PAPER

Solid-phase extraction, separation and preconcentration of titanium(IV) with SSG-V10 from some other toxic cations: a molecular interpretation supported by DFT†

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The present work reports the separation and preconcentration of titanium(IV) with functionalized silica gel (SSG-V10). A density functional theory (DFT) calculation has been performed to analyze the structure of both the extractor and the titanium(IV)-extractor complex to rationalize the sorption pathway. The systematic studies on the solid phase extraction of titanium(IV) ensured its quantitative sorption at solution pH: 5.0–6.0, influent volume: 1000 mL, analyte concentration: 23.95–35.92 μg mL^{-1}, flow rate: 2.5 mL min^{-1}, temperature: 27 °C, time of equilibration: 1.5 minutes and stress of foreign ions concentration (Cl$^-$, SO$_4^{2-}$, ClO$_4^-$ and NO$_3^-$): 200 μg mL^{-1}. The extractor, *i.e.*, SSG-V10 (29 567.465 eV; $\eta = 3.671$ eV), has a high BET surface area (149.46 m^2 g^{-1}), a good value of exchange capacity (2.54 meq. of H$^+$ g^{-1} of dry SSG-V10), break-through capacity ($Q_0 = 37.4$–40.7 μg mg^{-1}) and column efficiency (N: 108) with respect to titanium(IV). The +ve ΔH (0.048 kJ mol^{-1}), ΔS (5 J K^{-1} mol^{-1}) and −ve ΔG (−1.1488 kJ mol^{-1}) indicate that the sorption process was endothermic, entropy-gaining and spontaneous in nature. The DFT calculations reveal that the guest, [(OH)(H$_2$O)Ti(-μO)$_2$(OH)(H$_2$O)]$^{+2}$ (15 531.185 eV; $\eta = 3.39$ eV), is stabilized as a *syn* isomer. This *syn* isomer was then placed at the exchange site and a second DFT calculation was performed. It was found that the hydrogen bonded *anti* complex gets stabilized by 0.286 eV over the *syn* isomer as the extracted species. The loading of titanium(IV) has been confirmed by EDX. The sorbed titanium(IV) was eluted as a distinct and detectable color with 1 M HCl containing H$_2$O$_2$. The preconcentration factor has been optimized at 60.8 ± 0.5. Titanium(IV) amid congeners and other metal ions, associated with it in ores and alloy samples, have been separated from synthetic mixtures. Moreover, the method was found effective for alloy samples.

1. Introduction

Titanium is a relatively rare element (0.6%), but because of its unusual corrosion resistance and self-healing properties, it is in great demand for special applications in turbine engines, aircrafts, marine equipment, and in medical applications like hip and knee replacements.[1] The manufacture of the versatile white pigment TiO$_2$ through the 'chloride process' generates large amounts of acidic waste chloride liquors,[2] containing metal ions such as magnesium(II) (13.41 g dm^{-3}), aluminum(III) (13.36 g dm^{-3}), vanadium(V) (1.16 g dm^{-3}), chromium(III) (0.78 g dm^{-3}), manganese(II) (5.96 g dm^{-3}), iron(II) (215.66 g dm^{-3}) and iron(III) (48.67 g dm^{-3}) and a comparatively low amount of titanium(IV) (0.22 g dm^{-3}), which should be monitored to assess the efficiency of the titania production process. Thus, this

chloride process waste poses a challenge to the analytical chemist. Sample clean up, through the preconcentration and separation of an analyte, is required before its monitoring with sophisticated instruments. During enrichment, the target species is selectively gathered in a small volume, from a large volume of sample of complex nature. Small amounts of analyte can therefore be quantified by coupling a preconcentration system to a sensitive, selective detection/estimation technique.[3] The most widely used techniques for separation and pre-concentration of trace levels of titanium(IV) include liquid–liquid extraction,[4] differential thermal analysis,[5] reversed-phase high-performance liquid chromatographic separation,[6] ion exchange,[7] precipitation,[8] and inductively coupled plasma optical emission spectrometry (ICPOES).[9] Because of its unique features, ICPOES is able to work with trace level amounts of elements, but samples need severe digestion in 18 mol L^{-1} H$_2$SO$_4$ at 250 °C for 1 h in order to be analyzed. Moreover, prior to the operation a proper sample clean-up is required. Metal ion absorption on a solid polymer surface (solid phase extraction, SPE) is now considered as one of the most promising

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techniques for preconcentration, removal and recovery of metal ions from a wide variety of sources due to its eco-friendliness, fastness, simplicity and cost effectiveness. In our laboratory, Versatic-10 present on the surface of a hydrophobic silica support has been effectively used[10–12] for the extraction, preconcentration and separation of Cu(II), Bi(III) and V(IV). However, the systematic extraction chromatographic investigation for preconcentration and separation of titanium(IV) using silica gel-Versatic-10 composite has not yet been reported. Versatic-10, a high molecular mass liquid cation-exchanger (HMMLCE), containing a mixture of C_{10}-isomeric tertiary monocarboxylic acids, is soluble in several solvents like benzene, toluene, *n*-hexane, xylene, butanol, carbon tetrachloride, chloroform, nitrobenzene and diisopropyl ether.[10,11] It has a good thermal and chemical stability and efficiently extracts metal ions from aqueous solution over a wide range of pH.[12,13] The present work reports the separation and preconcentration of titanium(IV) with functionalized silica gel (SSG-V10) for the analysis. Global hardness (η) is a definite quantum mechanical descriptor and it is the cardinal index of chemical reactivity as well as stability of atoms and ions.[14] Thus, a density functional theory (DFT) calculation has been performed not only to analyze the structure of the extractor and the titanium(IV)–extractor complex but also to rationalize the sorption pathway in terms of hardness.

2. Experimental

The pH measurements were carried out with a digital Elico L1-120 pH meter combined with a glass electrode. The scanning electronic microscopy (SEM) image was obtained at 5.0 kV by JEOL JSM-6700-FESEM. Fourier transform infrared (FT-IR) spectra of SSG-V10 in its titanium(IV) loaded and unloaded forms were recorded on a Shimadzu FT-IR spectrophotometer (Model no. FT-IR-8400S) using KBr pellets. EDX spectra were recorded on a JEOL 2010 FEG microscope equipped with an EDX analyzer. The X-ray diffraction patterns were recorded on a Rigaku (Ultima IV) H-12 Japan (Kurary Co. Ltd. N) diffractometer in the 2θ range of 18°–50° using Cu (Kα) as its scattering X-ray line source. UV-visible spectra for the metal–ligand complexation were studied with a Shimadzu UV-visible spectrophotometer (Model no. UV-1800). The thermal stability of the SSG-V10 has been determined by TGA/DTA analysis with PerkinElmer (STA 6000) Simultaneous Thermal Analyzer in temperature range from 40 to 950 °C. BET experiments were carried out by using a Beckman Coulter SA 3100 surface area analyzer at 77 K in high vacuum. A liquid cation exchanger, Versatic-10 (Shell Chemical, London, England), which is a high molecular mass synthetic C_{15}–C_{16} monocarboxylic acid, was used without any further purification. Dimethyldichlorosilane (BDH, Bombay, India) was utilized as an end-capping reagent. A standard stock solution of titanium(IV) (5.5 mg mL^{-1}) was prepared by dissolving Ti(SO$_4$)$_2$ (E. Merc, Bombay, India) in water and estimated spectrophotometrically.[15] Buffer solutions of different pH values were prepared from acetic acid (0.2 M) and ammonium acetate (0.2) in proper ratios. For ion-exchange paper chromatography, 0.5 mL Versatic-10 was placed in 20 mL of diisopropyl ether solution and paper strips (Whatman no. 1) were immersed in it to achieve uniform

coating, and then dried in air.[10] The titanium(IV) solution (in μg) was taken on the paper strip containing Versatic10 and developed with acetate buffer (pH 5.5)–acetone (15 : 2 v/v) as the developing solvent (mobile phase).

