes), the deposited composite was washed thoroughly with distilled water and left to dry.

Table 2.1: Preparation of composite samples

sample	Chitosan solution in AA (g/ml)	CMC solution in AA (g/ml)	CA solution in AA (g/ml)	Total Volume (ml)	Amount of composite (g)
C1	0.1/40	0.9/50	0.0275/10	100	0.74
C2	0.1/100	0.9/90	0.0500/10	200	0.79
C3	0.5/150	0.5/140	0.0500/10	300	0.45
C4	0.1/100	0.9/95	0.0050/5	200	0.82
C5	0.9/150	0.1/140	0.0275/10	300	0.02
C6	0.5/150	0.5/145	0.0050/5	300	0.39
C7	0.5/100	0.5/90	0.0275/10	200	0.45
C8	0.5/40	0.5/50	0.0500/10	100	0.49
C9	0.9/100	0.1/90	0.0500/10	200	0.09
C10	0.1/150	0.9/140	0.0275/10	300	0.67
C11	0.9/40	0.1/50	0.0275/10	100	0.09
C12	0.5/100	0.5/90	0.0275/10	200	0.43
C13	0.5/45	0.5/50	0.0050/5	100	0.54
C14	0.9/100	0.1/95	0.0050/5	200	0.05
C15	0.5/100	0.5/90	0.0275/10	200	0.38

2.3 Removal of Cr (VI) from aqueous solution using chitosan/CMC composites

A 1000 ppm Stock solution of Cr(VI) was prepared by dissolving a 0.2829g of potassium dichromate in distilled water and completed to the mark in 1 liter volumetric flask. From the

previousstock solution of Cr(VI) another standard solution of Cr(VI) having 50 ppm concentration was prepared and used for adsorption experiments. In a typical experiment, 10 ml of 50ppmstock solution was taken into 50ml a plastic beakerand0.02 g of composite was added and

stirred well. The beaker with its content was left for 24 hours at ambient conditions and

Atomic absorption spectroscopy was used to determine the concentration of the remaining Cr(VI).

Determination of Cr(VI) by atomic absorption spectroscopy
AA500-Graphite Furnace-Atomic Absorption Spectrophotometer (PG Instruments) was used to determine the concentration of the remaining Cr(VI).The following analysis parameters were used:

Analytical line: 357.9nm
Bandwidth: 0.4nm
Filter factor: 1.0
Lamp current: 5.0ma
Integration time: 3.0sec
Background: None/SR
Flame type: N_2O/Acetylene
Flame setting: Reducing Red Feather
Sensitivity: 0.05mg/L
Detection limit: 0.005mg/L
Working Range: 0.04-8.0mg/L

A stock solution of Cr(IV) having 1000ppm concentration was used to prepare series of standard solutions (5, 10, 15, 20 and 25 ppm) of Cr(IV). All solutions were acidified with 1% nitric acid to avoid precipitation. The efficiency was determined using the following equation:

$$\%E = \frac{C_i - C_f}{C_i} \times 100 \dots\dots\dots\dots\dots\dots(2.1)$$

Where C_i and C_f represent the initial and final concentrations of Cr(VI).

Fourier Transform Infrared analysis
The infrared spectra ofCMC, chitosan and the composite (C11)were obtained using Fourier transform infrared spectrometer, FT-IR, Shimadzu (model 8400S - Japan). Few milligrams of the each sample were mixed thoroughly with sufficient amount of KBr and pressed to form a transparent disk. The infrared spectrumwasrecorded between 400 and 4000 cm^{-1} using a resolution of 4cm^{-1} and 8 numbers of scans.

Scanning electron microscopy
SEM was used to investigate the morphology of the composite sample (C11) through anInspect^{TM} Scanning Electron Microscope (Inspect S50, Japan). The sample was frozen under liquid nitrogen, mounted, sputter-coated with gold and allowed to dry in a vacuum system. The dried sample was viewed usingan accelerating voltage of 5.00 kV.

Thermogravimetric analysis
Thermogravimetric analysis was carried out using a Simultaneous Thermal Analyzer Neztsch STA449 F3 Jupiter. The analysis was

carried out under nitrogen gas flow from room temperature to 700°C at a heating rate of 10°C/min.

Effect of time on removal of Cr(VI) from aqueous solutions
The effect of contact time on removal of Cr(VI) was studied using C11. Contact times of 1,2,3,4,5,7,10,12 and 15 minutes were selected to carry out the experimental work. Standard solution of Cr(VI) with 50 ppm concentration was prepared from stock solution (1000 ppm) of Cr(VI) and used for adsorption experiments. In a typical experiment, 10 ml of 50ppm standard solution was taken into a plastic beaker and 0.02 g of composite was added and stirred wellfor 1 minuteusinga magnetic stirrerat ambient conditions and the remaining Cr(VI) was determined using UV/VIS spectrophotometry. Exactly typical steps were repeated but at different contact times of 2,3,4,5,7,10,12 and 15 minutes. A plot of the equilibrium adsorption capacity versus contact time was carried out.

