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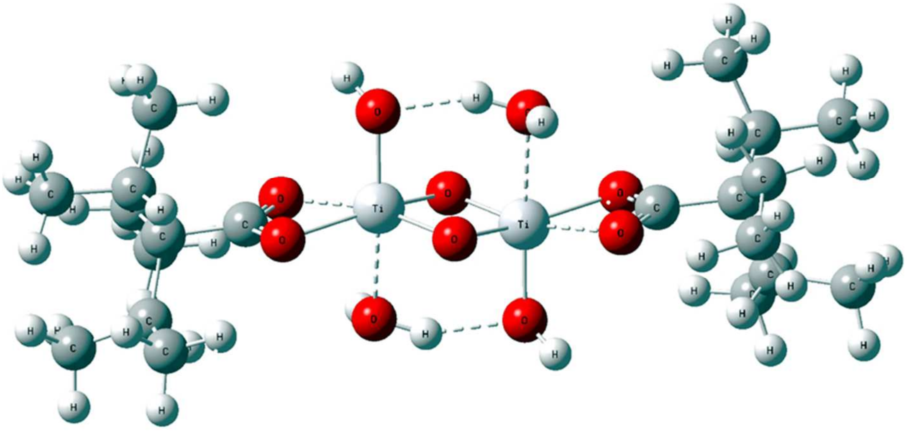

Ti-Versatic-10 anti-complex complex
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Solid phase extraction, separation and preconcentration of titanium (IV) with SSG-V10 from some other toxic cations: a molecular interpretation supported by DFT

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Abstract:

The present work reports the separation and preconcentration of titanium (IV) with functionalized silica gel (SSG-V10). 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, SSG-V10 (29567.465 eV; $\eta = 3.671$ eV) has a high BET surface area (149.46 m^2 g^{-1}), 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}) indicates that the sorption process was endothermic, entropy gaining and spontaneous in nature. The DFT calculations reveal that the guest, $[(OH)(H_2O)Ti(\text{-}\mu O)_2(OH)(H_2O)]^{+2}$ (15531.185 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 made. 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_2O_2. Preconcentration factor has been optimized at 60.8 ± 0.5. Titanium (IV) amid

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congeners and other metal ions associated with it in ores and alloy samples has been separated from synthetic mixtures. The method was found effective for alloy samples as well.

Keywords: Extraction chromatography, DFT optimized SSG-V10-(dinuclear titanium (IV)) composite, Preconcentration factor, Selectivity factor, selective separation of titanium (IV)

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 equipments, 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 intruments. 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 level 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_2SO_4 at 250 °C for 1h in order to be analyzed. Moreover, prior to operation a proper sample clean up is

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required. Metal ion a desorption on solid polymer surface (solid phase extraction, SPE) is now considered as one of the most promising 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 being present on the surface of hydrophobic silica support has been effectively used [10-12] for the extraction, preconcentration and separation of Cu(II), Bi(III) and V(IV). But, the systematic extraction chromatographic investigation for preconcentration and separation of titanium (IV) with Silica Gel-Versatic10 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 acid, 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) in order to be analyzed. 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]. So, Density Functional Theory (DFT) calculation has been performed to analyze the structure of both the extractor and the titanium (IV)-extractor complex in terms of hardness 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 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 form were recorded on Shimadzu FT-IR spectrophotometer (Model no FT-IR-8400S) using KBr pellets. EDX spectra were recorded on JEOL 2010 FEG microscope equipped with an EDX

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analyzer. The X-ray diffraction patterns were recorded on Rigaku (Ultima IV), H-12 Japan (Kurary Co. Ltd. N) defractometer at range of 2θ, 18-50 ° using Cu (Kα) as its scattering X-ray line source. UV-Visible spectra for the metal-ligand complexation were studied with 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 at the range of temperature 40 to 950 °C. BET experiments were carried out by using a Beckman Coulter SA 3100 surface area analyzer at 77 K at high vacuum. A liquid cation exchanger, Versatic-10 (Shell Chemical, London, England), being a high molecular mass synthetic C_{15}-C_{16} mono carboxylic acid 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^{-I}) was prepared by dissolving $Ti(SO_4)_2$ (E. Merc, Bombay, India) in water and estimated spectrophotometrically [15]. Buffer solutions of different pH were prepared from acetic acid (0.2 M) and ammonium acetate (0.2) in proper ratio. 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]. 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; 8.5g) was rendered hydrophobic by exposing it to vapor 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 was 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.

