



# Preparation and characterization of La(III) encapsulated silica gel/chitosan composite and its metal uptake studies

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## ABSTRACT

Lanthanum loaded silica gel/chitosan composite (LaSiCS) was prepared by mixing silica gel,  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  and chitosan which was then cross-linked with glutaraldehyde. The LaSiCS composite was characterized using FT-IR, SEM-EDAX, XRD and BET. The adsorption of chromium(VI) ions onto LaSiCS composite has been investigated. The LaSiCS composite was found to have excellent chromium adsorption capacity than the silica gel/chitosan composite (SiCS), silica gel (Si) and chitosan (CS). The sorption experiments were carried out in batch mode to optimize various parameters viz., contact time, pH, initial chromium ion concentration, co-ions and temperature that influence the sorption. Langmuir and Freundlich adsorption models were applied to describe isotherm constants. Equilibrium data agreed very well with the Langmuir model. Thermodynamic studies revealed that the nature of chromium sorption was spontaneous and endothermic. The LaSiCS composite removes chromium by electrostatic adsorption coupled reduction/ion-exchange.

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## 1. Introduction

The presence of hydroxyl and amino groups, which are excellent functional groups for anchoring a large variety of transition metals, makes chitosan a good candidate for metal sorption in aqueous solution. Different applications were reported in the literature concerning the involvement of chitosan/silica hybrid composite. Ayers and Hunt [1] synthesized chitosan/silica hybrid gels for wastewater treatment using the chelating effect of the included chitosan. Airoidi and Monteiro [2] prepared new organic–inorganic hybrids from chitosan and aminosilylating agents and cross-linked them through linear glutaraldehyde units and used for water treatment. Molvinger et al. [3] used porous chitosan–silica hybrid microspheres as a potential catalyst. Surface modification of silica and cellulose-based microfiltration membranes with functional polyamino acids were carried out for heavy metal sorption studied by Ritchie et al. [4]. A number of methods viz., precipitation, extraction, ion-exchange and reverse osmosis have been attempted for heavy metal removal. All these methods have limitations, such as metal solubility, finite aqueous solubility of extractants/dilutions, high-pressure operation and electric-field-assisted [5]. Among the methods reported adsorption seems to be the most attractive and selective technique for metal removal. Heavy metals are effectively removed by silica compounds functionalized with carboxylic acids,

sulfonic acids and quaternary ammonium groups. The support for these groups is often silica-based, because silica provides chemical resistance and is mechanically robust. Silica-based support structures are widely used in the field of selective separations because of their well-known acid and solvent stability, as well as their excellent mechanical properties and do not have the shrink/swell characteristics. Beauvais and Alexandratos [6] have provided an excellent overview on silica for selective complexation of metal ions. Among the inorganic ion-exchangers and adsorbents investigated for removing metals, silica based sorbents like natural and synthetic zeolites [7,8], titanites [9], silica [10], silicotitanites [11] and silica-orchabazite-supported metalhexacyanoferrates [12,13] have been identified as potential sorbents [14–16]. The surface chemistry of silica makes it an excellent candidate for modification. Some examples include vinyl groups [17], amine groups [18] and glycidoxo groups [6] have been studied.

In recent years, biosorption has been recognized as an effective method for the removal of heavy metals in water and industrial effluents. Silica supported polymeric hybrid materials using chitosan, polystyrene, etc., were used in the heavy metal removal, biosensor, catalyst, chromatography, tissue engineering etc., [3,19–21]. La(III) loaded materials increases Cr(VI) sorption due to its higher positive charge [22]. The application of silica gel/chitosan hybrid composite (SiCS) and La(III) loaded SiCS composite (LaSiCS) for chromium removal has not been studied so far. Hence it was aimed to prepare SiCS composite and LaSiCS composite for chromium removal studies. A comparative evaluation of adsorption capacity of Si, CS, SiCS composite and LaSiCS composite

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was also made and discussed. Various influencing parameters viz., contact time, initial chromium concentration, solution pH and the presence of co-ions on sorption capacity were optimized. The equilibrium sorption data was fitted with various isotherms to find the best fit model for the sorption system.

## 2. Materials and methods

### 2.1. Materials

Chitosan (85% deacetylated) was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). Silica gel GLR TLC grade was purchased from S.D. Fine-Chem Limited, Mumbai.  $K_2Cr_2O_7$ ,  $LaCl_3 \cdot 7H_2O$ , glacial acetic acid, glutaraldehyde were from Merck, Mumbai and all other chemicals used were of analytical grade.

### 2.2. Synthesis of SiCS composite

Silica was heated at  $110^\circ C$  for 1 h to activate the surface. 20 g of silica was immersed in 30 mL of distilled water to make slurry. 2 g of chitosan was dissolved in (2% v/v) aqueous solution of acetic acid and stirred for 1 h. This solution was added to the silica slurry and the mixture was stirred for 30 min and 5% of glutaraldehyde aqueous solution was added for cross-linking. The mixture was stirred for 2 h and soaked in an ultrasonic bath for 30 min. The wet mixture was kept in a refrigerator at  $4^\circ C$  for 24 h to undergo complete cross-linking reaction and then washed to neutral pH and dried in an oven at  $50^\circ C$ . Finally the dried hybrid composite was sieved to 60 mesh and used for chromium sorption studies.

### 2.3. Synthesis of LaSiCS composite

The LaSiCS composite was prepared as describe for SiCS. 2 g of chitosan and 5 g of  $LaCl_3 \cdot 7H_2O$  dissolved in (2%, v/v) acetic acid aqueous solution was mixed with silica gel slurry and stirred for 2 h and then the required amount of 5% glutaraldehyde for cross-linking was added. The LaSiCS composite was kept at  $4^\circ C$  and washed thoroughly with distilled water and dried in an oven at  $50^\circ C$ . Finally the dried hybrid composite was sieved to 60 mesh and used for chromium sorption studies.