2.1 Preparation of ion exchange material

Silica gel (60–120 mesh; 8.5 g) was rendered hydrophobic by exposing it to vapors of dimethyldichlorosilane (DMDCS) in N$_2$ atmosphere. It was then washed with anhydrous methanol and dried at 100 °C. Versatic-10 (0.5 mL (density: 0.92 g mL^{-1}) in 20 mL diisopropyl ether) was placed in an ultrasonic bath at 27 °C to achieve a homogenous solution. The silanized silica gel (SSG) was impregnated with Versatic-10 (SSG-V10; 5.411% w/w), diluted in diisopropyl ether and dried in a rotary vacuum evaporator to achieve uniform coating.[11] Each column could be used for at least 60 cycles without any loss of its exchange capacity.

2.2 UV-visible spectral study

UV-visible spectra were recorded for the solutions (pH 5.5) containing titanium(IV) (10^{-4} M) and Versatic10 (10^{-4}) at different molar ratios to obtain the composition of the extracted species.

2.3 Extraction procedure

An aliquot containing 5.5 μg mL^{-1} of titanium(IV) in acetate buffer was passed through the column at a flow rate of 2.0 mL^{-1} min at 25 °C. After extraction, titanium(IV) was stripped with 1 M HCl containing H$_2$O$_2$ and the amount of titanium(IV) from each fraction was determined spectrophotometrically.

2.4 Break-through capacity (BTC)

For the determination of break-through capacity (BTC), 200 mL fractions of metal ion solution (0.055 mg mL^{-1}) were passed through the column and the effluent was collected till the amount of metal ion concentration was the same both in feed and effluent. A breakthrough curve (Fig. 1) was obtained by plotting the ratio $\dfrac{C_e}{C_0}$ against the effluent volume, where C_0 and C_e are the concentrations of the initial solution and of the effluent, respectively. BTC is calculated using the formula $\left(\dfrac{CV(10\%)}{W}\right)$, where C_0 is the concentration of the metal ion in mg mL^{-1}, V (10%) is the volume of the metal ion solution passed through the column when the exit amount reaches 10% of the initial amount (mg) and W is the weight of the ion-exchange material in grams.

2.5 Computational methods

Standard density functional theory (DFT) calculations for all the structures were carried out with the Gaussian 09 package.[16] The geometries of all the species were fully optimized by using B3LYP[17,18] hybrid functional, LANL2DZ+ECP[19–21] basis set for titanium (Ti) and 6-31g(d) basis set for the other elements. All the optimized structures have been characterized by frequency analysis as energy minima in the absence of imaginary frequencies. In addition, neutral bond order (NBO)[22–24]
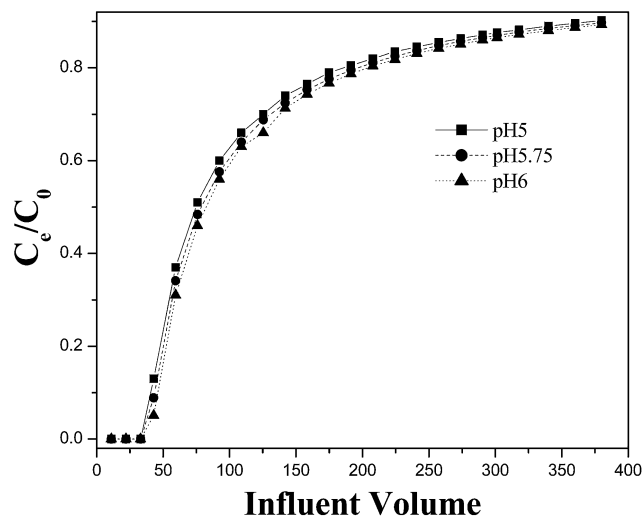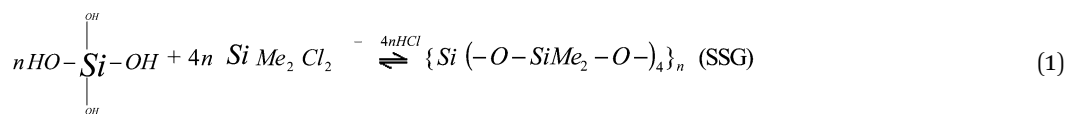
Fig. 1 Break through curve (■ = pH 5; ● = pH 5.75 and ▲ = pH 6).

Fig. 2 SEM image of SSG-V10.

calculations of the optimized structures were performed to determine the molecular orbital. The energies of the optimized structures were calculated after the ZPE (zero point energy) and thermal corrections.

3. Results and discussion

3.1 Silanization and the nature of the attachment of Versatic-10 leading to an ion-exchange material

The surface of the silica gel gets methylated (hydrophobic) during silanization (eqn (1)).[25] The silanised silica gel (SSG) surface immobilizes the hydrophobic part of Versatic-10 through weak hydrophobic interaction (eqn (2)).[10] The –COOH groups of Versatic-10 head towards the hydrophilic mobile phase and exist as dimers[26] with the formation of cavities through intermolecular hydrogen bonding.

hence, the standard methylene blue method[11] is used.[27] The SA is found to be much higher (280 m^2 g^{-1}) for the SSG-V10 composite. This SA obtained by methylene blue method is comparable to Versatic-911.[3] The surface area of the material increases with decrease in the concentration of Versatic-10 in diisopropyl ether as solvent. This indicates that the increased concentration of Versatic-10 is blocking the pores of the silica gel. Pore diameters were computed using eqn (3) (ref. 11) as 62.5 μm for a pore volume of 0.1 mL.

$$PD = \frac{4 \times PV}{SA} \times 10^4 \qquad (3)$$

[PD = Pore diameter, PV = Pore volume, SA = Surface area]

The BET study confirms that the adsorption hysteresis is H2 type, which is comprised of interconnectivity of pores in which the smaller pores act as a bottle-neck.[28]

$$nHO-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH + 4n\ SiMe_2Cl_2 \overset{4nHCl}{\underset{}{\rightleftharpoons}} \{Si(-O-SiMe_2-O-)_4\}_n\ (SSG) \qquad (1)$$

$$SSG + (RCOO^-H^+)_2 \rightarrow SSG\cdot(RCOO^-H^+)_2(s) \qquad (2)$$

3.2 Physicochemical characteristics of the ion-exchange material

The SEM image of the ion-exchanger (SSG-V10) (Fig. 2) shows that the size of the particles lies between 60 and 70 μm and their shapes are irregular in nature. BET (Fig. 3) surface area (SA), pore volume and average pore diameter were found to be 149.46 m^2 g^{-1}, 0.2001 mL g^{-1} and 4.1 nm, respectively. The nitrogen BET often does not access the internal surface areas;
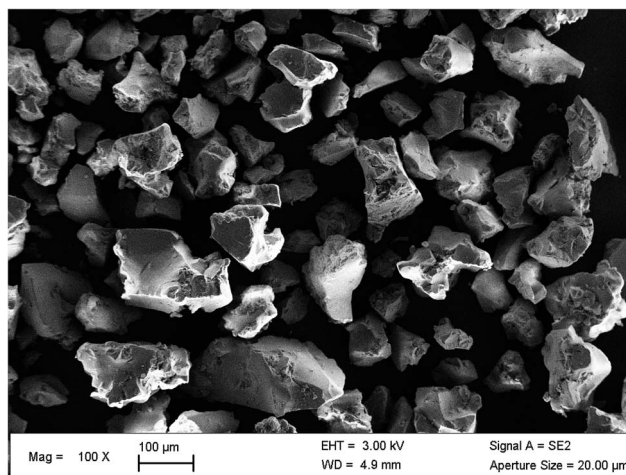
3.3 TGA and DTA analyses