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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 mole ratios to get 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_2O_2 and the amount of titanium (IV) from each fraction was determined spectrophotometrically.

2.4 Break through capacity (BTC): For the determination of breakthrough capacity (BTC), 200 mL fractions of metal ion solution (0.055 mg mL^{-1}) was passed through the column and the effluent was collected, till the amount of metal ion concentration was same both in feed and effluent. A breakthrough curve (Fig. 1) was obtained by plotting the ratio $\frac{C_e}{C_0}$ against the effluent volume, where C_0 and C_e are the concentrations of the initial solution and effluent, respectively. BTC is calculated using formula ($\frac{CV(10\%)}{W}$), 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 gram.

2.5 Computational Methods: Standard density functional theory (DFT) calculations for all the structures were carried out with Gaussian 09 package [16]. The geometries of all the species were fully optimized by using B3LYP [17, 18] hybrid functional and 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 by the absence of imaginary frequencies. In

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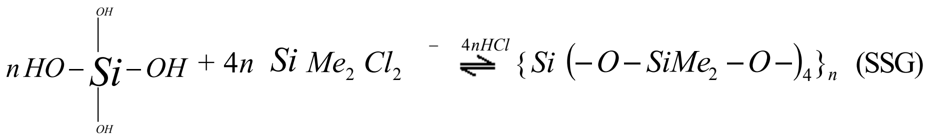
addition, neutral bond order (NBO) [22-24] calculations of the optimized structures were performed to find the molecular orbital. The energies of the optimized structures were calculated after the ZPE (zero point energy) and thermal corrections.

3. RESULTS AND DISCUSSION

3.1 Silanization and nature of attachment of Versatic 10 leading to an ion-exchange material: The surface of the silica gel gets methylated (hydrophobic) during silanization (eq. 1) [25]. The silanised silica gel (SSG) surface immobilizes the hydrophobic part of Versatic 10 through weak hydrophobic interaction (eq. 2) [10]. The -COOH groups of Versatic 10 point towards the hydrophilic mobile phase and exist as dimers [26] with the formation of cavities through intermolecular hydrogen bonding.



$$n\,HO-\underset{OH}{\overset{OH}{Si}}-OH + 4n\ Si\,Me_2\,Cl_2 \ \ -\ \overset{4nHCl}{\rightleftharpoons} \{Si\,(-O-SiMe_2-O-)_4\}_n \ \text{(SSG)} \qquad (1)$$

$$\text{SSG} + (\text{RCOO}^-\text{H}^+)_2 \rightarrow \text{SSG.}(\text{RCOO}^-\text{H}^+)_2\ \text{(s)} \qquad (2)$$

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 60-70 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, hence the standard methylene blue method [11] is used [27]. The SA is found to be much higher (280 m^2 g^{-1}) for SSG-V10 composite. It is comparable to Versatic 911 [3]. The surface area of the material increases with decrease in concentration of Versatic-10 in diisopropyl ether as solvent. This indicates that the increased concentration of Versatic-10 blocking the pores of the silica gel. Pore-diameters have been computed using eq. (3) [11] as 62.5 μm for a pore volume of 0.1 mL.

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

[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 where the smaller pores act as a bottle neck [28].

3.3 TGA and DTA analysis: The TGA and DTA analysis (Fig. 4) exhibit two regions of weight loss. Up to 150 °C the material (SSG-V10 composite) losing 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 becomes entirely for the decomposition of Versatic 10 loaded on SSG (eq.2) for the preparation of ion-exchanger. This is compatible with the TGA values (5.411% w/w). So, the prepared ion-exchange material is thermally stable up to 150°C.

