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Synthesis of novel aniline immobilized silica gel for the selective extraction of Cr(III)

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ABSTRACT

Aniline moiety was immobilized on the surface of silica gel (SG) through functionalizing the later by 3-chloropropyl trimethoxysilane (3-CPTS). The aniline immobilization was confirmed by chemical, Fourier transform infrared (FTIR), thermo gravimetric analysis (TGA), and scanning electron microscopy (SEM). Solid phase extraction (SPE) property of the synthesized product was studied in terms of Cr(III) uptake by batch and column methods. Metal ion adsorption and its isotherm, kinetic and thermodynamic parameters were evaluated. The mechanistic path involved in up taking metal ion has been suggested. The Cr(III) binding capacity was found to be 8.7 mg g^{-1} at trace level of chromium in aqueous medium. The presence of chloride ion improved the metal ion binding capacity as well as selectivity to a significant extent. The developed material and the selective extraction method were tested by applying it in real samples and the results were compared with the reported values.

Keywords: Solid phase extraction; Immobilization; Aniline; Silica gel; Cr(III)

1. Introduction

Solid phase extraction (SPE) is the most common technique for the treatment of environmental samples. It deserves the advantages of eco-friendliness, simplicity, short extraction time, high enrichment factor, and low consumption of organic solvents over liquid–liquid extraction [1,2]. Preparation of new selective adsorbent and development of selective extraction method is an important research area [3].

Silica gel (SG) is a widely used support material for its pendant Si-OH groups, allowing variety of ligands to be immobilized on the surface through coupling agents [4]. Aniline immobilized SG are expected to be good binder for Cr(III) due to availability of electron-rich nitrogen donor center. Pavan et al. [5,6] synthesized thermally stable aniline/silica composite through sol-gel technique for the adsorption of $CoCl_2$, $ZnCl_2$, and $CdCl_2$. Jacques et al. [7] grafted aniline moiety onto SG for the removal of Cu(II), Fe(III), and Cr(III) from aqueous solution. A new unbreakable solid-phase microextraction (SPME) fiber coating based on poly(aniline)-silica nanocomposite was electrodeposited on a stainless steel wire [8]. However, the low Cr(III) uptake capacity, poor selectivity, and slow adsorption rate make the reported materials unsuitable for practical applications. In fact, the reported materials are far from large enough to be utilized for the treatment of tannery effluent, which is the main source of chromium pollution. Cr(VI) is a well-known carcinogen and Cr(III) is relatively inert.

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However, aerial oxidation, particularly in presence of soil, Cr(III) is converted to Cr(VI) almost quantitatively [9]. Cr(III) is essential to mammals which helps the body to control blood-sugar levels in trace concentrations, but toxic to fish when present in water above 5.0 mg L^{-1} [10]. For compliance with this limit, it is essential for industries to treat their effluents to reduce the chromium to acceptable levels.

In the present study, we have immobilized SG with aniline through functionalization the former by (3-chloropropyl) trimethoxysilane (3-CPTS) to achieve selective solid phase adsorbent for simultaneous removal and recovery of Cr(III) from aqueous solution. The synthesized novel material and the developed extraction methodology have been tested in real environmental sample like tannery effluent.

2. Materials, instruments, and methods

2.1. Materials

Aniline (Merck, Mumbai, India) was purified by distillation over zinc dust. The middle fraction of the distillate was collected and stored in a refrigerator. 3-CPTS (97%) (Sigma, St. Loius, MO, USA), toluene (Merck, Mumbai, India), diethylether (Merck, Mumbai, India), ethanol (Jiangsu Huaxi International Trade Co. Ltd., China), and SG (60–120 mesh, Merck, Mumbai, India) were used as received. Chromate sulfate (Pfizer Ltd., Mumbai, India) was used for the preparation of stock solution of Cr(III) (300 mg L^{-1}). All the working solutions were prepared by proper dilution of the stock solution with double distilled water.

2.2. Instruments

The amount of metal ion in solution was measured using atomic absorption spectrophotometer (AAS, Shimadzu, AA 6300). An ELICO made pH meter (Model LI120) was used for the pH measurement. The Fourier transform infrared (FTIR) was recorded using KBr pellets by Shimadzu-8400S spectrometer. Thermogravimetric and differential thermal analysis were made using a Pyris Diamond TG/DTA (Perkin Elmer, STA-6000) thermal analyzer in nitrogen atmosphere at a heating rate of 20°C $\min^{-1}$. Scanning electron microscopy (SEM) of the solid phase was conducted by JEOL SEM 6360 machine. The magnetic susceptibility measurement was carried out using the Sherwood Scientific Balance, Cambridge, UK.