The TGA and DTA analyses (Fig. 4) exhibit two regions of weight loss. Up to 150 °C, the material (SSG-V10 composite) loses its trapped water and solvents (1.20%). The original weight reappears on restoring the material at room temperature. The second weight loss (5.404%) up to 850 °C, results entirely from the decomposition of Versatic-10 loaded on SSG (eqn (2)) for the preparation of the ion-exchanger. This is compatible with the TGA values (5.411% w/w); thus, the prepared ion-exchange material is thermally stable up to 150 °C.
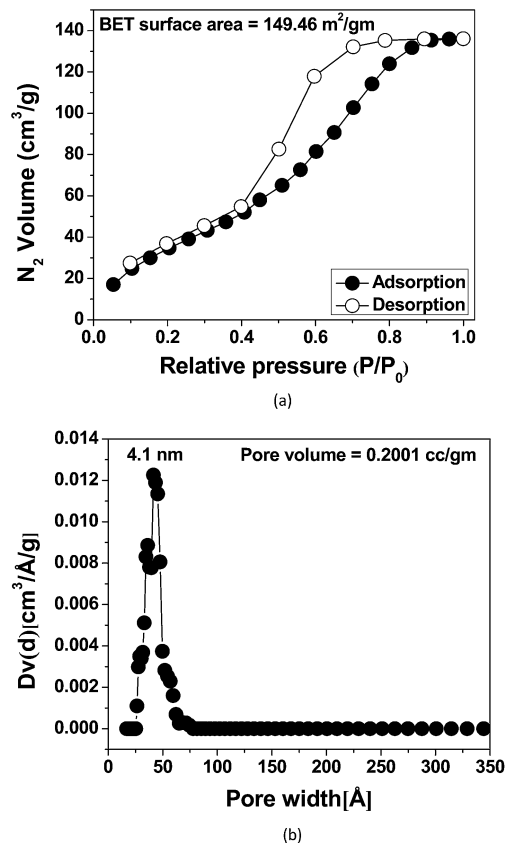
Fig. 3 BET surface properties of SSG-V10 (a) BET surface area (149.46 $m^2 gm^{-1}$); (b) pore volume (0.2001 $cm^3 gm^{-1}$).
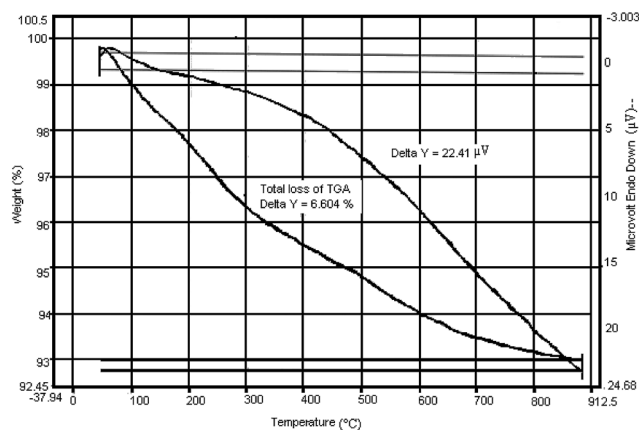

Fig. 4 TGA-DTA of Versatic-10; flow rate of nitrogen: 20 mL min^{-1}; temperature increment: 25 °C min^{-1}.

3.4 FT-IR analysis

FT-IR spectra of the composite SSG-V10 containing –COOH groups[29] showed a strong absorption band at 1688.4 cm^{-1}. While at 2580 cm^{-1} a broad peak appears due to intermolecular hydrogen bonding (Fig. 5) by –COOH. Both these peaks indeed vanished, suggesting the conversion of the –COOH group to the –COO$^-$ ion and the rupture of the hydrogen bonding,[29] thereby confirming the participation in the adsorption of titanium(IV).
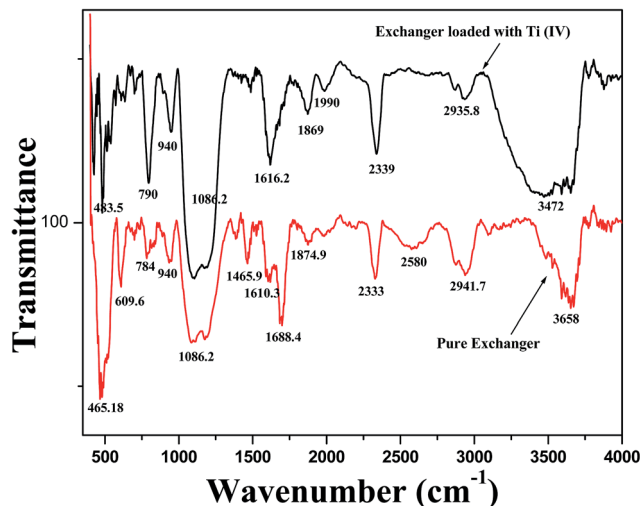

Fig. 5 FT-IR spectra of (a) the ion exchanger and (b) Titanium(IV)-loaded ion exchanger.

On the other hand, a sharp –OH peak at 3658 cm^{-1} appears as well as a broad peak at 3472 cm^{-1} in the loaded spectra due to intramolecular hydrogen bonding. The position of the peak at 1610 cm^{-1}, related to the carboxylic –C=O group of SSG-V10, was found to be shifted to a somewhat higher frequency at 1616.2 cm^{-1} and confirmed the conversion of –COOH groups to –COO$^-$ ions with higher bond orders.[29] EDX spectra of the loaded ion-exchange material also confirmed the presence of titanium(IV) in the sample (Fig. 6).

3.5 Exchange capacity (EC), break-through capacity (maximum uptake capacity) and preconcentration factor

The exchange capacity of the prepared ion-exchange material (SSG-V10), in the range of pH 10–12, was determined (2.54 milliequivalent of H$^+$/g at 25 °C), at different temperatures, by measuring the milliequivalent of sodium ions absorbed on 1 g of dry SSG-V10 in its H$^+$ form.[13] The ion-exchange material (1 g) becomes saturated at pH values of 5.0, 5.50 and 5.75 on
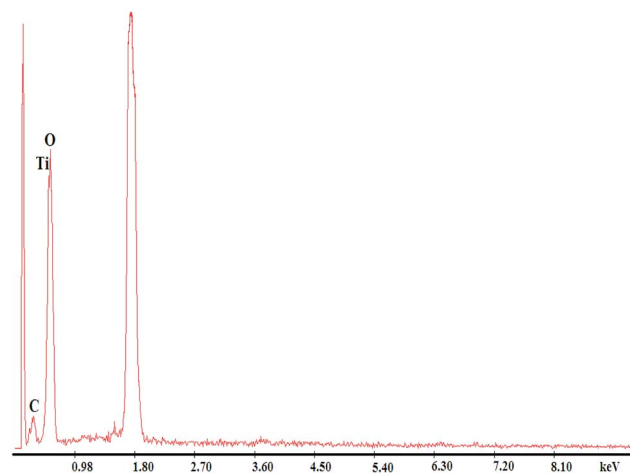

Fig. 6 EDX spectra of Versatic-10 loaded with Titanium(IV).

equilibration with 680 mL (37.4 mg), 710 mL (39.1 mg) and 740 mL (40.7 mg) of titanium(IV) (0.055 mg mL^{-1}) solution, respectively. However, the values (37.4–40.7 mg g^{-1}) were much lower than the projected value of the maximum uptake capacity (1.27 mmol g^{-1} (60.8 mg g^{-1})) for dinuclear bipositive cationic species $[(H_2O)(OH)Ti(\mu-O)_2Ti(H_2O)(OH)]^{2+}$ with respect to the exchange capacity (mono positive H$^+$ ion). Here, the working pH (5.0–5.75) for the sorption of titanium(IV) is much lower than the required pH (10–12) for the full functioning of the exchange site containing the –COOH group. As a result of which the efficiency of the ion-exchange material stands at a somewhat reduced level of 61.5–66.9% with respect to titanium(IV). Exchangeable sites for titanium(IV) uptake increase along with an increase in the pH value.