Determination of Cr(VI)by UV/Visible spectrophotometry
The Cr(IV) concentration in aqueous solutionswas determined by JENWAY 7205 UV/Visible-spectrophotometer at 540 nm using 1,5-diphenylcarbazide (DPC) method. Standard solution of Cr(VI) with 50 ppm concentration was prepared from 1000 ppm stock solution of Cr(VI).Series of standard Cr(VI) solutions having different concentrations of 0.2, 0.4, 0.5, 0.8, and 1 ppm were prepared from the 50 ppm stock solution of Cr(VI).1.0ml of each of the standard Cr(IV) was mixed with 9.0ml of 0.2 M H_2SO_4 in a 10 ml volumetric flask then 0.2 ml of freshly prepared 0.25% (w/v) DPC in acetone was added

into the volumetric flask. The mixture was stirred in a plastic beaker for 30s and then let to stand for 15 minutes for full color development. The absorbance of the colored solution was measured at λ_{max} 540nm using distilled water as a reference.The absorbance-concentrations calibration curvewas plotted with a correlation coefficient, of 0.9998. For the adsorption experiment, 10 ml of 50 ppmCr(IV)standard solution was taken into a conical flask and 0.02g of the composite (C11) sample was added. The content was stirred for 7 minutes and the concentration of the remaining Cr(IV) was determined following exactly the above given UV/Visible spectrophotometry method for the standard Cr(IV) solutions.

Absorbed Cr (VI) was calculated by equations 1 and 2:

$$q_e = \frac{(c_o - c_f)V}{m} \quad (1)$$

$$q_t = \frac{(c_o - c_t)V}{m} \quad (2)$$

Where $q_e$is the equilibrium adsorption capacity, q_t adsorption capacity at time t, C_o and C_f are the initial and final Cr(VI) concentrations, respectively, V is the volume of Cr(VI) solution in liter and m is the mass of the adsorbent in grams.

Effect of pH on removal of Cr(VI) from aqueous solutions

To determine the effect of pH the experiments were carried out at different pH values 2,4,6,8 and 10.Standard solution of Cr(VI) with 50 ppm concentration was prepared from 1000 ppm stock solution of Cr(VI) and used for adsorption experiments. In a typical experiment, 10 ml of 50ppm standard solution was taken into 50ml beaker and the pH was adjusted to 2,4,6,8 and 10 using 0.1M NaOH or 0.1M HClsolutions with the aid of a pH-meter.0.02 g of composite was addedto contents of the beaker and stirred for 5 min on a magnetic stirrer at 150rpm and then allowed to settle for 5 min to reach the equilibrium at ambient conditions. The remaining Cr(VI) was determined using UV/VIS spectrophotometry.A plot of the equilibrium adsorption capacity versus pH was carried out.

Effect of initial concentration of Cr(VI) on adsorption of Cr(VI) from aqueous solutions

The adsorption capacity of Cr(VI) was studied at different concentrations 10, 20, 30, 40, 50 and 70 ppm. Standard solution of Cr(VI) with 50 ppm concentration was prepared from stock solution (1000 ppm) of Cr(VI) and used for adsorption experiments. In a typical experiment, 10 ml of 10ppm standard solution was taken into a 50ml beaker and 0.02 g of the composite was added and stirred well for 7 minutes using a magnetic stirrer at pH 5 which was previously adjusted using 0.1M HCl or 0.1M NaOH with the aid of a pH-meter. The remaining Cr(VI) was determined using UV/VIS spectrophotometry. The whole experiment was repeated again but using 20, 30, 40, 50 and 70 ppm of Cr(VI) in each case.

Solubility and stability test

0.03g of the composite was suspended in distilled water after adjusting the pH to 2, 10 and 7 and kept for 24 hours. Then they were filtered, the residue was pressed with filter paper to remove water that is physically adhered to the samples, weighed and the solubility was checked using equation 5.The stability was checked by letting the samples to dry and werereweighed again.

$$\text{Solubility} = \frac{\text{wet weight after } - \text{dried weight before}}{\text{dried weight}} \times 100 \quad (5)$$

III. RESULTS AND DISCUSSION

To determine the polymer blend with the highest removal efficiency for Cr(VI), a series of experiments were carried out by varying the amounts of chitosan and CMC, the volumes of the stock solution of acetic acid that were used to dissolve the chitosan, CMC and citric acid and the amount of citric acid as a crosslinker. The initial and final concentrations of Cr(VI) were determined by atomic absorption spectroscopy and the results are shown in Table 3.2. As it is evident from the table, sample C11 has the highest removal efficiency and hence were selected for further experimental work regarding the effects of different parameters on removal efficiency as well as adsorption kinetic and adsorption isotherms.

Table 3.2: Initial concentration of Cr (VI), final concentration of Cr (VI) and maximum efficiency

Sample	C_i	C_f	%E
C1	51.866	34.348	34
C2	51.866	30.970	40
C3	51.866	37.726	27
C4	51.866	34.348	34
C5	51.866	34.911	33
C6	51.866	33.222	36
C7	51.866	30.970	40