3.4 FT-IR analysis: FT-IR spectra of composite, SSG-V10 containing –COOH group [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 of which indeed vanished suggesting the conversion of -COOH group to $-COO^-$ ion and rupturing the hydrogen bonding [29], thereby confirming the participation in the adsorption of titanium (IV). On the other hand, a sharp –OH peak at 3658 cm^{-1} appears 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 carboxylic -C=O group of SSG-V10 was found to be shifted to somewhat higher frequency at 1616.2 cm^{-1} and confirmed the conversion of -COOH group to $-COO^-$ ion with higher bond order [29]. EDX spectra of the loaded ion-exchange material also confirm 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 miliequivalent of H^+/g at 25^0C) at different temperatures

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by measuring the miliequivalent of sodium ions absorbed on 1 g of dry SSG-V10 in its H^+ form [13]. The ion-exchange material (1g) becomes saturated at pH values of 5.0, 5.50 and 5.75 on 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. But, the values (37.4-40.7 mg g^{-1}) were much lower than the projected value of maximum uptake capacity (1.27 mili mol. g^{-1} (60.8 mg g^{-1})) for dinuclear bipositive cationic species $[(H_2O)(OH)Ti(\mu\text{-}O)_2Ti(H_2O)(OH)]^{2+}$ with respect to 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 full functioning of the exchange site containing –COOH group. As a result of which the efficiency of the ion-exchange material stands at 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 pH value.

3.6 Effect of pH on extraction: As carboxlic acid groups are the exchange site on the sorbent investigated, 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 at the pH range 3.0 to 7.0 ensured its quantitative extraction at 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 [10] decrease the amount of $–COO^-$ ions and titanium extraction was poor. Moreover, the solubility of titanium (IV) increases in aqueous solution along with the decrease in pH values. Both the effects lower the values of log K_d (eq. S1 and Fig. S1; supplementary document) at low pH and corroborate the suggested mechanistic path (eq. 4).

The cationic dinuclear species, $[(H_2O)(OH)Ti(\mu\text{-}O)_2Ti(H_2O)(OH)]^{2+}$ is present [30] in the weakly

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acidic pH range of 4.0-6.0. Its structure has been optimized by DFT calculation (Fig. 7) and produced the *syn* compound (system energy: -15531.124 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 their different mole ratios were taken 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 slope = 1.029 between log K_d and log $C_{[\text{Versatic-10}]}$ 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 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), $[(H_2O)(OH)Ti(\mu\text{-}O)_2Ti(H_2O)(OH)]^{+2}$, 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:

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

Species such as $Ti_3O_4^{4+}$ appears at pH values higher than 6.5. They lead to the eventual formation of colloidal or precipitated as $TiO_2.nH_2O$ [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 forms dimmers and produce cavities (as is mentioned in sec. 3.1) in hydrophilic part of the ion-exchange material were 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 the core radius of the dimer as 167.05 pm. The value is much lower than the calculated radius (from both the DFT optimized structure and global hardness (η) considering, r = 1/2η) [32] of dinuclear *anti*

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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 (-29567.465 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 having a suitable shape in comparison to titanium (IV) ion itself ($\eta_{Ti(IV)}$ = 16.23 eV) [33] 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 and 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 changes 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 : $\eta_{V10-\mathrm{dimer}}$ = 5.143 eV) [32] and intra-molecular hydrogen bonding ($r_{O....H-O}$ = 183.65 pm) rationalized the formation of *anti*-complex (Fig 10). The strong absorption 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 scheme 1 and 2.