3.6 Effect of pH on extraction

As carboxylic acid groups are the exchange sites on the investigated sorbent, the pH of the influent solution is an important controlling parameter in the sorption process.[10] The systematic extraction chromatographic studies on titanium(IV) with SSG-V10, in the pH range 3.0 to 7.0, ensured its quantitative extraction in the optimum pH range 5.0–6.0 in 0.1 M acetate buffer. The retention of titanium increases with an increase in pH, reaches a maximum in the pH range 5.0–6.0, and then decreases with an increase in pH. Common anions like Cl$^-$, SO$_4$$^{2-}$, ClO$_4$$^-$ and NO$_3$$^-$ did not interfere. Quantitative retention of titanium was found up to a flow rate of 2.5 mL min^{-1}.

At lower pH (<5.0), the otherwise difficult deprotonation of the carboxylic acid moiety of SSG-V10 (ref. 10) decreases the amount of –COO$^-$ ions and titanium extraction was poor. Moreover, the solubility of titanium(IV) increases in an aqueous solution along with the decrease in pH values. Both the effects lower the values of log K_d (eqn S1 and Fig. S1; ESI† document), at low pH, and corroborate the suggested mechanistic path (eqn (4)).

The cationic dinuclear species, $[(H_2O)(OH)Ti(\mu-O)_2Ti(H_2O)(OH)]^{2+}$, is present[30] in the weak acidic pH range of 4.0–6.0. Its structure has been optimized by a DFT calculation (Fig. 7) and produced the *syn* compound (system energy: −15 531.124 eV; HOMO: −16.7623 eV; LUMO: −12.8711 eV and global hardness, η = 3.8912 eV). UV-visible spectra (Fig. 8) of the aqueous solutions containing metal–ligand (10^{-4} M) at different mole ratios were analyzed and the maximum absorbance at 1 : 1 mole ratio rationalizes the proper complex formation. A linear relationship (y = 1.029X + 1.6926; R^2 = 0.9889) with the slope = 1.029 between log K_d and log $C_{[Versatic-10]}$ is also obtained in the range of pH 4.0–6.0 at a fixed concentrations of acetate and titanium(IV). Thus, the probable composition of the extracted species comes out to be 1 : 1 (metal–extractant). Within the pH range of 4.5–6.5, Versatic10 exists as a dimer through intermolecular hydrogen bonding.[26] Bearing this in mind, it has been suggested that the dimer (*anti* compound), $[(H_2O)(OH)Ti(\mu-O)_2Ti(H_2O)(OH)]^{+2}$, having the suitable size and charge, moves to the dimeric core of the exchange site and probably stabilized as anatase (pH: 2–11)[31] with co-ordination number six, with one edge sharing (in this unit), at this recommended condition (pH: 4.0–6.0) as per the following proposed path:
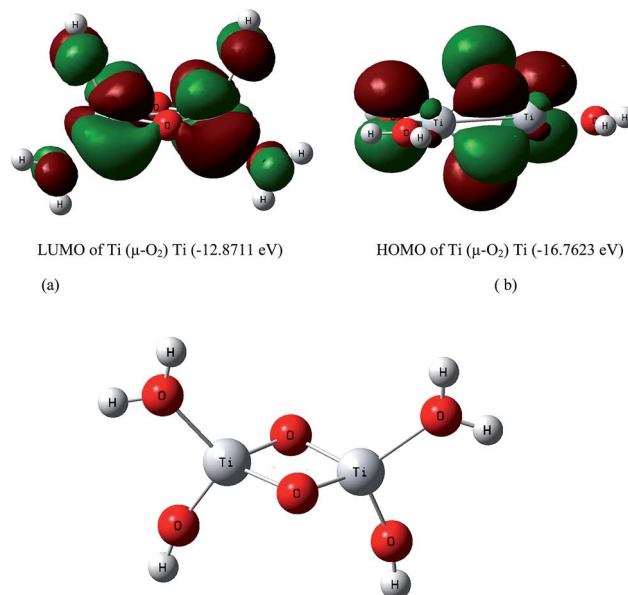
LUMO of Ti (μ-O$_2$) Ti (-12.8711 eV)   HOMO of Ti (μ-O$_2$) Ti (-16.7623 eV)

(a)   (b)

Fig. 7   DFT-optimized structure of $[(H_2O)(OH)Ti(\mu-O)_2Ti(H_2O)(OH)]^{+2}$ (η = 3.8912 eV); Ti–Ti: (bond distance) 265.99 pm; bond distance (Ti–O: 179.0 pm (bridge); Ti–O: 200.78 pm (terminal)); ∠Ti–O–Ti: 96.24°; ∠O–Ti–O: 106.4°; dipole moment: 4.2980 debye.

Fig. 8   UV-visible spectra of organic phase (ligand–Titanium(IV) (a) 1 : 1 (b) 1 : 2 (c) 1 : 3).

$$SSG \cdot (RCOO^-H^+)_2(s) + [(H_2O)(OH)Ti(\mu-O)_2Ti(H_2O)(OH)]^{2+}(aq.)$$
$$\rightleftharpoons SSG \cdot [Ti_2(\mu-O)_2(OH)_2(RCOO^-)_2](s) + 2H^+(aq.) \quad (4)$$

Species such as Ti$_3$O$_4$$^{4+}$ appear at pH values higher than 6.5, and they lead to the eventual formation of colloidal or precipitated TiO$_2 \cdot n$H$_2$O (ref. 30) and do not participate in the exchange process.
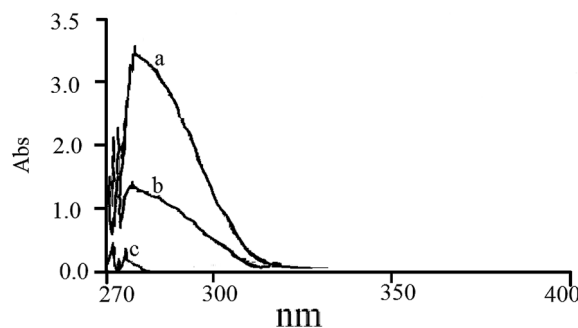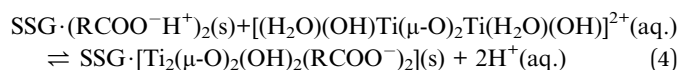
3.7 Rationalization of titanium sorption in terms of DFT calculation

The COOH of Versatic-10, impregnated on SSG, which forms dimers and produces cavities (as is mentioned in Section 3.1) in the hydrophilic region of the ion-exchange material, was optimized by DFT calculations (Fig. 9). In the DFT optimized structure, the bond length of O···H···O is 244.9 pm, C–O bond length is 122.5 pm and ∠OCO is 124.02°.[10] It generates a core
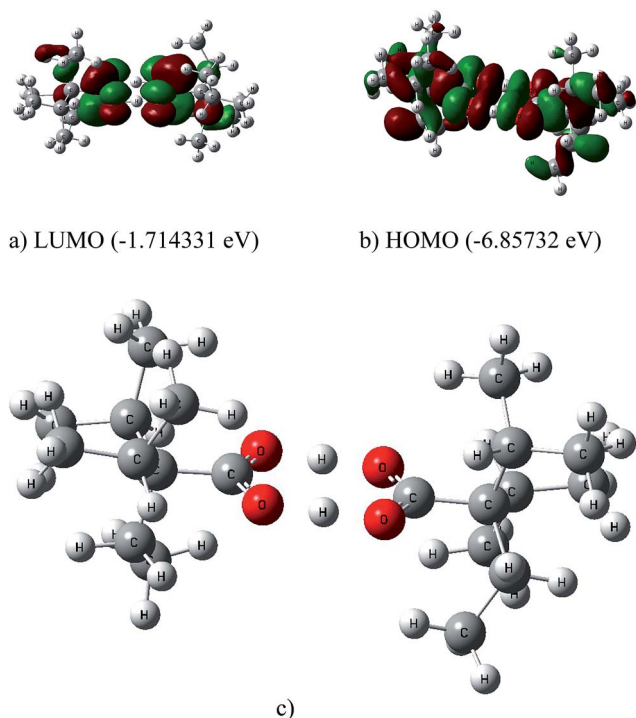
a) LUMO (-1.714331 eV)   b) HOMO (-6.85732 eV)

c)

Fig. 9 Hydrogen bonded dimer of Versatic-10 (η_{dimer} = 5.143 eV) (a) LUMO (b) HOMO and (c) optimized dimer *Syn*-Side-View *Syn*-Top-View.