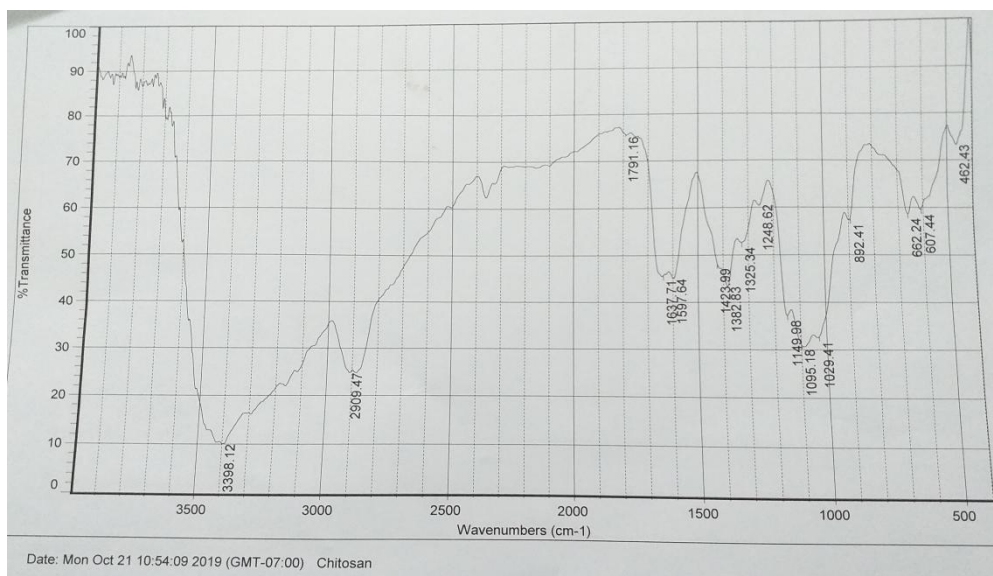| C8 | 51.866 | 23.652 | 54 |
C9	51.866	11.827	77
C10	51.866	17.907	65
C11	51.866	5.576	89
C12	51.866	21.622	58
C13	51.866	31.418	39
C14	51.866	17.907	65
C15	51.866	35.133	32

FTIR analysis

Figure 1: FTIR spectrum of chitosan polymer

(-NH$_2$, -OH, -CH and -CH$_2$, C-N, C-C, C-O-C) Figure 1, shows the infrared spectrum of chitosan. The band at around 3000 to 3600cm^{-1} is characteristic of aromatic secondary amine N-H and –OH stretching vibrations. The absorption band at 2909 cm^{-1} is attributed to the C-H stretching vibration. The band at 1637 is due to the bending vibration of –OH group. The adsorption band at 1598 cm^{-1} shows the presence Of C=C asymmetrical stretches. The presence of symmetrical band C=C are confirmed by the bands at around 1637 cm^{-1}. The CH$_2$ and –C-N bending are cleared by the presence of bands at around 1423 and 1382 cm^{-1}, respectively. The absorption band at 1149 cm^{-1} also showing the asymmetric stretching of the C-O-C bridge. The bands at 1095 and 1029 cm^{-1} correspond to C-O stretching. [8]
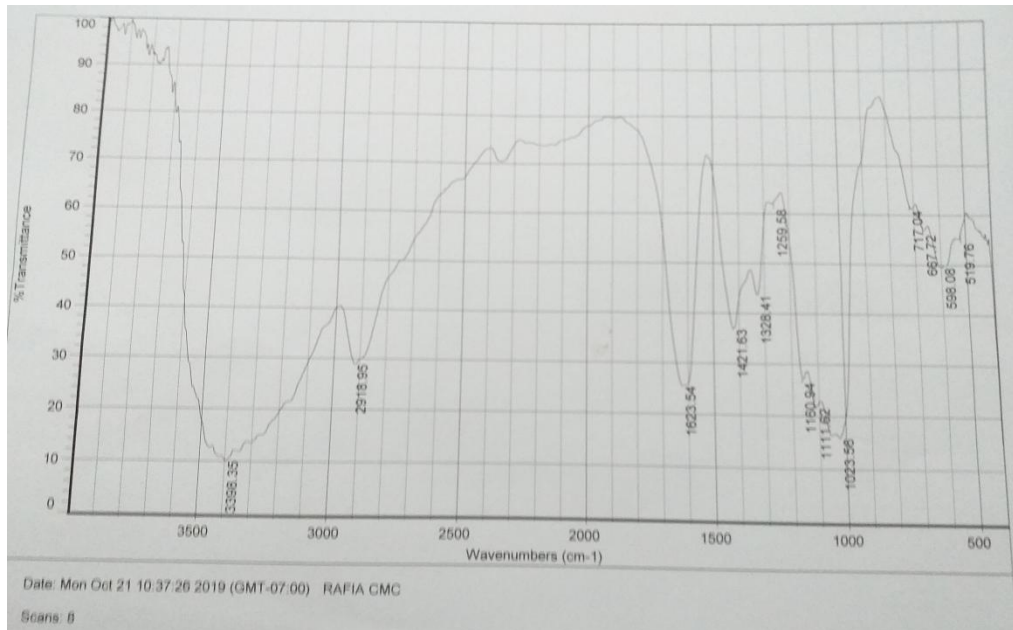
Figure 2: FTIR spectrum of CMC polymer

Figure 2 displays the FTIR spectrum of CMC. As can be seen from the spectrum, theband at 3398 cm^{-1} corresponds to O–H stretching vibrations. The band at 2918 cm^{-1} representssaturated C–H stretching vibration. Finally, peak 1075 cm^{-1} represent the C–O–C stretching vibration. [9]
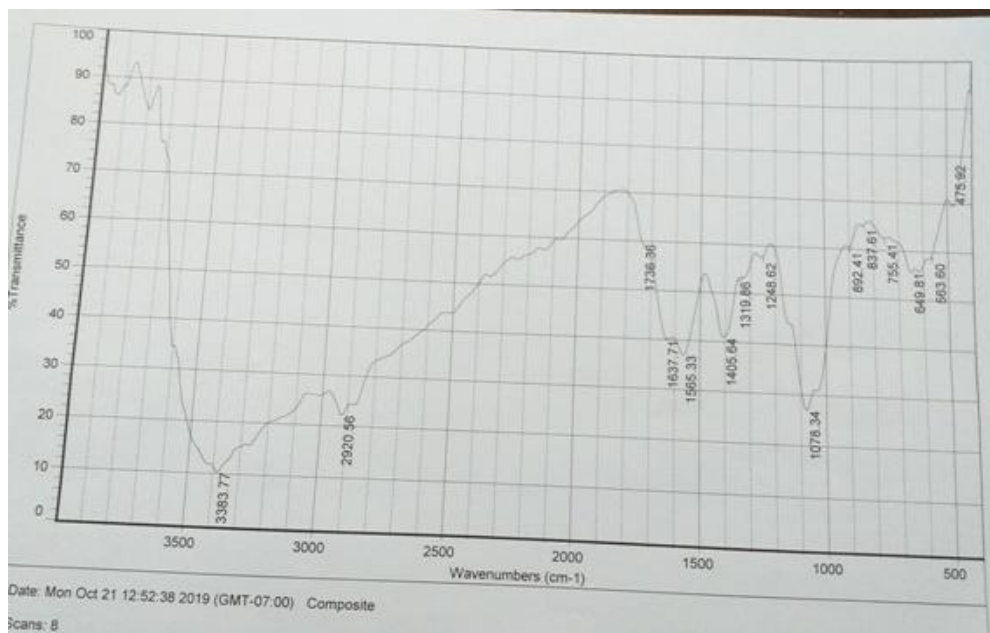