2.3. Immobilization of aniline onto silica gel

Immobilization of aniline and SG was carried out in two steps; viz. functionalizing of SG (Fig. 1) and covalently binding of aniline (Fig. 2). In the first step, the SG was subjected to acid treatment for 2 h and then heated at 150°C for 6 h to activate the material. About 10 g of activated SG having active Si–OH groups was suspended in 20 mL dry toluene containing 1 mL of 3-CPTS and the mixture was refluxed for 5 h. The weight ratio of 3-CPTS and SG was kept very low 0.1: 1 (i.e. 10 weight percentage of 3-CPTS with respect to SG), in accordance with the theoretical calculation of hydroxyl (Si–OH) groups present per nm^2 of SG used. However, more than 50 weight percentage of 3-CPTS was required in the sol-gel synthesis [5–7] of the same material. The functionalized silica gel (FSG) was filtered off, washed with ethanol, and dried in an oven at 60°C for 6 h.

In the next step, 5 g of the FSG was treated with 5 mL of distilled aniline dissolved in 10 mL of dry toluene and the suspension was refluxed for overnight. The resulted product (FSG–ANI) was then filtered off, washed, and dried in an oven at 60°C for 6 h. Novelty of the present scheme is that it did not require

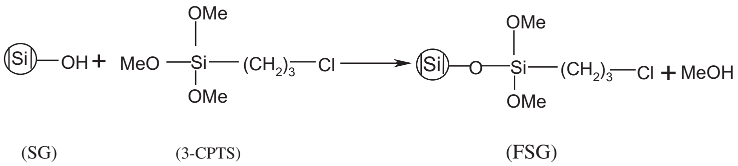


Fig. 1. Functionalizing of silica gel.

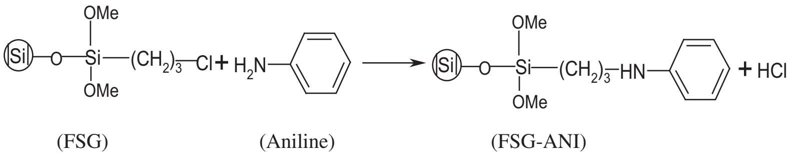


Fig. 2. Immobilization of aniline onto the FSG.

additives like NaH and HF, organic solvent like THF, and costly gas like Ar. The developed method eliminated the step of activation by prolonged acid treatment [5–7].

2.4. Extraction of Cr(III) ions

Selective extraction of Cr(III) uptake ability of the synthesized novel material was studied by batch method. In a batch method, 0.2 g adsorbent (FSG–ANI) was taken in a conical flask along with 20 mL Cr (III) solution. The mixture was stirred at the rate of 90–100 rpm. The pH of the system was adjusted using acetic acid and sodium acetate buffer. The initial concentration of Cr(III) was kept below 100 mg L^{-1} to assess the performance of the developed method at trace levels of metal ion. After suitable time interval, the adsorbent was filtered and the residual solution was analyzed for Cr(III) ions spectroscopically [7]. The amount of Cr(III) extracted was calculated using the relationship:

$$q_t = (W_i - W_t)/M$$

Here q_t is the amount of Cr(III) adsorbed per unit mass of adsorbent (mg g^{-1}) (uptake capacity). W_i and W_t are the initial and residual amount (mg) of Cr(III), respectively. M is the mass (g) of the adsorbent (FSG–ANI) added. The analysis was repeated at least thrice to determine the uncertainties values.

Preconcentration of Cr(III) was made by column method. In a column method, the chromatographic column (column = 0.8 × 8 cm) was filled up with the developed material (FSG–ANI). Then 150 mL sample containing Cr(III) ion was poured in the column (pH was adjusted to 3.1). Then system was kept for certain time to reach to equilibrium at room temperature. The extracted Cr(III) was eluted with several eluents at the flow rate 1 mL min^{-1}.

2.5. Isotherm study

Isotherm studies were conducted by batch method at different temperatures 8, 30, and 55°C. The low temperature was monitored through ice-cold water and the high temperature was maintained by water bath. The initial concentrations of Cr(III) taken for this study was 5, 20, 40, 60, 75, and 90 mg L^{-1}, and the solution was adjusted to pH 3.1. After equilibrium adsorption, the samples were separated and analyzed for Cr(III) content.

2.6. Kinetic study

Kinetic study was performed by batch method at room temperature. The initial concentration of Cr(III) and pH of the solution were 40 mg L^{-1} and 3.1 respectively. One mL sample solution was withdrawn each time from the reaction mixture by a syringe at a gap of fixed interval and Cr(III) was analyzed. The time-dependent metal ion uptake data were then used to fit various kinetic models to understand the selective extraction mechanism.

2.7. Selectivity test

To measure the selectivity, Cr(III) ion sorption was measured in the presence of 200-fold molar excess of Cr(VI), Fe(III), Al(III), and Na(I) ions at a constant pH (3.1), temperature (30°C), sorbent dose (10 g L^{-1}), and time (1 h). The selected competitive ions (Fe(III), Al (III), and Na(I)) are commonly found in tannery effluent. The selectivity (S) defined as:

S = (Cr(III) sorption in the presence of competitive ion)/(Cr(III) sorption in the absence of competitive ion).