### 2.4. Sorption experiments

Sorption experiments were carried out by batch equilibration method in duplicate. About 0.1 g of each sorbent was added to 50 mL of chromium(VI) solution of initial concentration 10 mg/L at 4 pH. The contents were shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm and the filtrate was analyzed for Cr(VI). The influence of various parameters like contact time, pH, the presence of co-ions and temperature on sorption capacity of the sorbent was investigated. The solution was then filtered and the residual chromium(VI) ion concentration was measured.

$$q = \frac{(C_i - C_e)}{m} V \text{ mg/g} \quad (1)$$

where  $q$  is the adsorption capacities of adsorbents (mg Cr(VI) ion/g adsorbent),  $V$  is the volume of Cr(VI) solution (L),  $C_i$  is the concentration of Cr(VI) ion before adsorption (mg/L),  $C_e$  is the concentration of Cr(VI) after adsorption (mg/L) and  $m$  is the weight of adsorbents (g). Adsorption isotherms were studied at different initial chromium concentrations viz., 8, 10 and 12 mg/L at different temperatures viz., 303, 313 and 323 K.

### 2.5. Analysis

The concentration of chromium(VI) was measured using UV-visible spectrophotometer (Pharo 300 Merck) at 540 nm,

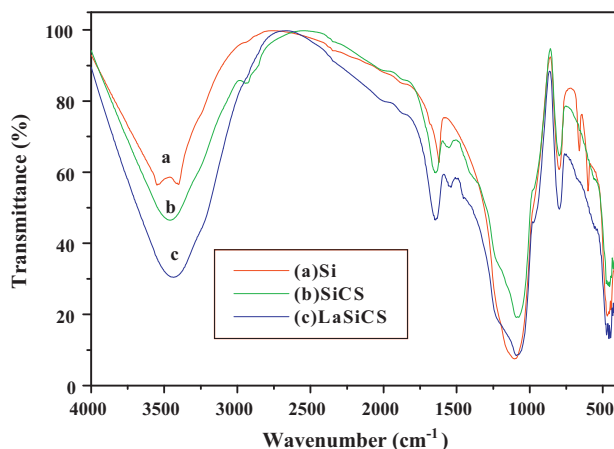


Fig. 1. FTIR spectra of Si, SiCS composite and LaSiCS composite.

according to the 1,5-diphenylcarbazide method [23]. The pH measurements were carried out with an expandable ion analyzer EA 940 with pH electrode.

### 2.6. Characterization

Fourier transform infrared spectroscopy (FTIR) was carried out on JASCO-460 plus model to obtain the structural information of SiCS and LaSiCS composites. The surface morphology of the sorbent was studied with scanning electron microscope (SEM) with HITACHI-S-3400 model. Elemental spectra were obtained using an energy dispersive X-ray analyzer (EDAX) during SEM observations which allowed qualitative detection and localization of elements in the composite. Surface area of the composite was obtained using Micromeritics – Tristar 3000 model. X-ray diffraction (XRD) measurements were obtained using X'per PRO model-PANalytical to determine the crystalline phases present in sorbents.  $pH_{zpc}$  (pH of zero point charge) was determined by a pH drift method [24].

### 2.7. Statistical tools

Computations were made using Microcal Origin (Version 6.0) software. The goodness of fit was discussed using regression correlation coefficient ( $r$ ), chi-square ( $\chi^2$ ) analysis and standard deviation (sd).

## 3. Results and discussion

### 3.1. Characterization of LaSiCS composites

The LaSiCS has particle size as 163 nm, density as  $0.99 \text{ g/cm}^3$ , BET surface area as  $119.29 \text{ m}^2/\text{g}$ . The surface morphological change of LaSiCS composite was confirmed by the shifting of  $pH_{zpc}$  values. The  $pH_{zpc}$  of Si and SiCS composite are 7.05 and 6.70 respectively where as for LaSiCS composite it was shifted to 5.30 which clearly indicate the occurrence of structural changes in LaSiCS composite [24]. Fig. 1 represents the FTIR spectra of CS, Si, SiCS and LaSiCS. Figs. 2 and 3 represent FTIR spectra of SiCS, LaSiCS and chromium-sorbed SiCS and LaSiCS composite respectively. The bands at 3436, 1070, 950 and  $790 \text{ cm}^{-1}$  are assigned to the stretching vibration of the surface hydroxyl, asymmetric Si–O–Si bond stretching and Si–OH bond stretching and symmetric Si–O–Si bond stretching respectively [21,25]. The band at  $2921 \text{ cm}^{-1}$  indicates the –CH stretching vibration in –CH and – $CH_2$ . A band at  $1639 \text{ cm}^{-1}$  corresponds to –NH bending vibration in – $NH_2$  and  $1650 \text{ cm}^{-1}$  indicates the presence of –CO stretching vibration in –CONH– (amide I band) [26]. A slight

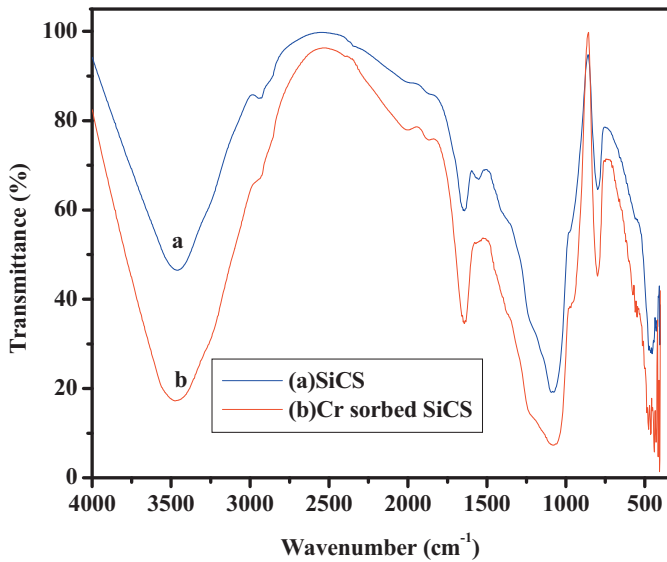


Fig. 2. FTIR spectra of SiCS composite and chromium sorbed SiCS composite.