Figure 3: FTIR spectrum of composite sample (C11)

Figure 3 shows the FTIR spectrum of the composite sample (C11). As it is evident from the figure, the presence of a peak at 1736 cm^{-1} represents the formation of ester linkages between the two polymers (the citrate crosslinks). The remaining peaks are typically similar to the ones that are shown already in Figures 1 and 2. The comparison between the FTIR spectra of chitosan and CMC clearly indicated a significant reduction in the absorption band at 1030 cm^{-1} associated with -OH group, which is a strong evidence of the carboxymethylation reaction occurring on the primary alcohol of chitosan [10]

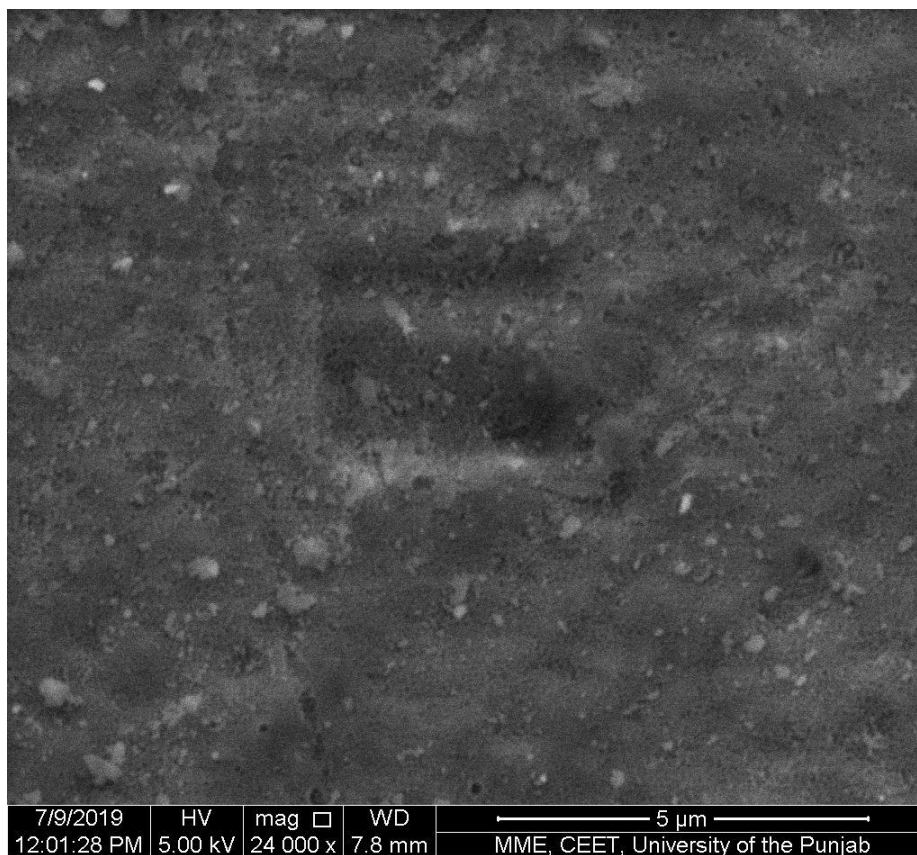**Scanning electron microscopy**

Figure 4: SEM micrograph of composite sample (C11)

In SEM analysis the Figure 4 shows the morphology of the composite. The homogeneity of composite proves that composite have smooth large surface area for the adsorption of Cr (IV). The composite homogeneous structure made the chitosan/cellulose composite film. However, the porosity of surface can also be seen because of crosslinker particles. [11]

Thermogravimetric analysis

As shown in figure 5a and 5b the initial degradation rate is $100C^o$. At this stage the CMC and chitosan did not decompose properly and shows only the free water loss. The onset temperature for CMC and chitosan is $277C^o$ and $274C^o$ respectively which shows the complete mass loss which is 27.01% and 19.80%. The composite TGA spectrum shows the two clear peaks. The first peak is at about $100C^o$ to $150C^o$ and second peak rangis $250C^o$ to $350\ C^o$, shows the mass change 24.82%.The second peak range also shows that it is the main peak where the decomposition occurred

due the breaking of bonds. After $350C^o$ the mass changes is negligible. The composite TGA spectrum also shows that the temperature degradation rate at second peak is less than the second peak degradation rate of CMC and chitosan due to less mass loss of composite and because of crosslinker which provide the stability of the composite. [11, 12]