2.8. Magnetic susceptibility measurement

Magnetic susceptibility [11] was measured using the following equation:

$$\chi_g = \frac{C \times L(R - R_0)10^{-9}}{M} \tag{1}$$

where C = calibration const. of instrument = 0.8–1.2; L = length of sample in tube = 2.0 cm; R = weight of the sample filled tube = 162 g; R_0 = weight of the empty tube = −32 g; and M = weight of the sample taken = 0.131 g.

3. Results and discussion

3.1. Evidence for aniline immobilization and chromium binding

Immobilization of aniline on FSG was confirmed by the FTIR spectrum of FSG–ANI (Fig. 3(a)). The spectrum showed the characteristic peaks at 3,454, 1,637, 1,230, and 800 cm^{-1}, which were absent in the spectra of both SG and FSG. The peaks at 3,454, 1,637, 1,230, and 800 cm^{-1} may be assigned to N–H stretching, benzene ring vibration, C–N stretching, and N–H bending, respectively [12]. The characteristic new peaks thus provided to strong evidence of aniline immobilization on FSG. The uptake of Cr(III) by FSG–ANI was confirmed by the appearance of a new

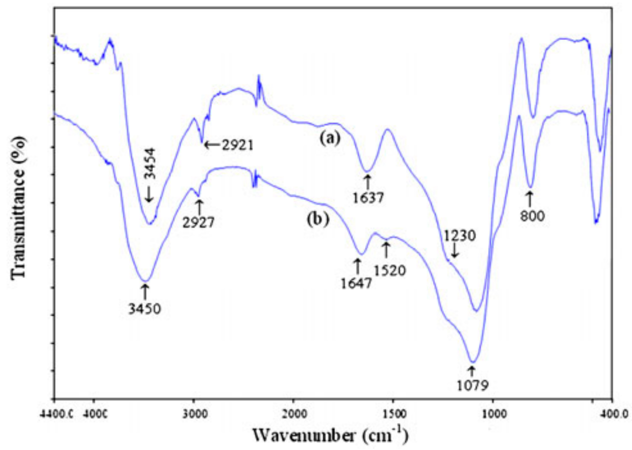


Fig. 3. FTIR spectra of (a) FSG–ANI and (b) FSG–ANI–Cr (III).

peak at 1,520 cm^{-1} in the spectrum of FSG–ANI–Cr (III) (Fig. 3(b)). The new peak was due to Cr–N linkage [13]. The chromium binding was confirmed by the magnetic susceptibility data, which was a 2.369465×10^{-6} cgs unit.

The TGA traces of SG, FSG, FSG–ANI, and FSG–ANI–Cr(III) are presented in Fig. 4. SG exhibited two-stage weight losses while its derivatives showed thrice. The initial weight loss of all the materials (from 40 to 100°C) was mainly due to the loss of water [14]. The initial weight losses of SG (11.048%) was greater than its all the derivatives (1.8794, 1.509, and 2.062% weight reduction for FSG, FSG–ANI, and FSG–ANI–Cr(III), respectively). The less-weight loss in the later case suggested the conversion of Si–OH group of SG into Si–O–Si linkage in the derivatives (Fig. 1). In fact, the formation of Si–O–Si linkage explains the better thermal stability of the derivatives over SG. It was evident that the product FSG–ANI showed better thermal stability than FSG (the former undergoes less weight loss than later). FSG contains covalent chlorine, which is probably responsible for its relatively higher weight loss. Thus the result supports the reaction (Fig. 2), which deals with the conversion of C−Cl into C−N bond. The less thermal stability of the chromium loaded sample (FSG–ANI–Cr(III)) compared to both FSG and FSG–ANI may be due to enhanced thermal degradation in presence of metal ion.

The surface morphology of the bare SG and synthesized FSG–ANI were investigated by SEM (Fig. 5 (A) and (B)), which showed irregular shape of the product beads. However, shape of the used SG was a granular form of silica and regular spherical [15]. Thus, the irregular shape confirms the successful capping of aniline (Figs. 1 and 2).