Syn-Side-View

Syn-Top-View

Fig. 10 Ti-Versatic-10 *anti*-complex complex: bond distances (Ti–O: 179.0 pm (bridge); Ti–O: 260.05 pm (terminal); Ti–O: 213.61 pm (axial)); ∠Ti–O–Ti: 94.56°; ∠ –Ti–O: 63.02°.

radius of the dimer of 167.05 pm. The value is much lower than the calculated radius (from both the DFT optimized structure and global hardness (η) considering, $r = 1/2\eta$)[32] of dinuclear *anti* compound of titanium(IV) (r_{DFT} = 285.02 pm; $r_{\frac{1}{2\eta}}$ = 369.93 pm). To elucidate the hardness behavior, the hydrogen bonded dimeric structure of Versatic-10 (Fig. 9) was optimized by DFT calculations (−29 567.465 eV), and from the HOMO (−6.85732 eV)–LUMO (−1.714331 eV) gap, the global hardness was calculated[32] (η = 5.143 eV). The dinuclear titanium(IV) complex is a soft acid ($\eta_{Ti-syn-complex}$ = 3.8912 eV) and has a suitable shape in comparison to the titanium(IV) ion itself ($\eta_{Ti(IV)}$ = 16.23 eV),[33] which is trapped inside the co-ordination sphere with an anatase structure by one edge sharing at the recommended pH (2–11).[31] Here, the stable dinuclear *syn* compound of titanium(IV), having comparable η values, is trapped inside the co-ordination sphere of a number of hard donor *O*-sites present in the ion-exchange core (inherent η = 5.143 eV) (Fig. 10). During the insertion of the larger-sized dinuclear *syn* compound of titanium(IV), the dimeric core of the ion-exchanger becomes ruptured, which is confirmed by the disappearance of the FT-IR peak at 2580 cm^{-1} in the titanium(IV)-loaded spectra (Fig. 5). Interestingly, this dinuclear *syn* isomer changed its conformation and stabilized as an *anti*-complex in the DFT optimized exchanger-metal complex entity. Lower steric crowding, comparable acid-base character ($\eta_{Ti-Ti-complex}$ = 3.8912 eV: $\eta_{V10-dimer}$ = 5.143 eV)[32] and intramolecular hydrogen bonding ($r_{O\cdots H-O}$ = 183.65 pm) rationalized the formation of the *anti*-complex (Fig. 10). The strong absorptio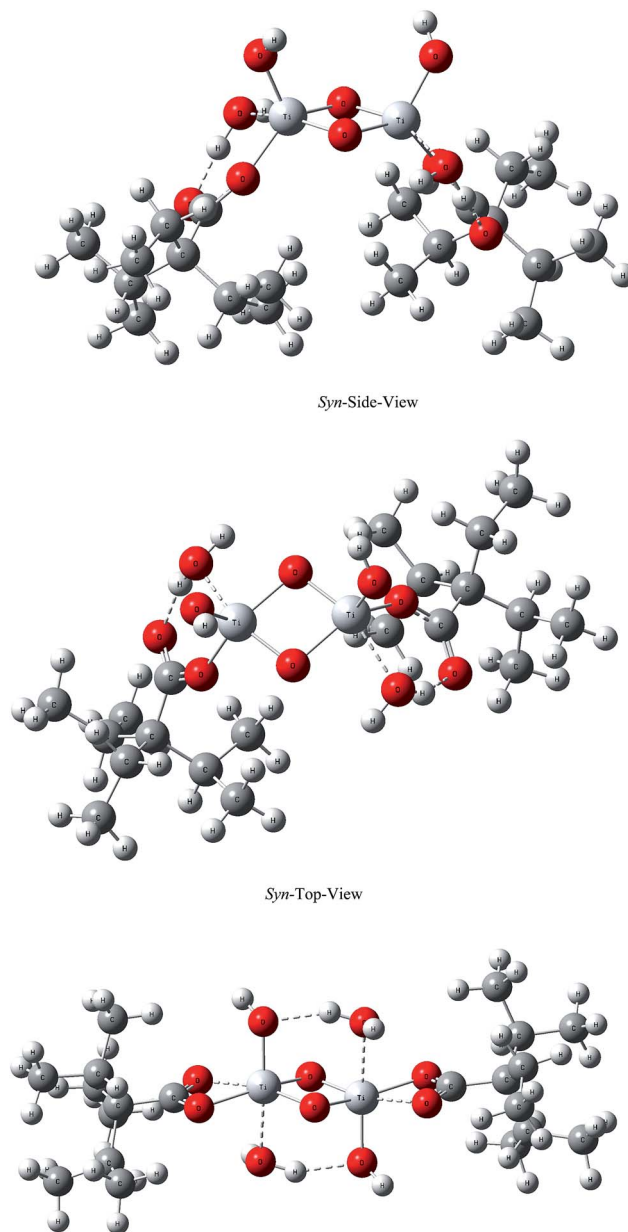n band at 3658 cm^{-1} suffers a shift to 3472 cm^{-1} as a broad band in the loaded FT-IR spectrum (Fig. 5), thereby confirming the formation of intramolecular hydrogen bonding in the extracted species (Fig. 10). The plausible mechanistic path is depicted in Schemes 1 and 2.

The core diameter (Fig. 10) (*i.e.*, the distance between two carboxylic carbon atoms) is 746.2 pm and in 1 g of dry SSG-V10 having the BET surface area of 149.46 m^2 g^{-1} generates 3.42 × 10^{20} such cores. In each core, titanium is present as a dinuclear complex [(H$_2$O)(OH)Ti(μ-O)$_2$-Ti(H$_2$O)(OH)]$^{+2}$ and it corresponds to 1135.64 μM (54.36 mg) of titanium(IV) g^{-1} of dry SSG-V10. The experimental value (37.4–40.7 mg g^{-1}) is effectively 69–75% of this theoretically calculated value.
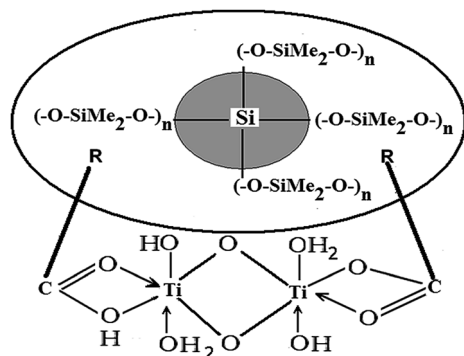
Scheme 1 Probable attachment of titanium(IV) at the hydrophilic region of the ion-exchange material; $R = -C\{CH(CH_3)_2\}_2CH_2CH_3$: silica gel (shaded area); methylated surface: (open area).
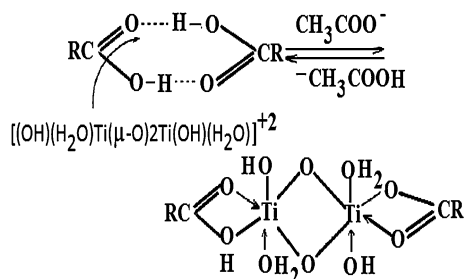
Scheme 2 Probable mechanism of titanium(IV) trapping in dimeric cavity of the ion-exchange material; $R = -C\{CH(CH_3)_2\}_2CH_2CH_3$.