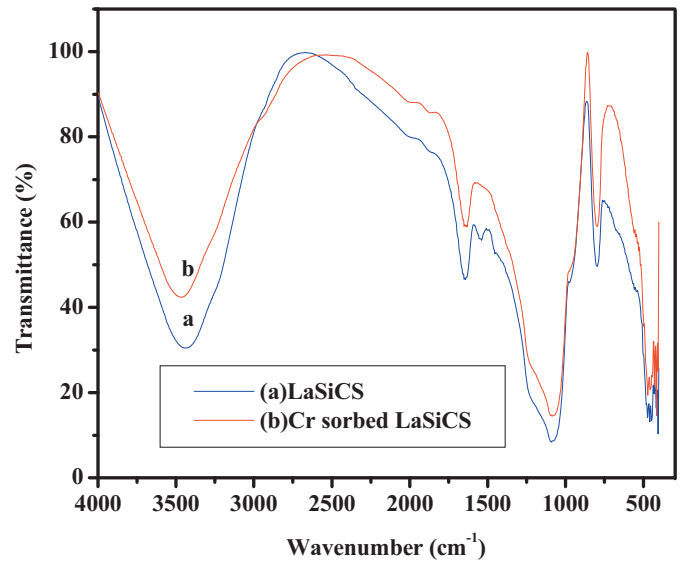


Fig. 3. FTIR spectra of LaSiCS composite and chromium sorbed LaSiCS composite.

broodening of band at  $3436\text{ cm}^{-1}$  in the chromium sorbed SiCS and LaSiCS composite may be taken as indicative of electrostatic adsorption between the sorbent and the chromium. These figures reveals that all functional groups originally present in chitosan are also present after blending with Silica. The band at  $540\text{ cm}^{-1}$  indicates

the presence of  $\text{Cr}(\text{OH})_3$  in the chromium treated composites (cf. Figs. 2b and 3b) [27,28].

SEM images of LaSiCS and SiCS composites are shown in Figs. 4a and 5a and the chromium sorbed LaSiCS and SiCS composites are shown in Figs. 4b and 5b respectively. The change in the SEM

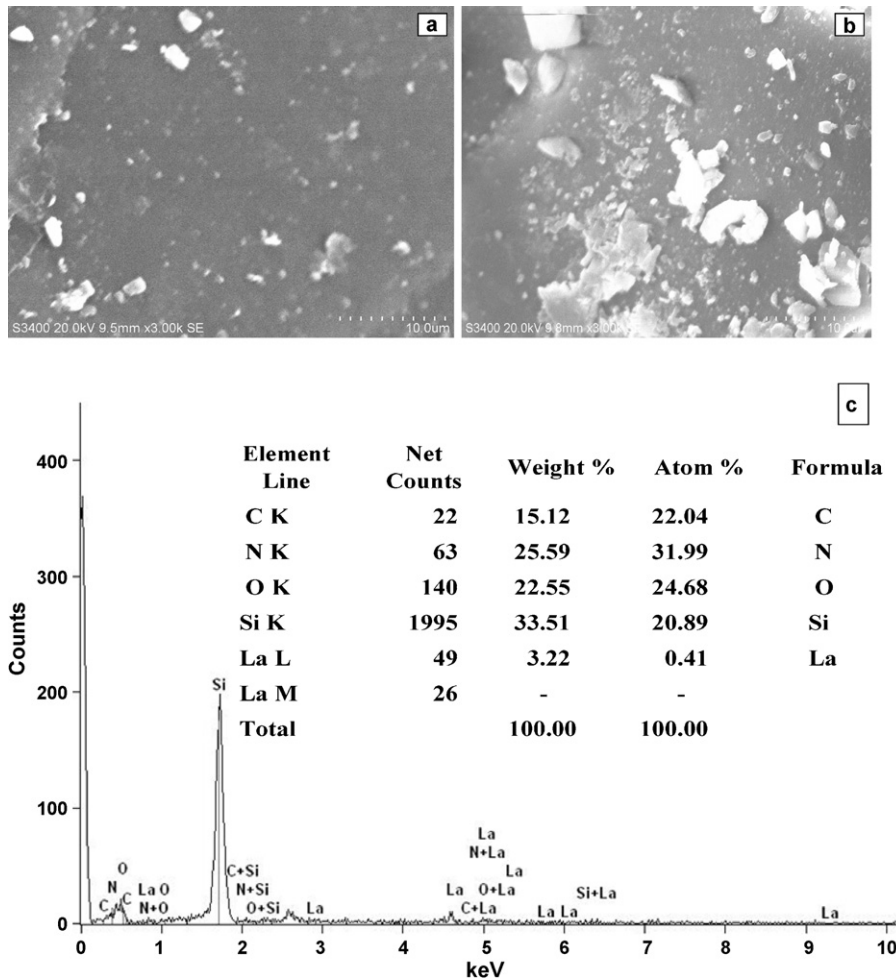


Fig. 4. SEM micrographs of (a) LaSiCS composite, (b) chromium sorbed LaSiCS composite and EDAX spectra of (c) LaSiCS composite.