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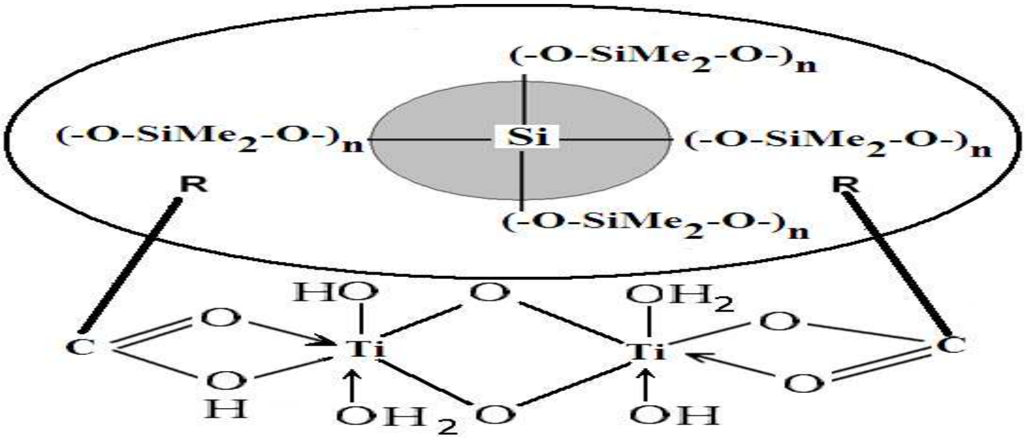
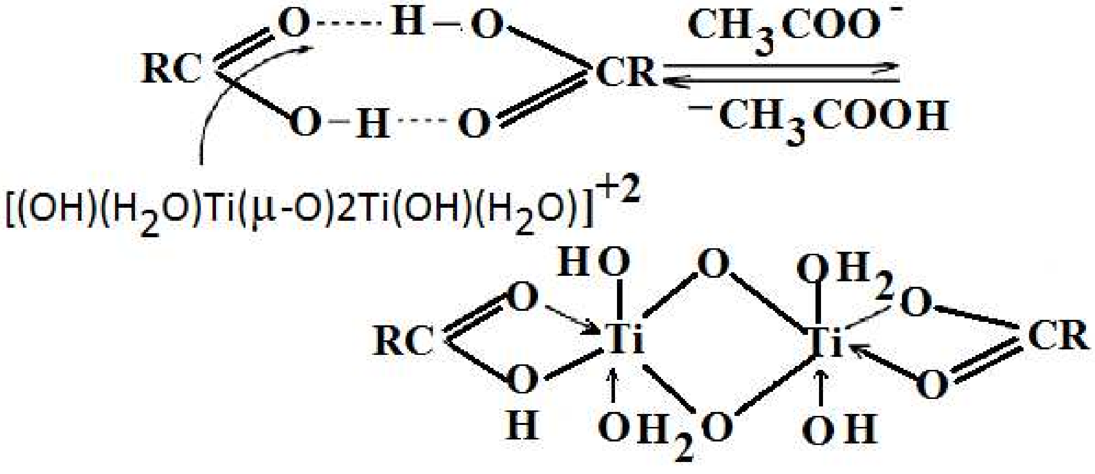


Scheme-1: Probable attachment of titanium (IV) at the hydrophilic part of the ion-exchange material; R= $-C\{CH(CH_3)_2\}_2CH_2CH_3$: Silica gel (shaded area); Methylated Surface: (open area)



Scheme-2: Probable mechanism of titanium (IV) trapping in dimeric cavity of the ion-exchange material; R= $-C\{CH(CH_3)_2\}_2CH_2CH_3$

The core diameter (Fig 10) (i.e., the distance between two carboxylic carbon) is 746.2 pm and in 1 g of dry SSG-V10 having BET surface area 149.46 m^2 g^{-1} generates 3.42×10^{20} number of such cores. In each core titanium is present as a dinuclear $[(H_2O)(OH)Ti(\mu\text{-}O)_2Ti(H_2O)(OH)]^{+2}$ and it corresponds to

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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.

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 have two reflections (a broad, strong reflection (2θ =21.83; 2θ=22.16; 2θ=21.82) and a weak & sharp reflection (2 θ =48.56; 2θ= 48.55; 2θ=48.52) and the corresponding reflections of SSG, SSG-V 10 and SSG-V10-titanium (IV) were found to be almost at 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 SSG-Versatic-10 composite. Here, the binding between SSG and Versatic-10 is 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.