3.8 XRD analysis

The XRD patterns of silanized silica gel (SSG), SSG-V10 composite and SSG-V10-titanium(IV) are shown in Fig. 11. Each of them has two reflections: a broad, strong reflection ($2\theta = 21.83°$; $2\theta = 22.16°$; $2\theta = 21.82°$) and a weak and sharp reflection ($2\theta = 48.56°$; $2\theta = 48.55°$; $2\theta = 48.52°$) and the corresponding reflections of SSG, SSG-V10 and SSG-V10-titanium(IV) were found to be almost in the same position in their XRD patterns. The SSG network does not get influenced by impregnation with Vesatic-10 or by the sorption of titanium(IV) on the surface of the SSG-Versatic-10 composite. Here, the binding between SSG and Versatic-10 is caused by a hydrophobic interaction only (Scheme 1), and it takes place at the surface of the hydrophobic SSG. After that, the metal ion, titanium(IV), is placed at the exchange site of Versatic-10.

3.9 Selection of stripping agents

At low pH, TiO^{2+} is in equilibrium with $[Ti(OH)_2]^{2+}$ and $[Ti(aq.)]^{4+}$. Thus, in the elution process (back extraction) extracted titanium elutes as TiO^{2+}, which is in equilibrium with $[Ti(OH)_2]^{2+}$ and $[Ti(aq.)]^{4+}$ in such strong acid media, and H^+ acts as an eluent. After extraction, titanium(IV) was stripped from the column using various acids of different concentrations (Fig. S2†). Quantitative elution of titanium(IV) has been achieved with HNO_3 (0.5–1 M), $HCl + H_2O_2$ (0.5–1 M) and H_2SO_4 (1–1.5 M) (Table S1†). Acetic acid weakly dissociates in aqueous solution; thus, it performs poorly in the recovery of titanium from the

extractant compared to the strong inorganic acids like HCl, H_2SO_4 or HNO_3. Moreover, the strongly basic Ti=O group is very much susceptible to an electrophilic attack by protons and titanium(IV) leaves the cavity of the ion-exchange core (Scheme 2) through the formation of large polymeric species like $[Ti=O \rightarrow Ti–O–Ti \leftarrow O=Ti]_n$ or $[–O–Ti–O–Ti–OH]_n$ (ref. 30) in mineral acids. Column efficiency (N) for these eluents has been calculated[10] with respect to titanium(IV) ($N_{H_2SO_4} = 88$; $N_{HNO_3} = 60$; $N_{HCl+H_2O_2} = 108$) (eqn (5)). It was found that 1 M HCl containing H_2O_2 as an eluent gave a symmetric elution profile (Fig. S2†). It requires less volume (15 mL) and provides the highest column efficiency. Moreover, 1 M HCl along with H_2O_2 gave a distinct and detectable bright yellow color with titanium(IV)[15] during its elution. This colored complex has been utilized for the spectrophotometric estimation of titanium(IV). These features justify the use of 1 M HCl containing H_2O_2 as a stripping agent for the further steps of experiments.

$$N = 4 \times \left[\frac{y}{x}\right]^2 \tag{5}$$

where $y =$ distance for peak elution, $x = \frac{1}{2} \times W_{0.6065}$ and $W_{0.6065} =$ width of the peak at 0.6065 times the peak height.

3.10 Optimization of column flow rate and time

Systematic studies on flow rate show that with the increase of flow rate (mL min^{-1}) the retention of titanium(IV) decreases linearly. This was quantitative (<96%) up to the flow rate of 4.0 mL min^{-1}. Since the reaction kinetic was found to be very fast, the effect of equilibration was investigated at a high flow rate (6–8 mL min^{-1}), and it was observed that 1.5 min was sufficient for its extraction from aqueous solution at pH 5.0–5.75.

3.11 Effect of pH, volume and concentration of influent on recovery and preconcentration factor (PF)

During the extraction of titanium(IV) (23.95–35.92 µg mL^{-1}) in the range of pH 5.0–5.75, it was found that an influent volume up to 1000 mL, PF (ratio of effluent concentration, C_f to influent concentration, C_s) increased with the increase in effluent concentration (Table 1). Although at a particular volume, PF was not depending on either the concentration or the pH of the influent. Recovery decreased with the increase in influent volume, and for an influent volume up to 1000 mL recoveries were quantitative (>90%). To attain the break-through values (as 37 400 µg g^{-1} at pH 5.0, 39 100 µg g^{-1} at pH 5.5 and 40 700 µg g^{-1} at pH 5.75), respectively, 1561, 1306 and 1133 mL of titanium(IV) solution were passed through the column. However, due to the volume effect[10] recoveries were much poorer (<80%); consequently, PF did not attend its maximum possible values (104.1, 87.1 and 75.5 for 100% recovery). It was optimized at a value of 60.8 ± 0.5. Plot of V_S (sample volume) *versus* $R_{Ti(IV)}$ (recovery of titanium(IV)) produced two linear segments ($y = -0.0094x + 99.4$; $R^2 = 0.963$ and $y = -0.0637x + 153.8$; $R^2 = 0.999$) intersecting at a volume of 890 mL (Fig. S2†). The slopes of the corresponding segments were the measures of desorption efficiency and yielded the desorption constants[8]
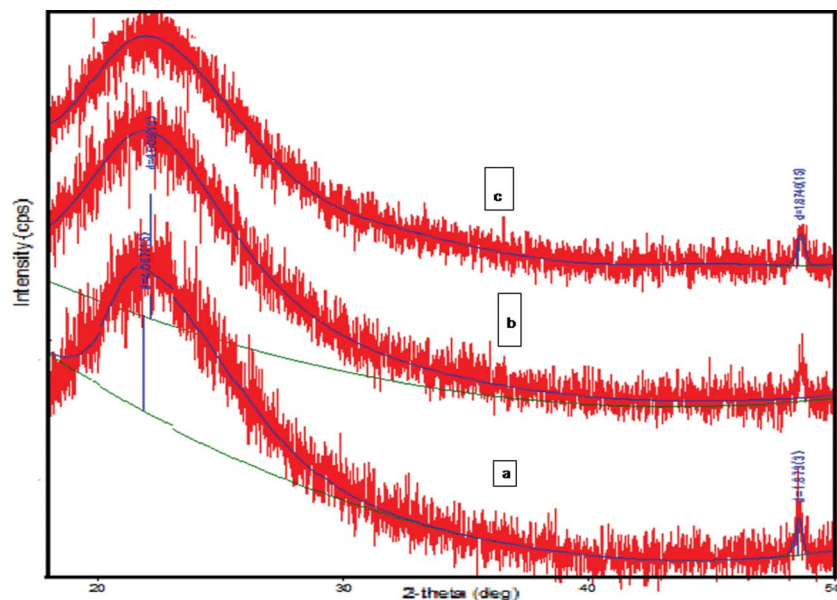
Fig. 11 XRD pattern of (a) SSG (b) SSG V10 and (c) SSG V10 Titanium(IV).

$K_{desorption}{}^1(9.4 \times 10^{-3})$ and $K_{desorption}{}^2(6.37 \times 10^{-2})$, respectively. For influent volumes higher than 1000 mL, the rate of desorption was much higher, and the recovery would become zero at an influent volume of 1628.5 mL (extrapolated value). The cationic components of the solvents and the metal ions took part in the sorption and desorption process by replacing each other during the movement of the mobile phase. With the increase in the volume of the solvent, the extent of desorption of the metal ion becomes predominant and it becomes complete at a volume of 1628.5 mL. This indicates that at this very condition the influent solvent itself will act as an eluent.

3.12 Effect of temperature on extraction

The extraction equilibrium constant (K_{ex}) has been computed at different temperatures using the following equation (eqn (6))[10] and plot of $\log K_{ex}$ vs. $1000/T$ gives a linear relationship ($y = -2.523x + 8.66$; $R^2 = 0.996$) (Fig. S4†). It was observed that the separation efficiency, C/C_0 (Fig. S5†) increased with sharply increasing temperature in the temperature range of 293–310 K. The equilibration time decreased with increasing temperature, in the mentioned interval and became nearly constant at the final equilibrium state.