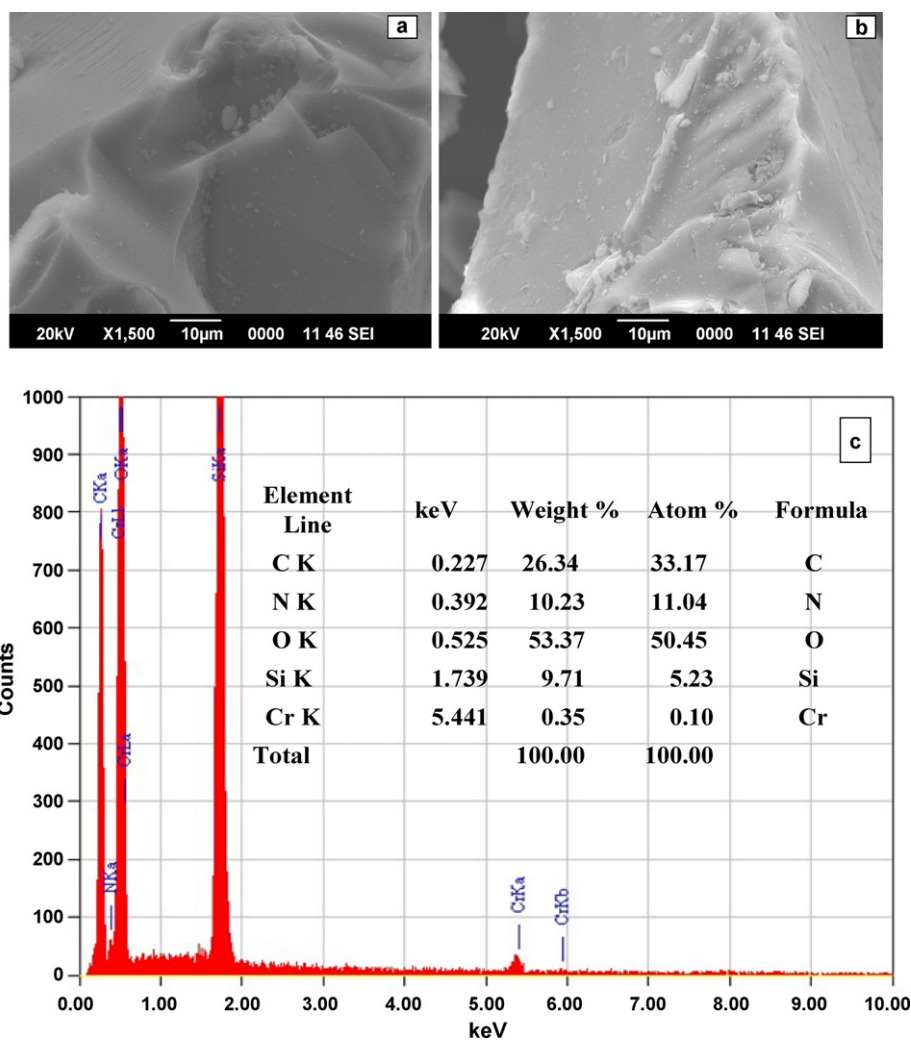


Fig. 5. SEM micrographs of (a) SiCS composite, (b) chromium sorbed SiCS composite and EDAX spectra of (c) chromium sorbed SiCS composite.

micrographs of the sorbent before and after chromium treatment indicates the structural changes in the sorbent. It is evident that the composites are porous in structure before sorption which has been blocked after sorption of chromium that indicates the structural changes in the composites. EDAX methods were employed to establish whether the electron-dense portions of the composites surfaces were composed of Cr(VI) ions. The EDAX spectra of the LaSiCS composite is depicted in Fig. 4c confirm the presence of C, N, O, Si and La. The EDAX spectra of the chromium sorbed SiCS composite is depicted in Fig. 5c. Fig. 5c confirms the presence Cr in the composite after chromium sorption. The quantitative elemental compositions of the composites are listed in their respective figures. The chromium sorption has occurred on SiCS composite which was confirmed by the presence of chromium and Si+Cr peaks in the EDAX spectra of chromium treated SiCS composite (cf. Fig. 5c).

X-ray power diffraction patterns of Si, CS, SiCS and LaSiCS were presented in Fig. 6a–d. Silica gel characteristic peaks at  $2\theta = 11.6^\circ$ ,  $20.7^\circ$ ,  $25.6^\circ$ ,  $29.7^\circ$ ,  $31.7^\circ$  and  $49.2^\circ$  and chitosan flakes showed characteristic peaks at  $2\theta = 10.1^\circ$ ,  $20.3^\circ$ ,  $26.0^\circ$  and  $42.0^\circ$ . These peaks correspond to a crystalline structure of Si and CS respectively [29,30]. XRD spectra of SiCS and LaSiCS composites more or less amorphous in nature with small crystalline area between  $2\theta = 20\text{--}29^\circ$ . The decrease in the crystallinity may be due the introduction of bulky chitosan polymeric chain and lanthanum ion loading, which demonstrates that the conjugation of silica and chitosan suppressed the crystallization of both chitosan and silica to

some extent. It suggests that silica and chitosan polymeric chain were mixed well at a molecular level. More importantly, the peak at  $2\theta = 21^\circ$  in SiCS was shifted to  $25^\circ$  after incorporation of La(III) resulted in the significance decrease in the crystallinity of composite. Figs. 7 and 8 show the SiCS/LaSiCS composites and after sorption

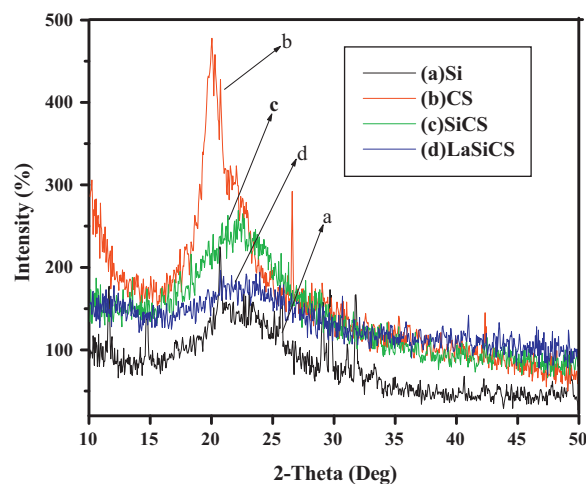


Fig. 6. XRD Spectra of (a) chitosan, (b) silica, (c) SiCS and (d) LaSiCS.