Effect of time on removal of Cr(VI) from aqueous solutions

The effect of time on removal of Cr(VI) from it is aqueous solutions were investigated using three different concentrations. The initial and the final concentrations of Cr(VI) were determined using UV/Visible spectrophotometry. The results are displayed in Figure 3.1. As can be seen from the Figure, the equilibrium adsorption capacity was increased with time gradually and reached its plateau between 6 to 8 minutes, so 7minutes were chosen as the optimum time for adsorption experiments.
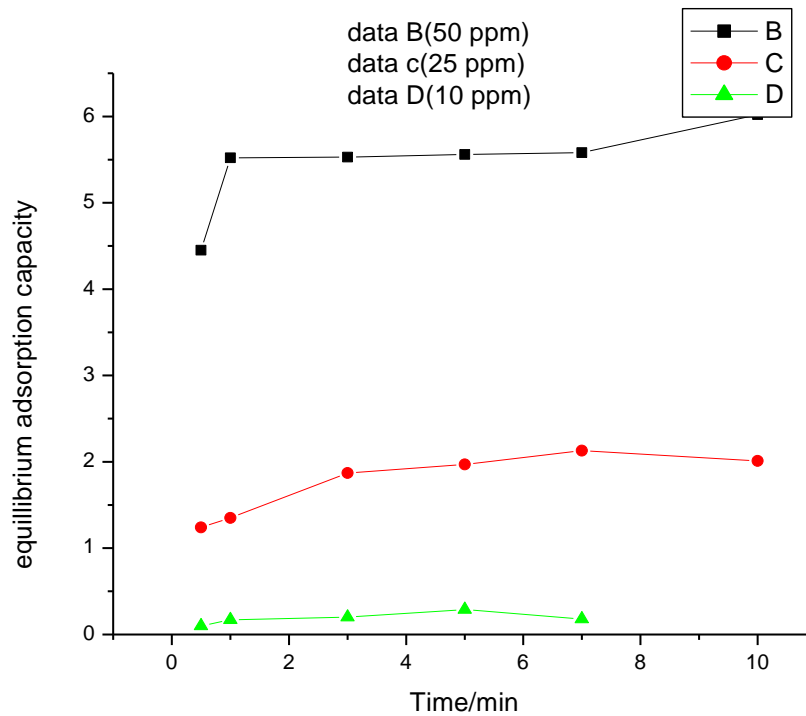
Figure 3.1: Effect of time on removal of Cr(VI)

Figure illustrates the result of comparative study of contact time by using composite. It is evident that optimum contact time for the composite was found to be 7 min with maximum removal. The trend of percentage adsorption was shown that with increased contact time there is more time for the Cr (VI) to make complex with the adsorbent.

Adsorption isotherms

The behaviors like capacity and the interaction between the adsorbent (C11) and ions [Cr (VI)]at moderate temperature can be described by adsorption isotherms. The adsorption process has been interpreted by applying many isotherms like Langmuir [Eq. (3)],Freundlich [Eq. (5)],Temkin [Eq. (6)] and Dubinin– Radushkevich (DR) adsorption isotherms [Eq. (7)] to deduce the adsorption of Cr(VI) ions on the composite. Linear form of Langmuir adsorption isotherm is given as follow.

$$\frac{Ce}{qe} = \frac{1}{KLqm} + \frac{Ce}{qm} \quad (3)$$

$$RL = \frac{1}{1+KLCo} \quad (4)$$

In equation 3, qe(mg/g) is the amount of chromiumadsorbed at equilibrium per unit mass of adsorbent, Ce(mg/L)is the   concentration in aqueous solution of Chromium ions at equilibrium, qm gives the theoretical maximum adsorption capacity, KL describes the affinity of the surface for the solute and Co is the initial Cr (VI) concentration.The Langmuir isotherm model indicates formation of a monolayer of adsorbed molecules on the surfaces of adsorbent, with adsorption sites equally available for adsorption and non-interaction between adjacent adsorbed molecules [13] as well as it is also applied to explain the equilibrium inveterate between substance metal ions in solution and the amount of metal ions adsorbed on the surface of composite. [14].Experimental data (ce/qe verses ce) was fitted onto Langmuir isotherm model. The value of RL (separation factor) in equation 4 gives the information about the adsorption process.RL values indicate the adsorption to be unfavorable when RL> 1, linear when RL = 1, favorable when 0 <RL<1, and irreversiblewhen RL = 0.[15] The RL values calculated are represented in Table 2which are between 0 and 1 indicating that, the adsorption of metal ions are favorable. [16] Similar results are available in the literature.[22,23,24,25]
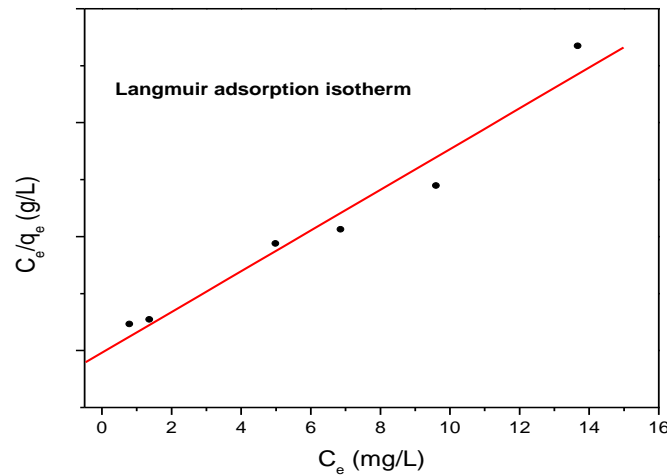
Figure 1: Langmuir adsorption isotherm