Table 1 Effect of volume, sample concentration and pH on the preconcentration factor. [Flow rate: 3.5 mL min^{-1}; pH: 5.0–6.0; Titanium(IV): 23.95–35.92 µg mL^{-1}; # average of three determinations; standard deviation <0.04]

pH	Sample conc. (C_S) (µg mL^{-1})	Sample volume, V_S (mL)	Amount of Ti(IV) (µg)		Effluent conc. (C_f) (µg mL^{-1})	Recovery[a] (%)	PF (C_f/C_s)
			Added	Recovered			
5.0	23.95	200	4790	4732.5	315.5	98.8	13.2
		400	9580	9311.8	620.8	97.2	25.9
		800	19 160	18 393.6	1226.2	96.0	51.2
		1000	23 950	21 674.7	1445.0	90.5	**60.3**
		1300	31 135	21 888.0	1459.2	70.3	**60.9**
		1561	37 386	20 487.5	1365.8	54.8	57.0
5.5	29.93	200	5986	5938.1	395.9	99.2	13.2
		400	11 972	11 684.6	778.9	97.6	26.0
		800	23 944	23 201.7	1546.8	96.9	51.7
		1000	29 930	21 595.5	1839.7	92.2	**61.4**
		1200	35 916	27 511.7	1834.1	76.6	**61.2**
		1306	39 088	27 010.0	1800.7	69.1	60.2
5.75	35.92	200	7184	7083.4	472.2	98.6	13.1
		400	14 368	14 080.6	938.7	98.0	26.1
		800	28 736	27 988.8	1865.9	97.4	51.9
		1000	35 920	32 759.0	2183.9	91.2	**60.8**
		1100	39 512	32 874.0	2191.6	83.2	**61.0**
		1133	40 698	23 884.0	2192.2	80.8	61.0

[a] Average of five determinations; PF = ratio of effluent conc. to sample conc. (C_f/C_s).

$$K_{ex} = \frac{E_R}{[(RCOO^-H^+)_2]}[H^+]^2 \tag{6}$$

where $[(RCOO^-H^+)_2(s)]$ denotes the concentration of SSG-V10 in its dimeric form, which participated in the ion-exchange process, and E_R is the ratio of extracted metal ion to its un-extracted portion.

The enthalpy change (ΔH) was evaluated from the plot of $\log K_{ex}$ versus $1000/T$ (eqn (7)). The effect of temperature on the extraction of titanium(IV), in the range of pH 5.5–5.75, has been performed for the determination[34] of different thermodynamic parameters (ΔG and ΔS at 300 K) using the standard van't Hoff equation (eqn (8) and (9)).

$$\Delta H = -(slope) \times 2.303 \times R \tag{7}$$

$$\Delta G = -2.303RT \log K_{ex} \tag{8}$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \tag{9}$$

where R (8.314 J K^{-1} mol^{-1}) is the gas constant.

The positive ΔH (0.048 kJ mol^{-1}) and smaller ΔS (5 J K^{-1} mol^{-1}) rationalize the endothermic nature of the extraction process. During the adsorption of titanium(IV), H$^+$ is released in the solution phase and increases the number of neutral CH$_3$COOH. This effect correlates with the positive value of ΔS. The higher negative value of ΔG (-1.1488 kJ mol^{-1}) suggests the spontaneity and tendency for chemisorptions of the equilibrium,[34] and this is in agreement with the Langmuir isotherm.

3.13   Ion-exchange paper chromatography

At pH 5.75, the R_f values and selectivity factors (α) (ratio of the R_f values) of metal ions were determined in an acetate buffer–acetone mixture (15 : 2 v/v) using chromatograms (Table S2†). The results show that, under this recommended condition, Sn(II), Cr(III), Ca(II), Mg(II), Co(II), Zn(II), Cd(II) are very weakly bound (R_f value ~0.9), metal ions like titanium(IV), Pb(II), Al(III), Cu(II), Ga(III) are moderately bound (R_f value 0.3–0.6) while Hg(II), Bi(III), Tl(III) is tightly bound (R_f value < 0.2) with the stationary phase. At pH 2.5, binding strength of Zr(IV) (R_f value = 0.06) is much higher than that of Fe(III) (R_f value = 0.41) and under this condition, large polymeric species like [Ti=O–Ti–O–Ti–O=Ti]$_n$ do not participate in the exchange process (R_f value = 0.93). Selectivity factors for most of the studied metal ions were appreciably higher ($\alpha \geq 2.17$), and this suggests their easy separation from titanium(IV).

3.14   Effect of pH on selectivity factors (α)

Systematic studies on R_f values of metal ions (except Fe(III) and Zr(IV)) in the range of pH 5.0–5.75 have been performed. The selectivity factors (α) (separation efficiency) with respect to titanium(IV) have been computed, and they were appreciably higher (≥ 2.17) at pH 5.75 (Table 2). The values of separation factors for Fe(III) and Zr(IV) were found to be the best at pH 2.5.

3.15   Separation of titanium(IV) from binary and multicomponent mixtures

In order to access the possible analytical applications, different binary and multicomponent mixtures (Table 3; Table 4) of titanium(IV) containing diverse metal ions (elements present in the acidic waste of "chloride process for titania production": Ti(IV), Fe(III), Cr(III), V(V), Al(III); elements of Gr III in analytical table: Ti(IV), Zn(II), Ce(IV), Th(IV), U(VI); elements of periodic table: Ti(IV) and Zr(IV)) having widely different R_f values (appreciably higher ($\alpha \geq 1.5$))[11] have been formed. Then, from these important synthetic mixtures, viz., mixture number 4 containing Zr(IV), V(IV), Al(III), Ti(IV); mixture number 1 containing Fe(III), Cr(III), Ti(IV) etc. (Table 4) metal ions from one to another have effectively been separated. The binary and ternary separations from diverse metal ions were achieved either by exploiting the differences in the pH for extraction or by using suitable eluting agent utilizing the selectivity factors ($\alpha \geq 1.5$)[9] (Tables 3 and 4) (separation procedure is given as ESI file (f. 1)†). After recovery, except Ti(IV) the different metal ions (diverse ions) which have been selectively separated from the synthetic mixtures (Table 3 and Table 4) were determined complexometrically.[9] In almost all the cases, fairly good reproducibility with respect to quantitative extraction, separation and recovery have been achieved.

3.16   Application of the method of extraction in an alloy sample of titanium

A titanium, Ti6Al–4V alloy (V, Al, Ti and Fe) sample was treated[15] with 10 mL 1 : 1 nitric acid and 10 mL of 70% perchloric acid. The analyte solution (80 mL) was evaporated to dryness. The mass was dissolved in 25 mL distilled water. Any residue that remained was filtered (Whatman no. 42) and diluted to 100 mL with distilled water and extracted at pH 2.5, whereas Fe(III) was extracted and eluted with 0.5 M H$_2$SO$_4$. The effluent containing V, Al and Ti was passed through the column at pH 5.75 and

Table 2   Effect of pH on R_f values and selectivity factors ($\alpha = (R_f)_i/(R_f)_{Ti(IV)}$) of different metal ions obtained on Whatman no. 1 impregnated with Versatic-10; [time = 2.5 hours; developing solvent = acetate buffer: acetone (25 : 1) v/v]

pH	Metal ion	R_f values	Selectivity factors (α)
5.0	Zn(II)	0.82	10.25
	Cd(II)	0.86	10.75
	V(IV)	0.38	4.75
	U(VI)	0.09	1.13
	Ti(IV)	0.08	1.00
	Cr(III)	0.96	2.34
	Th(IV)	0.05	1.20
5.75	Zn(II)	0.88	14.66
	Cd(II)	0.84	14.00
	V(IV)	0.34	5.67
	U(VI)	0.14	2.33
	Ti(IV)	0.06	1.00
	Cr(III)	0.86	14.33
	Th(IV)	0.02	3.00

Table 3 Separation of Titanium(IV) from synthetic metal ion mixtures [Titanium(IV) taken: 2.2 mg mL^{-1}, column: 0.8 × 8 cm, flow rate: 1 mL min^{-1}, pH-2.5*, 5.0; temp: 25 °C; RSD = Relative Standard Deviation]