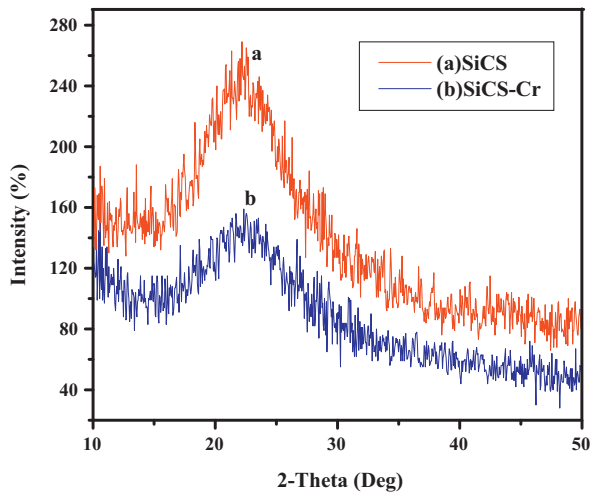


Fig. 7. XRD Spectra of (a) SiCS and (b) chromium sorbed SiCS.

of chromium. The adsorption of chromium leads a very significant change in the morphology of the composites. In both the composites after chromium sorption the intensity of peaks decreased and the characteristic  $2\theta$  at  $20^\circ$  shifted to  $23\text{--}25^\circ$  due to the sorption of chromium ion.

### 3.2. Effect of contact time

The  $q$  values of Si, SiCS composite and LaSiCS composite vary with the period of time of contact with sorbate solution. So the experiments were carried out with different contact time in the range of 10–100 min with 50 mL of 10 mg/L initial chromium concentration at 303 K. As it is evident from Fig. 9, that all the sorbents reached saturation at 60 min and hence for further studies the contact time was fixed as 60 min. The  $q$  values of LaSiCS composite and SiCS composite are 5.31 and 3.5 mg/g respectively whereas the Si and CS possess 1.08 and 0.7 mg/g respectively at 60 min contact time.

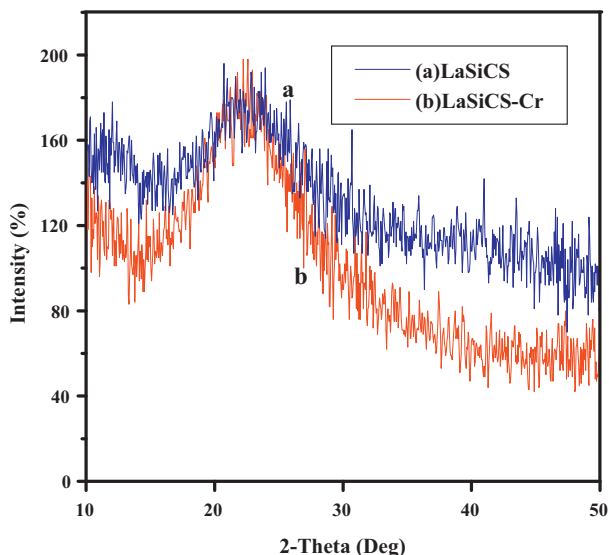


Fig. 8. XRD Spectra of (a) LaSiCS and (b) chromium sorbed LaSiCS.

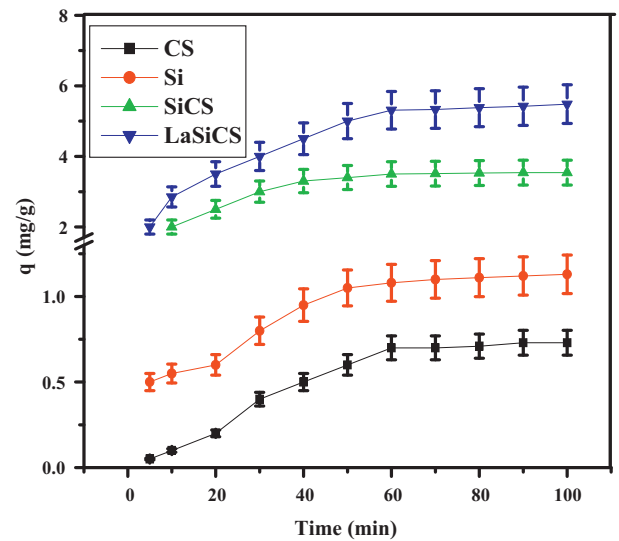


Fig. 9. Effect of contact time on  $q$  value of the sorbents at 303 K.

### 3.3. Effect of pH

The pH is an important parameter affecting metal sorption at water-adsorbent interfaces. Hence sorption of chromium ions onto the sorbents was analyzed at five different initial pH levels viz., 2, 4, 6, 8, 10 and 12 keeping other parameters like contact time as 30 min, 0.1 g dosage and 10 mg/L as initial chromium concentration at 303 K as constant. The pH of the working solution was controlled by adding HCl/NaOH solution. Fig. 10 shows the  $q$  value of sorbents was influenced by the pH of the medium. Maximum  $q$  value was observed at pH 4 and minimum at alkaline pH ranges. In all the pH ranges studied, the LaSiCS composite was found to possess higher  $q$  value than that of SiCS composite, Si and CS. The effect of pH on the sorption of Cr (VI) onto the sorbents is higher at low pH levels and decreases with the increase in solution pH. The reason could be at lower pH levels, the sorbents acquire a positive charge due to the protonation of amino groups except Si and the predominant species of chromium in the form of  $\text{HCrO}_4^-$  ion has been adsorbed through electrostatic attraction by the sorbent [31,32] which results in an increased adsorption. There is a gradual decrease in the  $q$  value of the sorbents as the pH of the solution increases, which may be due to the competition of  $\text{OH}^-$  ion for the sorption sites of the sorbent