Freundlich isotherm explains the adsorption processes on heterogonous surfaces as well as it also specifies the relative distribution of the energy and the heterogeneity of the adsorbate sites [17].The linear form of Freundlich adsorption isotherm is given as follow:

$$\ln q_e = \frac{1}{n}\ln C_e + \ln K_F \qquad (5)$$

Where C_e is the equilibrium concentration of the adsorbate in mg/L, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), 1/n is the adsorption intensity and K_F is the relative adsorption capacity. The plot of lnqe against lnCe according to Eq. (5) is shown in Figure 2.The values of Freundlich constants such as 1/n and K_F were calculated from slope and intercept of the plot, respectively and their values are given in Table 1.The smaller the value of1/n means greater extent of heterogeneity of adsorbent surface [18].The experimental data did not show best fit for Freundlich isotherm model for chromium ions adsorption on C11.
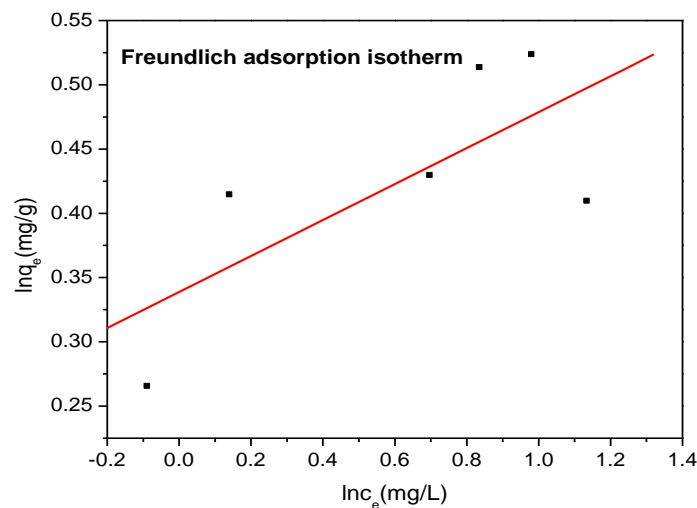

Figure 2: Freundlich adsorption isotherm

Temkin isotherm interprets the interactions between adsorbents and metal ions to be adsorbed in adsorption process. It is expected that all the molecules in the layer decreases the heat of adsorption (ΔH_{ads}) in a line which resulted the increase surface coverage[19]. The linear form of the Temkin isotherm is represented as:

$q_e = \beta \ln K_T + \beta \ln C_e$ (6)

Where C_e is the equilibrium concentration of the adsorbate in mg/L, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), β (J/mol) is a heat adsorption constant and K_T is the equilibrium binding constant (L/min) parallel to the maximum binding energy[20]. A plot of q_e versus $\ln C_e$ assists the determination of constants β and K_T via slope and intercept. The values of R^2, K_T(L/g), β(J/mol) are given in Table 2. Fitting the obtained experimental data to Temkin model demonstrated that the adsorption of Cr(IV) onto C11 obeys this modelto a greater degree.
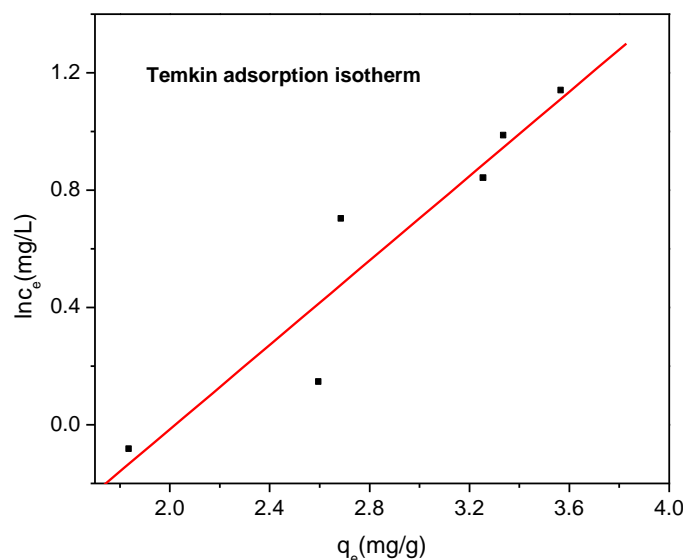

Figure 3: Temkin adsorption isotherm

Dubinin-Radushkevich model evaluates the heterogeneity of the surface energies [17]. The linear form of DR isotherm equation is represented as:

$\ln q_e = \ln q_{DR} - \beta_D \varepsilon^2$ (7)

$\varepsilon = RT \ln[1 + \frac{1}{Ce}]$ (8)

$E_S = \frac{1}{\sqrt{2\beta D}}$ (9)