Mixture	Cations	Added (mg mL^{-1})	Recovered (mg mL^{-1})	R.S.D. (%)	Eluent vol. (mL)
1	*Fe(III)	2.85	2.87	1.74	0.1 M HCl (30)
	Titanium(IV)	2.20	2.22	3.73	1 M HCl + H$_2$O$_2$ (15)
2	Th(IV)	1.8	1.88	3.80	2.5 M HNO$_3$ (25)
	Titanium(IV)	2.20	2.16	1.53	1 M HCl
3	Pb(II)	2.20	2.24	2.41	0.005 M CH$_3$COOH (60)
	Titanium(IV)	2.15	2.17	3.22	1 M HCl + H$_2$O$_2$ (15)
4	Ni(II)	2.15	2.12	1.50	Mobile phase
	Titanium(IV)	2.20	2.24	2.41	1 M HCl + H$_2$O$_2$ (15)
5	Zn(II)	2.63	2.62	2.17	Mobile phase
	Titanium(IV)	2.20	2.22	3.73	1 M HCl + H$_2$O$_2$ (15)
6	*Zr(IV)	2.08	2.06	2.12	4 M HNO$_3$ (20)
	Titanium(IV)	2.20	2.21	3.48	1 M HCl + H$_2$O$_2$ (15)
7	Cd(II)	1.80	1.83	3.87	Mobile phase
	Titanium(IV)	2.20	2.22	3.73	1 M HCl + H$_2$O$_2$ (15)

Table 4 Separation of Titanium(IV) from synthetic metal ion mixtures [Titanium(IV) taken: 2.2 mg mL^{-1}, column: 0.8 × 8 cm, flow rate: 1 mL min^{-1}, pH: 2.5*, 5.0; temp: 25 °C; RSD = Relative Standard Deviation]

Mixture	Cations	Added (mg mL^{-1})	Recovered (mg mL^{-1})	R.S.D. (%)	Eluent vol. (mL)
1	*Fe(III)	2.85	2.87	1.74	0.1 M H$_2$SO$_4$ (20)
	Cr(III)	2.15	2.12	1.50	Mobile phase (25)
	Titanium(IV)	2.20	2.24	2.41	1 M HCl + H$_2$O$_2$ (15)
2	U(VI)	2.90	2.98	2.21	0.25 M HNO$_3$ (30)
	V(IV)	2.20	2.14	3.48	0.1 M CH$_3$COOH (50)
	Titanium(IV)	2.20	2.26	3.60	1 M HCl + H$_2$O$_2$ (15)
3	*Zr(IV)	2.98	3.04	2.45	4 M HNO$_3$ (20)
	Cr(III)	2.15	2.20	1.66	Mobile phase (25)
	Titanium(IV)	2.20	2.18	2.13	1 M HCl + H$_2$O$_2$ (15)
4	*Zr(IV)	2.98	3.02	1.68	4 M HNO$_3$ (20)
	V(IV)	2.20	2.15	1.68	0.1 M HNO$_3$ (05)
	Titanium(IV)	2.20	2.26	2.54	1 M HCl + H$_2$O$_2$ (15)
5	*Zr(IV)	2.98	3.08	3.12	4 M HNO$_3$ (20)
	U(VI)	2.90	2.96	1.98	0.25 M HNO$_3$ (30)
	Titanium(IV)	2.20	2.12	2.78	1 M HCl + H$_2$O$_2$ (15)
6	*Zr(IV)	2.98	3.08	3.08	4 M HNO$_3$ (20)
	V(IV)	2.20	2.13	3.11	0.1 M HNO$_3$ (05)
	Al(III)	1.80	2.00	2.69	1 M CH$_3$COOH (20)
	Titanium(IV)	2.20	2.12	3.22	1 M HCl + H$_2$O$_2$ (15)

sequentially eluted by the developed method (Table 4), and the recovery was quantitative (Table 5).

3.17 Estimation of an unknown concentration

For an unknown solution (200 mL), the recovered amount was estimated in the effluent. The recovered amounts of titanium(IV) were equated with the average recovery of 98.8%, for a sample volume of 200 mL the concentration for 100% recovery was

calculated. The predicted concentration agreed well with observed values obtained by AAS and spectrophotometry (relative error <7.02%) (Table 6). The preconcentration process gave slightly lower recovery with respect to 98.8%, probably because of the loss of analyte in both the extraction and elution steps, during its recovery, and all the recovery values were found to be about 4.0% ± 0.5% lower than AAS.

The separation of titanium(IV) and Cr(III) from water (pond and well water) samples was performed by applying the proposed method (PF: 59.1 ± 0.3) (Table S3†). The amounts of recovered titanium(IV) were equated with the average recovery of 95% for a sample volume of 800 mL^{-1}, and the projected concentrations were calculated to get an idea about the concentrations of the mother samples. The calculated values were highly compatible with the observed values obtained by spectrophotometry (relative error <2.8%) (Table S4†).

Table 5 Separation of Titanium(IV) from real sample

Sample				
Ti6Al–4V	Metal ion	V(IV)	Al(III)	Titanium(IV)
	Recovered	3.79	7.26	86.18
	Certified	4.50	6.75	88.42

Table 6 Comparison of the estimated conc. (AAS and Spectrophotometry) with the preconcentration technique, in the concentration range of 20.4–40.8 μg mL^{-1}; sample volume: 200 mL[a]

Amounts of Titanium(IV) (μg)

Standard	Estimated AAS	Spectrophotometry	Predicted (preconcentration technique)
4080	4026 (1.32)	3929 (3.70)	3848 (5.69)
6120	5982 (2.25)	5892 (3.73)	5726 (6.44)
8160	7948 (2.60)	7822 (4.14)	7668 (6.03)

[a] Values in the parentheses represent the relative errors (%).

4. Conclusions

According to the DFT optimized structure, the dimer complex, $[(OH)(H_2O)Ti(-\mu O)_2(OH)(H_2O)]^{+2}$, exists as a *syn* isomer, but in the extracted species it is the *anti*-form, which is stabilized by 0.286 eV over the *syn* isomer due to intra-molecular hydrogen bonding. DFT-optimized extracted complex turned out to be anatase. The loading of titanium(IV) on to SSG-V10 has been confirmed by EDX. The ion exchange material, SSG-V10 has a high BET surface area of 149.46 m^2 g^{-1}. The positive values of ΔH (0.048 kJ mol^{-1}) and ΔS (5 J K^{-1} mol^{-1}) and negative value of ΔG (-1.48 kJ mol^{-1}) indicated that the interaction process is endothermic, entropy-gaining and spontaneous in nature. A clean separation of titanium(IV) has been achieved from several toxic and heavy metal ions like Pb(II), Fe(III), Cr(III), Zn(II), Cd(II), Hg(II), Tl(III), Zr(IV), Ce(IV), and Th(IV) having very high selectivity factor ($\alpha \geq 1.24$) values. Very minute amounts (~0.2 mL) of liquid extractant in the developed ion-exchange material can selectively separate titanium(IV) from wide varieties of multi-component mixtures containing cations (Table 4), present in the acidic waste of "chloride process for titania production" (Ti(IV), Fe(III), Cr(III), V(V), Al(III)) and also from Gr III in the analytical table (Ti(IV), Zn(II), Ce(IV), Th(IV), U(VI)). Regarding the estimation of an unknown sample of titanium(IV) in its microgram level, the method was highly compatible with other sophisticated techniques. Estimation of the components of a mixture in the conventional spectrophotometric method fails if the absorption of the metal ions in presence of ligands occurs in the overlapping region. However, the present method does not face any such inconveniences as interfering ions are already separated. The ion-exchange material developed is chemically stable (up to 6 M HNO$_3$, 4 M CH$_3$COOH, 4 M HCl and 2 M H$_2$SO$_4$) and effective over a wide range of pH. It can be used for more than 30–40 cycles without any loss in its exchange capacity.

Acknowledgements

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