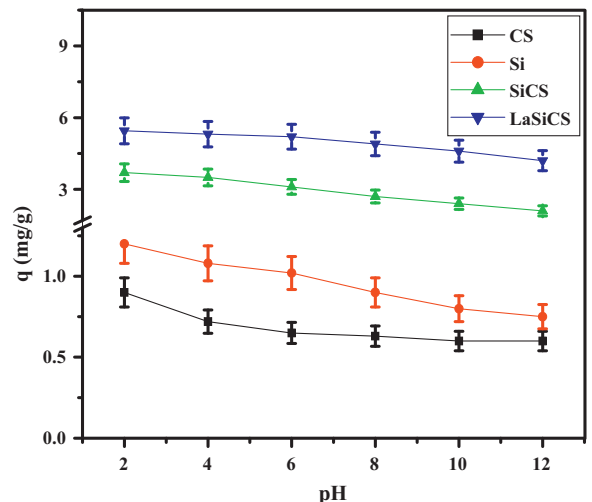


Fig. 10. Influence of pH on the  $q$  value of the sorbents at 303 K.

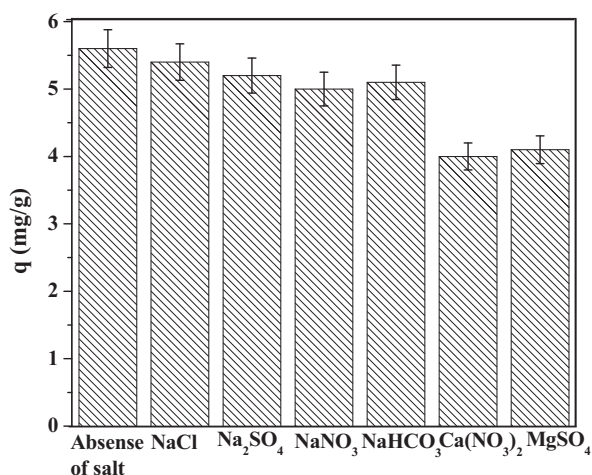


Fig. 11. Effect of co-ions on the  $q$  value of LaSiCS composite at 303 K.

surface. For further experiments, pH of the solution was fixed as 4. Irrespective of the initial pH ranges studied, the final pH of the treated water reached neutral pH for all the sorbents studied. In all the pH ranges studied, the LaSiCS composite was found to possess higher  $q$  value than that of SiCS, Si and CS. Further studies were focused on LaSiCS composite.

#### 3.4. Effect of co-ions

Chromium removal studies of LaSiCS composite were carried out in the presence of common ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  which are normally present in water which may compete with the active sites in the sorbent during chromium sorption. Fig. 11 shows the dependence of  $q$  value of LaSiCS composite in the presence of co-ions with a fixed initial concentration of 400 mg/L and other parameters such as time as 60 min, 4 pH, 0.1 g dosage and initial chromium concentration as 10 mg/L. In absence of co-ions  $q$  value of the sorbent was 5.6 mg/g. It was inferred that there was no remarkable influence on the  $q$  value of the sorbent in the presence of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  ion is due to large charge density and higher valency of chromate when compared to other co-anions. However the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions resulted in the decrease of  $q$  value from 5.6 to 4.0 mg/g. This may be due to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ion exchange with the LaSiCS composite.

#### 3.5. Sorption isotherms

To quantify the  $q$  value of LaSiCS composite for the removal of chromium, two commonly used isotherms namely Freundlich and Langmuir have been adopted.

##### 3.5.1. Freundlich isotherm

The linear form of Freundlich [33] isotherm is represented by the equation,

$$\log q_e = \log k_F + \left(\frac{1}{n}\right) \log C_e \quad (2)$$

**Table 1**  
Freundlich and Langmuir isotherms parameters of LaSiCS on the removal of chromium.

Temp. (K)	Freundlich isotherm					Langmuir isotherm				
	$1/n$	$n$	$k_F$ (mg/g) (L/mg) <sup>1/n</sup>	$r$	$\chi^2$	$Q^\circ$ (mg/g)	$b$ (L/g)	$R_L$	$r$	$\chi^2$
303	0.251	3.984	4.946	0.887	0.00196	6.127	0.574	0.126	0.989	0.00154
313	0.162	6.172	5.146	0.937	0.00061	8.152	1.138	0.068	0.998	0.00039
323	0.193	5.181	5.231	0.999	0.71500	9.216	0.981	0.078	0.999	0.00170

where  $q_e$  is the amount of chromium adsorbed per unit weight of the sorbent (mg/g),  $C_e$  is the equilibrium concentration of chromium in solution (mg/L),  $k_F$ , a measure of adsorption capacity, and  $1/n$ , the adsorption intensity, were calculated from the slope and intercept of the plot  $\log q_e$  vs  $\log C_e$ . The values of  $1/n$ ,  $n$  and  $k_F$  of LaSiCS composite are listed in Table 1. The values of  $1/n$  are lying between 0 and 1 and the  $n$  values lying in the range of 1–10 confirm the favorable conditions for adsorption. With the rise in temperature, the  $k_F$  values get increased which indicate that the chromium uptake by LaSiCS composite is a temperature dependent process.

##### 3.5.2. Langmuir isotherm

Langmuir [34] isotherm model can be represented in the form of equation,

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \quad (3)$$

where  $Q^\circ$  is the amount of adsorbate at complete monolayer coverage (mg/g), which gives the maximum sorption capacity of sorbent and  $b$  (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption calculated from the slope and intercept of the plot  $C_e/q_e$  vs  $C_e$  and the values are shown in Table 1. The increase in values of  $Q^\circ$  with the rise in temperature indicates that the uptake amount of sorbate increased with the rise in temperature [34]. The value of  $b$  which is the energy of adsorption increases with the increase in temperature and is a temperature dependent process. The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter  $R_L$  [35].