3.2. Effect of initial Cr(III) concentration

The effect of initial Cr(III) concentration on its uptake by the synthesized novel material was investigated within the range 5–90 $\mathrm{mg\,L}^{-1}$ keeping other parameters unchanged (sorbent = 10 $\mathrm{g\,L}^{-1}$, pH = 3.1, temperature = 30°C, and time = 1 h). The metal ion uptake increased steeply with the increase of metal ion concentration. The uptake capacity was found to be 2.5 $\mathrm{mg\,g}^{-1}$ even at very low level of Cr(III) (5 $\mathrm{mg\,L}^{-1}$) in absence of chloride. The value is considerably higher than commercially available ion exchange resin at similar conditions [14]. The metal

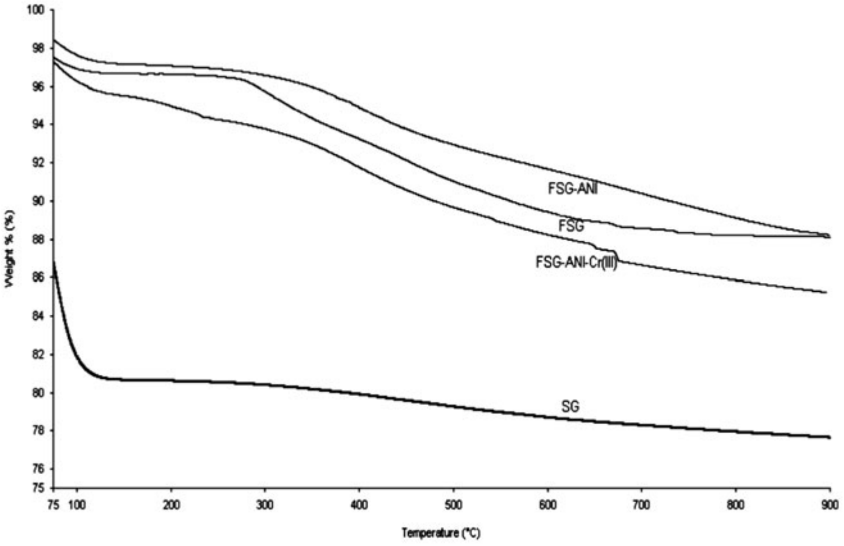


Fig. 4. TGA curves of SG, FSG, FSG–ANI, and FSG–ANI–Cr(III).

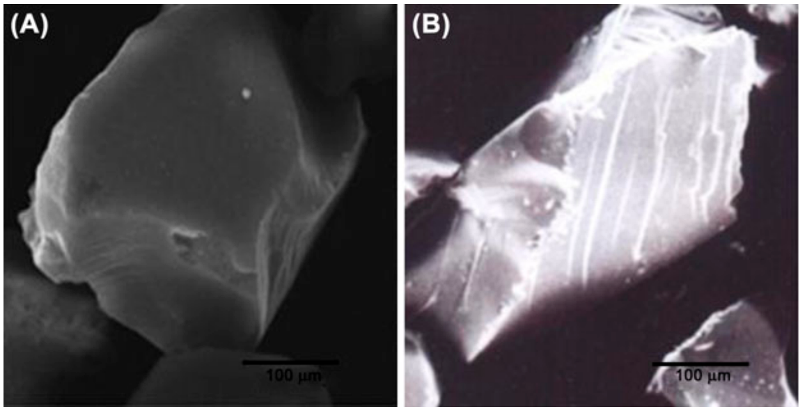


Fig. 5. SEM images of (A) bare SG and (B) FSG–ANI.

ion uptake capacity of non-immobilized SG was found to be 0.05 mg g^{-1}.

3.3. Optimization of pH and mechanism of Cr(III) binding

The uptake of Cr(III) ion as a function of pH is shown in Fig. 6. The uptake capacity increased with the increase of pH up to 3.1 and then decreased gradually. The observation may be explained on the basis of the Eqs. (2) and (3). At very low pH (less than 3.1), the equilibrium (Eq. (2)) shifted towards left, probably due to breaking of the complex through protonation of FSG–ANI at N centre. At higher pH (beyond 3.1), Cr(III) undergone hydrolysis (Eq. (3)), which diminished the positive charge of the metal ion. As a consequence, the metal ion uptake capacity decreased. So the optimized pH value was 3.1.The FTIR spectral as well as thermal analysis (Section 3.1) indicated the N → Cr coordinate covalent bond formation in the complex as shown in Eq. (2). The molecular mass of the complex was found to be 2,612, which supported the assignment of the complex. The gradual hydrolysis (Eq. (3)) of Cr(III) with pH was studied by several researchers [7,16,17]. In order to continue rest of the work, all adsorption studies were carried out at the optimum pH of 3.1.

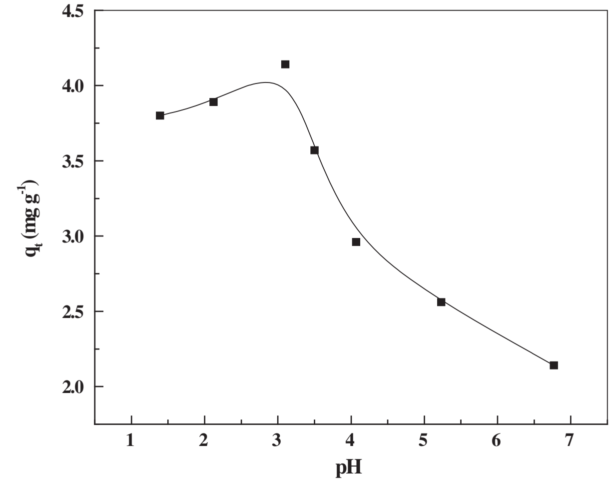
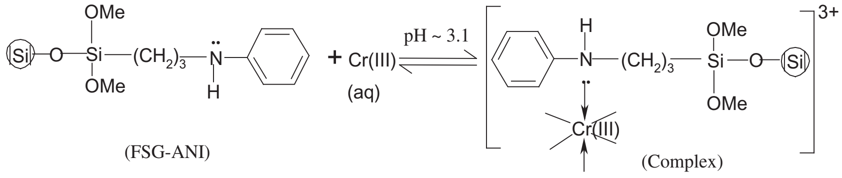