Where q_m is the theoretical saturation capacity (mol/g), β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol /J) and ε is the potential, C_e is the equilibrium concentration of adsorbate in solution (mol/L), R ($Jmol^{-1}K^{-1}$) is the gas constant and T(K) is the absolute temperature. The DR constants q_m and β were calculated from the linear plots of $\ln q_e$ versus ε^2 and are given in Table 1. Value of E_S was calculated from Eq. (9) using the value of β_D. It gives information about the nature of adsorption process. Value of E_S (kJ/mol) found to be less than 8 specify the presence of physical interactions and existence of van der wall's forces between adsorbate and adsorbent [16]. In this study, value of E_S was found to be 0.13 kJ/mol which was proof of formation of physical interaction between Cr (VI) ions and functional groups of composite (C11). Decreasing order of validity of various adsorption isotherms in term of their value of correlation coefficient (R^2) to best interpret the adsorption of Cr (VI) ions from aqueous medium on composite(C11) was found to be Langmuir >Temkin>Freundlich>DR with R^2 values 0.9797 > 0.9437 > 0.7301 > 0.3751, respectively.
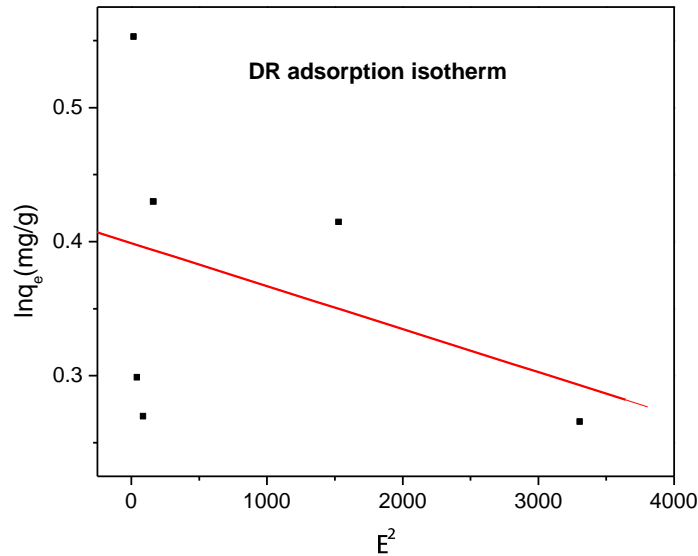
Figure 4: Dubinin-Radushkevich adsorption isotherm

Tab.1: DifferentisothermparametersforCr(IV)ionsoncomposite (C11)at 293K.

Langmuir isotherm parameters
R^2 0.9797
q_m(mg/g)   0.37
b(L/mg) 71.12
R_L 0.271
Freundlich isotherm parameters
R^2 0.7301
n   7.17
1/n   0.14
K_F(L/g) 1.17
Temkin isotherm parameters
R^2 0.9437
K_T(L/g) 1.378
β(J/mol)0.716
DR isotherm models
R^2 0.3751
E_S(kJ/mol)   0.13
q_{DR}(mg/g)   0.89

Kineticstudyofadsorptionprocess
        To investigate the rate of adsorption and the adsorption mechanism of Cr(VI) onto composite11, the pseudo first order, pseudo second order, Intraparticle diffusion and Elovich kinetic models were applied to adsorption data[21]. Linear forms of pseudo first order kinetic equation is given as follow:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (10)$$

In the Eq. (10), q_e (mg/g) refers to the concentration of Cr (VI) ions adsorbedon the active sites of composite at equilibrium while q_t (mg/g) is the concentration of chromium ion adsorbed on biomass at any time. $k_1$is first order rate constant and its unitsare min^{-1}. The value of $\ln(q_e - q_t)$ was plotted against t using Eq. (10) to find thepseudo

first order kinetics parameters. Values of k_1 and q_e were calculated from the slope and the intercept of

the plot and their values are given in Table 2.
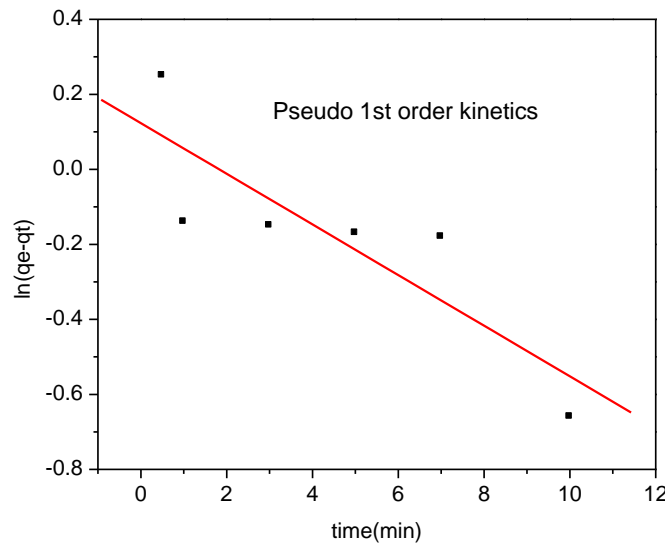
Linear formof pseudo second order kinetic equation is as follow:

$$t/qt = \frac{1}{K2.qe2} + \frac{t}{qe} \quad (11)$$

In Eq. (11), k_2 is pseudo second order rate constant and its unitis g/mg·min. The plot of t/q_t vs. t according to Eq. (11) is shown in Figure 6 and value of q_e and k_2 were calculated from the slope and the intercept of the plot, respectively. The initial adsorption rate represented by ho is defined as follow:

$$ho = k_2qe^2 \quad (12)$$

While the time required attaining the half of the equilibrium concentration of Cr (VI) ions adsorbed on composite (C11) was calculated using the relation as given below:

$$t_{1/2} = 1/k_2q_e^2 \quad (13)$$

In equations, (12) and (13), k_2 and q_e are the pseudo second order rate constant and equilibrium concentration of Cr (VI) ions adsorbed on composite(C11). Value of k_2, q_e, R^2, ho and $t_{1/2}$ for pseudo second order kinetic model are given in Table 2.
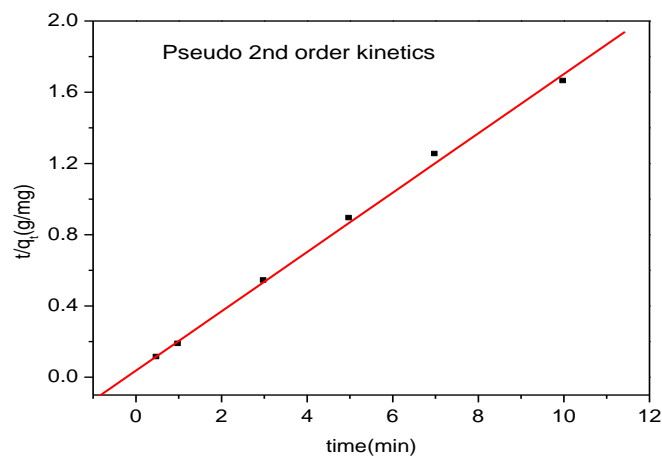
Intra-particle diffusion model was applied to elaborate the diffusion mechanismof adsorption of Cr (VI) ions on composite(11) using Eq. (12) as given below:

$q_t = k_{ipd}t^{1/2} + C$ (14)

In Eq. (14), k_{ipd} (mg/g·min1/2) is intra-particle diffusion constant while C is the constant which is relevant to thickness of the boundary layer[16]if the value of C is greater, it interprets the higher surface adsorption[16].The value of k_{ipd} and C was determined from slope and intercept of the plot of $q_t$vs. $t^{1/2}$, respectively. Values of parameters of intra-particles diffusion model are given in Table 2.
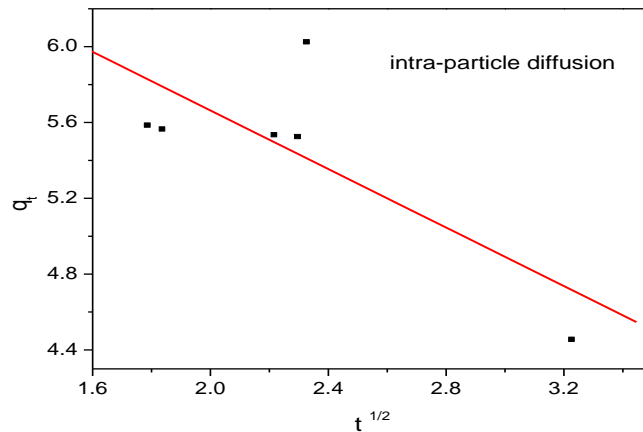

Linear form of Elovich model is as follow:

$q_t = 1/\beta ln(\alpha\beta) + 1/\beta lnt$(15)

In Eq. (15), α (mg/g·min) and β (g·mg) are the Elovich parameters. α represents the initial adsorption rate while β designates the desorption constant. Elovich parameterssuch as β and α was determined from slope and intercept of plot of q_t vs. lnt according to Eq.(15) and their values are given in Table 2.Values of regression factor (R^2) for Cr (VI) ions adsorption on composite (C11) were found to be 0.83, 0.99, 0.76 and 0.83 for pseudo first order, pseudo second order, intra-particle diffusion model and Elovich model, respectively. Value of regression factor (R^2) for adsorption of Cr (VI) ions on composite (C11) approaches to unity for pseudo second order kinetics which indicates that it best interprets the adsorption process as compared to pseudo first order, intra-particles diffusion and Elovich models.
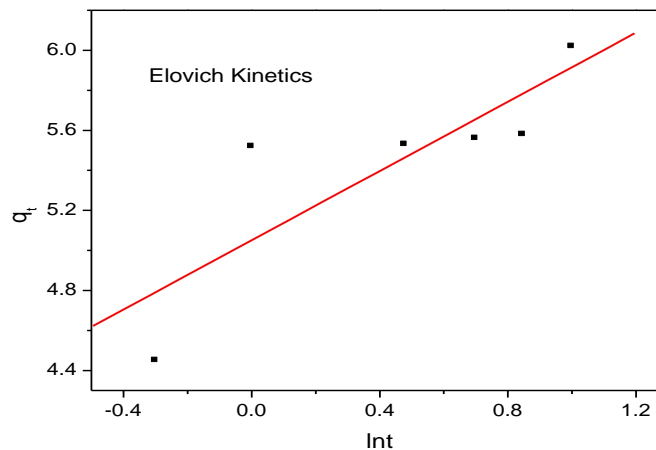
Tab.2: Kinetic parameters for adsorption of Cr (VI) ions on composite (C11)

Pseudo 1st order

R^2 0.8356

q_e(mg/g) 0.909

k_1(min^{-1})   0.0675

Pseudo 2nd order

R^2 0.9987

q_e(mg/g) 4.53

h(mg/g·min)   3.427

$t_{1/2}$(min) 27.1

k_2(g/mg·min)   0.167

Intra-particles diffusion model

R^2 0.7660

C(mg/g) 0.773

k_{ipd}(mg/g·min)   0.266

Elovich model

R^2 0.8399

α(mg/g·min)   31.0

β(g/mg) 0.865

IV. CONCLUSION

In conclusion, C11composite was successfully prepared andthe results have shownthe surface morphology, functional groups, and chemical compositions were well characterized. The results from characterization indicated thathomogeneous structure.The solution pH had a significant impact on the Cr (VI) removal performance, and the optimum pH was 2. Kinetics study indicated the adsorption ofCr (VI) onC11 can be well described by the pseudo-second-order model rather than the pseudo-first-order model. Further analysis suggested that the adsorption process was not governed by intraparticle diffusion. Isotherms data fitted well with the Langmuir isotherm model, which suggested that the adsorption is a favorable monolayer process. Furthermore, the positive value of ΔH0 and the negative value of ΔG0 revealed that the adsorption process ofCr (VI)onC11composites is endothermic and spontaneous.

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