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

The  $R_L$  values at different temperatures studied were calculated and are listed in Table 1. The  $R_L$  values lying between 0 and 1 indicated that the conditions were favorable for adsorption. The higher  $r$  values of Langmuir over Freundlich isotherm indicated the suitability of Langmuir isotherm than the Freundlich isotherm.

##### 3.5.3. Chi-square analysis

To identify the suitable isotherm for sorption of chromium onto LaSiCS, chi-square analysis was carried out. The mathematical statement for chi-square [36] analysis is

$$\chi^2 = \sum \left( \frac{(q_e - q_{e,m})^2}{q_{e,m}} \right) \quad (5)$$

where  $q_{e,m}$  is equilibrium capacity obtained by calculating from the model (mg/g) and  $q_e$  is experimental data on the equilibrium capacity (mg/g). The values of  $\chi^2$  are presented in Table 1. The low chi square values of Langmuir isotherm than Freundlich isotherm for LaSiCS indicates the applicability of Langmuir isotherm.

##### 3.5.4. Different initial chromium concentration

Increasing the concentration of the chromium with the fixed dosage as 0.1 g and 100 mL of chromium(VI) solution at pH 4 sorption studies were conducted in order to know the maximum efficiency of the LaSiCS for chromium removal. The concentration of the chromium solution viz., 200, 400 and 600 mg/L with the 0.1 g

**Table 2**  
Thermodynamic parameters of LaSiCS on the removal of chromium.

Thermodynamic parameters	LaSiCS	
	303 K	−4.62
$\Delta G^\circ$ (kJ mol <sup>−1</sup> )	313 K	−4.74
	323 K	−5.24
$\Delta H^\circ$ (kJ mol <sup>−1</sup> )		14.67
$\Delta S^\circ$ (kJ mol <sup>−1</sup> K <sup>−1</sup> )		0.03

of LaSiCS and 60 min as contact time, the maximum adsorption capacity ( $q_m$ ) was found to be 110, 224 and 240 mg/g respectively and after which a tendency of saturation was observed. It is obvious a concentration of 600 mg/L onwards, all the active sites of LaSiCS composite was occupied, which restrict further sorption of chromium after this concentration.

### 3.6. Thermodynamic treatment of the sorption process

The effect of temperature is a major influencing factor in the sorption process. The chromium sorption onto LaSiCS was monitored at three different temperatures viz., 303, 313 and 323 K under the optimized conditions and thermodynamic parameters like standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change

( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ ) were calculated as follows,

The change in free energy of sorption is given by

$$\Delta G^\circ = -RT \ln K_o \quad (6)$$

where  $K_o$  is the sorption distribution coefficient,  $\Delta G^\circ$  is the free energy of sorption (kJ/mol),  $T$  is the temperature in Kelvin and  $R$  is the universal gas constant (8.314 J mol<sup>−1</sup> K<sup>−1</sup>). The sorption distribution coefficient  $K_o$  was determined from the slope of the plot  $\ln(q_e/C_e)$  against  $C_e$  at different temperatures and extrapolating to zero  $C_e$  according to Khan and Singh method [37]. The sorption distribution coefficient can be expressed in terms of enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) as a function of temperature,

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where  $\Delta H^\circ$  is the standard enthalpy change (kJ/mol) and  $\Delta S^\circ$  is standard entropy change (kJ/molK). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from the slope and intercept of a plot of  $\ln K_o$  against  $1/T$ . The values of thermodynamic parameters are shown in Table 2. The negative values of  $\Delta G^\circ$  confirm the spontaneous nature of chromium sorption. The value of  $\Delta H^\circ$  is positive indicating that the sorption process is endothermic. The positive value of  $\Delta S^\circ$  which is a measure of randomness at the solid/liquid interface