Fig. 6. Variation of uptake capacity (q_t) with pH. (Adsorbent = 10 g L^{-1}, $C_0 = 40$ mg L^{-1}, temperature = 30°C, time = 1 h) (RSD: 2.5 ± 0.2%, confidence level: 98%).

3.4. Evaluation of adsorption isotherm

Isotherms for the metal ion adsorption were studied in the light of Langmuir [18] and Freundlich [19] models within the temperature range 8–55°C (Fig. 7). The Langmuir equation [18] was basically derived for



(2)

$$[Cr(H_2O)_6]^{3+} \xrightleftharpoons{\text{pH 3-4}} [Cr(H_2O)_5OH]^{2+} \xrightleftharpoons{\text{pH 6-7}} [Cr(H_2O)_4(OH)_2]^{1+} \xrightleftharpoons{\text{pH 8}} [Cr(H_2O)_2(OH)_4]^{1-} \qquad (3)$$

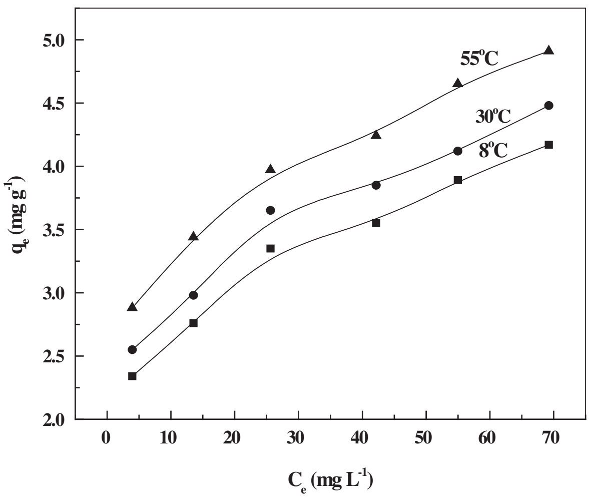


Fig. 7. Equilibrium adsorption isotherms. (Adsorbent = 10 g L^{-1}, pH = 3.1, time = 1 h) (RSD: 3.5 ± 0.3%, confidence level: 97%).

the sorption of gases on the solid surface. Nevertheless, it has been extended to include the sorption of solute at solid–liquid interface. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites and the standard mathematical representation is:

$$C_e/q_e = 1/(Q_m \times b) + C_e/Q_m \tag{4}$$

where C_e is the equilibrium concentration of chromium in the solution (mg L^{-1}); q_e, the amount of the retained chromium (mg g^{-1}); Q_m is the maximum sorption capacity (mg g^{-1}) and b is the Langmuir constant related to the affinity of binding sites. The essential feature of Langmuir adsorption can be expressed by means of R_L, a dimensionless constant referred to as a separation factor or equilibrium parameter for the prediction if the adsorption system is favorable or not. R_L can be calculated using the equation:

$$R_L = 1/(1 + b \times C_0) \tag{5}$$

C_0 is the initial concentration of the chromate solution (mg L^{-1}).

The Freundlich isotherm model [19] assumes that the sorption of metal ions occurs on a heterogeneous adsorbent surface. Freundlich equation is expressed as:

$$\log q_e = \log K_F + (1/n) \log C_e \tag{6}$$

q_e is the amount of retained chromium (mg g^{-1}); C_e is the concentration at equilibrium (mg L^{-1}); K_F and n are Freundlich constants.

Table 1
Values of Langmuir and Freundlich constants for the adsorption of Cr(III)

T (K)	Langmuir constants				Freundlich constants		
	R_L	Q_m	b	R^2	n	K_F	R^2
281	5.88×10^{-1}	4.37	0.14	0.9758	4.98	1.72	0.9685
303	5.40×10^{-1}	4.70	1.7	0.9881	4.94	1.89	0.9649
328	5.0×10^{-1}	5.17	0.20	0.9883	5.12	2.21	0.9839

The Langmuir and Freundlich sorption parameters were determined by plotting the experimental data (Fig. 7) based on Eqs. (4) and (6), respectively. The relevant parameters were determined and their corresponding correlation coefficients (R^2) are listed in Table 1. The R_L values were less than 1 and very close to 0, and the values of n where between 1 and 10 in the present case. These values indicated a favorable adsorption.

3.5. Thermodynamic parameters

According to the lower limit of the Langmuir isotherm (i.e. $bC_e << 1$), the Langmuir isotherm can be simplified to a linear adsorption isotherm equation as follows:

$$K_c = C_{Ae}/C_e \tag{7}$$

where K_c is the equilibrium constant, C_{Ae} is the amount of Cr(III) ion (mg) adsorbed on the adsorbent per liter of the solution at equilibrium, and C_e is the equilibrium concentration (mg L^{-1}) of the Cr(III) ion in the solution. Thermodynamic parameters such as free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) change of adsorption can be evaluated from the Van't Hoff equation [19].

$$\ln K_c = -\Delta H^\circ/RT + \Delta S^\circ/R \tag{8}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). The Gibbs free energy change ($\Delta G°$) is related to enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) at constant temperature by Eq. (9).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

The values of ΔH° and ΔS° were calculated from the slope and intercept of the Van't Hoff plot (ln K_c vs. $1/T$). The calculated values are given in Table 2. The Gibbs free energy change ($\Delta G°$) values were

Table 2
Thermodynamic parameters for the adsorption of Cr(III) on the FSG–ANI

T (K)	Ln K_c	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} k^{-1})
281	1.78	−6.60	0.61	25.6 9
303	1.85	−7.17		
328	2.06	−7.81		

found to be negative, which indicated the spontaneous nature of the adsorption process. In addition, more negative value of ΔG° with the increase of temperature justified the results of higher extent of adsorption at higher temperature. The positive value of ΔH° (0.61 kJ mol^{-1}) suggested an endothermic nature of Cr(III) adsorption. The positive values of ΔS° (25.69 J mol^{-1} K^{-1}) showed the increased randomness at the solid–solution interface during the adsorption process.

3.6. Evaluation of equilibrium time and kinetic models

Fig. 8 shows the amount of Cr(III) uptake (q_t, mg g^{-1}) at different contact time. Almost 95% uptake took place within 35 min and the time required to reach the equilibrium was 40 min. The rapid uptake was probably due to the availability of electron-rich nitrogen donor center of FSG–ANI. The time-dependent experimental data (Fig. 8) were used to fit various kinetic models [10] (Table 3) through linear regression plots. The linear regression values ($R^2 > 0.95$) indicated that the Cr(III) adsorption fitted second order, power function, and simple Elovich equation satisfactorily. Fitting of second-order equation justified the observed metal ion binding mechanism (Eq. (2)).

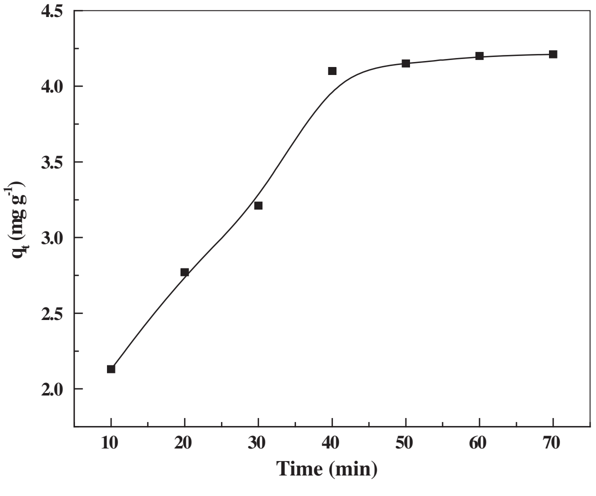


Fig. 8. Metal ion uptake at room temperature (Adsorbent = 10 g L^{-1}, C_o = 40 mg L^{-1}, pH = 3.1) (RSD: 2.5 ± 0.2%, confidence level: 97%).

Table 3
Kinetic models and other statistical parameters at room temperature (30°C) and at pH 3.1

Kinetic models	Parameters and values
First-order equation	$k_1 = 7.07 \times 10^{-3}$
$-\ln(C/C_0) = k_1 t$	$R^2 = 0.8918$
Lagergren equation	$k_1 = 7.83 \times 10^{-2}$
$\log(q_e - q) = \log q_e - (k_1/2.303)t$	$R^2 = 0.8452$
Second-order equation	$k_2 = 2.8 \times 10^{-4}$
$1/C - 1/C_0 = k_2 t$	$R^2 = 0.9572$
Pseudo-second-order equation	$k_2 = 5.28 \times 10^{-1}$
$1/q_e - q = 1/q_e + k_2 t$	$R^2 = 0.5845$
Power function equation	$a = 0.9078$
$\log q = \log a + b \log t$	$b = 0.3744$
	$R^2 = 0.9846$
Simple Elovich equation	$a = 6.3734 \times 10^{-2}$
$q = a + 2.303\, b \log t$	$b = 1.1705$
	$R^2 = 0.9810$