**Table 3**  
Toxic ions removal using the metal loaded sorbents.

S. no.	Adsorbent	Toxic ion removed	Reference
1	Zr-loaded lysine diacetic acid resin	As(V) and As(III)	[43]
2	Porous resin loaded with crystalline hydrous zirconium oxide	As(V) and As(III)	[44]
3	Zr-loaded activated charcoal	As(V), As(III), SeO <sub>4</sub> <sup>2−</sup> and Hg(II)	[45]
4	Chelating polymer-gel loaded with Zr(IV)	As(V), As(III) and PO <sub>4</sub> <sup>3−</sup>	[46]
5	Porous resin loaded with $\alpha$ -zirconium phosphate crystals	Pb(II)	[47]
6	Orange waste gel loaded with Zr	PO <sub>4</sub> <sup>3−</sup>	[48]
7	Zr(IV) loaded phosphoric chelate adsorbent	As(V)	[49]
8	Activated carbon fiber loaded with lanthanum oxide	PO <sub>4</sub> <sup>3−</sup>	[50]
9	Lanthanum hydroxide	F <sup>−</sup>	[51]
10	La(III) doped mesoporous silicates material	PO <sub>4</sub> <sup>3−</sup>	[52]
11	La(III)-coordinated diamino-functionalized 3D hybrid	PO <sub>4</sub> <sup>3−</sup>	[53]
12	La/Al pillared montmorillonite	PO <sub>4</sub> <sup>3−</sup>	[54]
13	Cotton cellulose based Fe(III)-loaded adsorbent	As(V)	[55]
14	La(III) incorporated chitosan beads	F <sup>−</sup>	[56]
15	La-modified chitosan	F <sup>−</sup>	[57]
16	Zr(IV) entrapped chitosan polymeric matrix	F <sup>−</sup>	[58]
17	Na <sup>+</sup> and Al <sup>3+</sup> incorporated ion exchange resin	F <sup>−</sup>	[59]
18	La(III) incorporated carboxylated chitosan beads	F <sup>−</sup>	[22]
19	Fe(III) loaded carboxylated chitosan beads	F <sup>−</sup>	[60]
20	La <sup>3+</sup> , Fe <sup>3+</sup> , Ce <sup>3+</sup> and Zr <sup>4+</sup> ion loaded resin	F <sup>−</sup>	[61]
21	La-Treated lignocellulosic sorbent	PO <sub>4</sub> <sup>3−</sup>	[62]
22	Zr(IV)-impregnated collagen fiber	F <sup>−</sup>	[63]
23	Fe(III)/Cu(II)-EDA complexes anchored inside mesoporous silica MCM-41	PO <sub>4</sub> <sup>3−</sup>	[64]
24	Bead cellulose loaded with iron oxyhydroxide	As(V) and As(III)	[65]
25	Fe-Ce bimetal oxide	As(V)	[66]
26	Fe(III)-loaded open-celled cellulose sponge	As(V) and As(III)	[67]
27	La(III)-loaded adsorbents with different functional groups and polymer matrices	F <sup>−</sup>	[68]
28	La-loaded zeolite	As(V)	[69]
29	La(III) hydroxide and lanthanum (III)-loaded ion exchangers	As(V), As(III) and Cr(VI)	[70]
30	La(III)- and cerium(III)-loaded orange waste gels	As(V) and As(III)	[71]
31	Novel polysulfone capsules containing zirconium phosphate	Pb <sup>2+</sup>	[72]
31	Zirconium phosphate supported by a cation exchanger	Pb <sup>2+</sup> , Zn <sup>2+</sup> and Cd <sup>2+</sup>	[73]
32	Chitosan supported zirconium(IV) tungstophosphate composite	F <sup>−</sup>	[74]
33	Hydrous zirconium oxide	Cr(VI)	[75]
34	Alumina/chitosan composite	Cr(VI)	[76]
35	Zr(IV) and Fe(III)-loaded saponified orange waste	Sb(III) and Sb(V)	[77]
36	Mesoporous ZrO <sub>2</sub>	PO <sub>4</sub> <sup>3−</sup>	[78]
37	Aluminum-loaded shirasu-zeolite	As(V)	[79]
39	Inorganic exchanger Zr(HPO <sub>3</sub> S) <sub>2</sub>	Pb(II), Cd(II) and Zn(II)	[80]
40	Iron-doped activated carbons prepared by impregnation with Fe(III) and Fe(II)	As(V) and As(III)	[81]
41	Fe(III)-loaded chelating resin having lysine-N <sup>o</sup> diacetic acid moiety	As(V) and As(III)	[82]
42	Oxide-loaded slag	As(V) and As(III)	[83]
43	Fe(III)-entrapped $\gamma$ -alumina nano sorbent	As(V)	[84]
44	Fe-chitosan composite	As(III) and As(V)	[85]

during chromium sorption indicates the sorption is irreversible and stable.

### 3.7. Sorption mechanism

Chromium removal by LaSiCS composite was mainly governed by adsorption mechanism. The positively charged  $\text{La}^{3+}$  surface in the hybrid composite attracts the negatively charged chromium ions by means of electrostatic attraction. The chromium removal by Si is mainly due to its porous nature which entraps chromium by means of electrostatic attraction. Amino groups present in chitosan get protonated in solution pH (pH 4) and remove chromium by electrostatic adsorption. The enhancement in  $q$  value of SiCS composite over Si may be due to the combined advantages of both chitosan and Si. The strong electrostatic adsorption and complexation between  $\text{La}^{3+}$  and  $\text{HCrO}_4^-$  ion are mainly responsible for the significant enhanced  $q$  value of La(III) incorporated hybrid composite. The FTIR spectra of Cr(VI) loaded sorbent have a new band at  $540\text{ cm}^{-1}$  and composite turning light green color confirms the formation of  $\text{Cr}(\text{OH})_3$  in the chromium sorbed composite [26,27,38]. The reactive  $-\text{OH}$  and  $-\text{NH}_2$  electron donor groups present in the LaSiCS composite reduce the toxic Cr(VI) to less toxic Cr(III) compounds confirms the adsorption coupled reduction [26,38]. In addition, Cr(VI) is also reduced to Cr(III) by glutaraldehyde molecules (cross-linker) [39].

### 3.8. Comparison of Cr(VI) removal with different adsorbents reported in literature

The adsorption capacities of the LaSiCS for the removal of Cr(VI) have been compared with those of other sorbents reported in literature. The experimental data of the present investigations are comparable with the reported one. The  $q$  value varies and depends on the characteristics of the individual adsorbent, the extent of surface/surface modification, pH and the initial concentration of the adsorbate. However, the present experiments are conducted to find the technical applicability of the adsorbents to remove Cr(VI).

### 3.9. Toxic metal ions removal using the metal loaded adsorbents and their advantages

The use of transition metals in the field of water treatment is well established as it does not leach into water due to its higher positive charges [40]. Mostly mesoporous silicates materials, cation-exchange resins, ion-exchangers macroporous polymers, chelating resins and biopolymers have been used as a base in the preparation of metal-loaded polymers. These metal-loaded polymers [41,42] have then been used to adsorb toxic ions and an extensive review of literature for the removal of ions is shown in Table 3. Metal loaded materials have been used mostly for the removal of phosphate, arsenic, fluoride and only a few reports for chromium.

## 4. Conclusions

LaSiCS composite possessed higher  $q$  value than SiCS composite, Si and CS. The  $q$  value of LaSiCS composite was influenced by pH of the medium and decreased in the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The optimum pH for removal of chromium (VI) is pH 4. After sorption, irrespective of initial pH ranges, the final pH of the treated water was found to be neutral. The sorption of chromium on LaSiCS composite followed Langmuir isotherm. The mechanism of chromium sorption was mainly governed by electrostatic adsorption coupled reduction/ion-exchange. The nature of chromium sorption was spontaneous and endothermic. LaSiCS composite can be effectively utilized for the wastewater containing toxic ions.

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