3.7. Selectivity

The selectivity test was performed with the competitive cations like Cr(VI), Fe(III), Al(III), and Na(I), commonly found in tannery effluent. The selectivity value was found to be 1.0, 1.0, 0.8, and 0.7 for Cr(VI), Na(I), Fe(III), and Al(III), respectively. Since the selectivity value was greater than 0.5, it may be concluded that the material exhibits higher preference [14] towards chromium metal. The synthesized material showed the selectivity order as: Cr(III) > Fe(III) > Al (III) >> Cr(VI), Na(I). The higher preference of Cr(III) may be explained on the basis of complex formation as described in (Eq. (2)). Fe(III) and Al(III) did not form similar type of complex due to low CFSE and devoid of d-orbitals, respectively. Na(I) ion is not a transition metal and Cr(VI) exists as anion in aqueous medium. So, the ions that are commonly present in tannery effluent did not affect the uptake of Cr(III).

3.8. Effect of chloride ion on Cr(III) binding

The effect of Cr(III) uptake capacity in presence of chloride ions shown in Fig. 9. The Cr(III) binding capacity of the synthesized material was increased almost two folds in presence of 0.004 M chloride ions. The observed uptake capacity was enhanced to 8.7 mg g^{-1} (at trace level chromium), which was higher than many synthetic adsorbents and commercially available cation exchangers (Table 4). The chloride ions

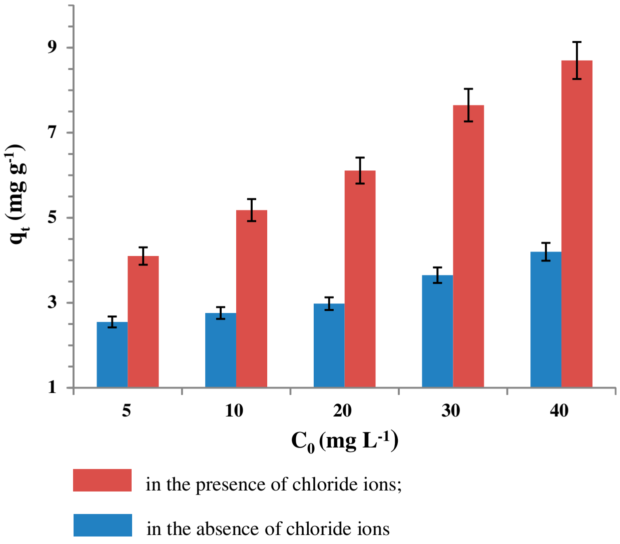


Fig. 9. Variation of uptake capacity (q_t) with chloride anions (Adsorbent = 10 g L^{-1}, anions conc. = 0.004 M, temperatue = 30˚C, time = 1h] (RSD: 2.5 ± 0.2%, confidence level: 98%).

probably helps in binding the Cr(III) through occupying thrice the coordination sites with the immobilized aniline (Fig. 10). The structure A suggested the binding of one Cr(III) atom per two nitrogen center while the B indicated one Cr(III) atom per each nitrogen center. Then structure B explained the two-fold increase of Cr (III) uptake. It is noteworthy to mention here that the presence of chloride not only helped in increasing Cr (III) binding, but also influenced the selectivity of the material. Literature survey also revealed that there are thousands of Cr(III) complexes with amines and chlorides having the formula $CrCl_3.3L$ (Octahedral) (where L = amines) [20].

3.9. Preconcentration of Cr(III)

The extracted Cr(III) was eluted by NaOH, NH_3 solution, Na_2CO_3, and $Na_2S_2O_3$ in a chromatographic column (Table 5). It was found that eluents having more than hundred times higher concentrations

Table 4
Comparision of uptake capacities of Cr(III) with various adsorbents

Adsorbents	Uptake capacity (mg g^{-1})	pH	Time (h)	C_0 (mg L^{-1}) (Initial concentration of Cr(III))	Reference
Aniline grafted SG	16.02	4.5	2	1,000	[7]
Chelating b-DAEG-sporopollenin and CEP-sporopollenin resings	4.4 5.2	5.0	24	52	[17]
Bis(2,4,4-trimetylpentyl) phosphinic acid	5.83	4.6	4	60	[23]
Active sludge of a biogas plant	7.8	2.5	3	⩾40	[24]
3-Mercaptopropyl trimethoxysilane	13.84	–	–	–	[25]
Coir pith	11.44	3.3	1.30	⩾50	[26]
Cross-linked chitosan	5.72	4.0	96	20	[27]
Aspergillus sp. biomass	2.24	4	48	⩾50	[28]
Chinese reed (Miscanthus Sinensis)	1.32	4	1	40	[29]
Aniline immobilized onto FSG (present material)	8.7	3.1	0.66	40	Present work

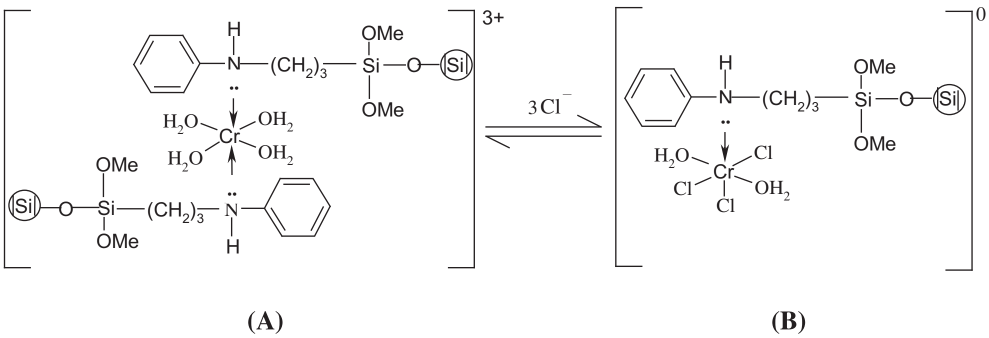


Fig. 10. Uptake capacity of Cr(III) in the presence of chloride ions.

Table 5
Elution of extracted Cr(III)

Eluents	V_t (mL)[a]	C_i (mg mL^{-1})[b]	C_f (mg mL^{-1})[c]	Recovery (%)[d]	PF[e] (C_f/C_i)	RSD[f] (S/p) × 1,000
0.1 M NaOH	19	0.04	0.31	98.16	7.75	0.51
25% NH_3 Sol.	22	0.04	0.24	88.00	6.00	0.46
0.05 M Na_2CO_3	24	0.04	0.21	84.00	5.25	0.49
5% $Na_2S_2O_3$	27	0.04	0.12	54.00	3.00	0.52

[a]Total volume of eluent (mL); [b]Initial concentration of Cr(III) in the influent; [c]Final concentration of Cr(III) in the effluent; [d]Metal ion eluted/metal ion loaded × 100, Percentage of recovery for each cases taken average of three determinations; [e]Pre-concentration factor; material weight = 2.50 g; flow rate = 1.0 mL min^{-1}; column = 0.8 × 8 cm; [f]Relative Standard Deviation (RSD) = Standard deviation(S)/mean(p) × 1,000.

compared to Cr(III) is required for effective elution. The table shows that NaOH is the most effective eluent. The preconcentration factor is the highest for 0.1 M NaOH system. The concept of preconcentration factor has been utilized in the removal and recovery of Cr(III) from tannery effluent.

3.10. Removal and recovery of Cr(III) from tannery effluent

To evaluate the accuracy and applicability of the developed material and method, it was tested with simulated tannery effluent. The Cr(III) containing synthetic tannery effluent was prepared as per literature [21] and its composition and results were presented in Table 6. It was found that the chromium contamination became below permissible limit [10] after successful treatment of the effluent by column method. The materials showed little loss of efficiency after each cycle of operation. It was observed that there was a loss of 10% efficiency after 30 cycles. Moreover, the extracted Cr(III) was eluted quantitatively by IERECHROM process [22]. The efficiency of the present removal and recovery method (8.7 mg g^{-1}) is superior to other natural and synthetic adsorbents (Table 4).

Table 6
Treatment of synthetic tannery effluent

Parameter	Value (mg L^{-1}) (before applying synthetic sample)	Value (mg L^{-1}) (after applying synthetic sample)
Cr^{3+}	40	1.50
Fe^{3+}	0.4	0.29
Al^{3+}	11.0	10.98
Na^+	2,810	2,800
Cl^-	3,654	1,200
SO_4^-	1,180	1,175
TOC (as acetic acid)	170	168

4. Conclusions

A new solid phase adsorbent based on immobilizing aniline onto SG surface through functionalizing the later by 3-CPTS has been synthesized through green approach. The metal ion uptake capacity was found to be as high as 8.7 mg g^{-1} even at trace level of Cr(III). The presence of chloride makes the system suitable for selective binding of Cr(III). The metal-aniline (anchored) interaction and molecular mass of the resulted complex was confirmed by magnetic susceptibility data. The most suitable pH, time, and temperature for Cr(III) uptake using the synthesized material was 3.1, 40 min, and 30°C, respectively. The material may be used up to 30 cycles with the little loss of efficiency. The developed material and the extraction method may be applied successfully for the removal and recovery of chromium from the tannery effluent. It is noteworthy to mention here that the further work is going on to improve the uptake capacity as well as selectivity of the studied material for commercial use.

Abbreviation

3-CPTS — (3-chloropropyl) trimethoxysilane
FSG — functionalized silica gel
FSG–ANI — aniline onto functionalized silica gel
CFSE — crystal field stabilization energy

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