3.8 Selection of Stripping Agents: At low pH TiO^{2+} is in equilibrium with $Ti(OH)_2^{2+}$ and $Ti_{(aq)}^{4+}$. So, 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 (0.5-1M), $HCl+H_2O_2$ (0.5-1M) and H_2SO_4 (1-1.5 M) (Table S1). Acetic acid dissociates weakly in aqueous solution and that is why, it performs poorly in recovery of titanium from the extractant compared to the strong inorganic acids like HCl, H_2SO_4 or HNO_3. Moreover, strongly basic Ti=O group is very much susceptible to 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 $[Ti{=}O \rightarrow Ti\text{-}O\text{-}Ti \leftarrow O{=}Ti]_n$ or $[\text{-}O\text{-}Ti\text{-}O\text{-}Ti\text{-}OH]_n$ [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) (Eq. 5). It was found that 1M HCl containing H_2O_2 as an eluent gave a symmetric elution profile (Fig. S2). It requires least volume (15

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mL) and provides the highest column efficiency. Moreover, 1M 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 1M 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 of the peak height.

3.9 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. It was quantitative (< 96%) up to the flow-rate of 4.0 mL min^{-1}. Since the reaction kinetic found to be very fast the effect of equilibration was investigated at a high flow-rate (6-8 mL/min) and it is observed that 1.5 min was sufficient for its extraction from aqueous solution at pH 5.0-5.75.

3.10 Effect of pH, volume and concentration of influent on recovery and preconcentration factor (P.F.): During extraction of titanium (IV) (23.95-35.92 µg mL^{-1}) at the range of pH 5.0-5.75, it was found that up to an influent volume of 1000 mL, P.F. (ratio of effluent concentration, C_f to influent concentration, C_s) increases with increase in effluent concentration (Table1). Although, at a particular volume, P.F. was not depend on either concentration or pH of the influent. Recovery decreased with increase in influent volume. Up to an influent volume of 1000 mL recoveries were quantitative (> 90%). To attain the break-through values (as 37400 µg g^{-1} at pH 5.0, 39100 µg g^{-1} at pH 5.5 and 40700 µg g^{-1} at pH 5.75), respectively, 1561, 1306 and 1133 mL of titanium (IV) solution were passed through the column. But, due to volume effect [10] recoveries were much poor (< 80 %). As a result of which, P.F. did not attend its maximum possible values (104.1, 87.1 and 75.5 for 100%

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recovery). It was optimized at a value of 60.8 ± 0.5. Plot of V_S (sample volume) vs. $R_{Ti(IV)}$ (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] $K_{desorption}{}^1(9.4\times10^{-3})$ and $K_{desorption}{}^2(6.37\times10^{-2})$ respectively. After 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 were in sorption and desorption process by replacing each other during the movement of the mobile phase. With the increase of 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. That is at this very condition the influent solvent itself will act as an eluent.

3.11. Effect of temperature on extraction: The extraction equilibrium constant (K_{ex}) has been computed at different temperatures using the following equation (eq. 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 is observed that the separation efficiency, C/C_0 (Fig. S5) increased with increasing temperature sharply in the range of temperature 293-310 K. The equlibration time decreased with the increasing temperature at the said interval and becomes nearly constant at the final equlibrium state.

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

Where, $[(RCOO^-H^+)_2\ (s)]$, denotes the concentration of SSG-V10 in its dimeric form, participated in 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} vs. 1000/T (eq. 7). The effect of temperature on extraction of titanium (IV) in the range of pH 5.5-5.75 has been made for the

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determination [34] of different thermodynamic parameters (ΔG and ΔS at 300 K) using the standard van't Hoff equation (eq. 8 and eq. 9).

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

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

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

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

The positive ΔH (0.048 kJ mol^{-1}) and smaller ΔS (5 J K^{-1}mol^{-1}) rationalizes the endothermic nature of the extraction process. During the adsorption of titanium (IV), H^{+} is released in the solution phase and increase the number of neutral CH_3COOH. This effect corelates with positive value of ΔS. The higher negative value of ΔG (-1.1488 kJ mol^{-1}) suggests the spontaneity and tendency of chemisorptions of the equilibrium [34], and is an agreement of Langmuir isotherm.

3.12 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 acetate buffer-acetone mixture (15:2 v/v) on chromatogram (Table S2). Result shows 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 very much higher than that of Fe(III) (R_f value = 0.41) and under this condition, the large polymeric species like $[Ti{=}O{-}Ti{-}O{-}Ti{-}O{=}Ti]_n$ does not participated 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 it suggests their easy separation from titanium (IV).

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3.13 Effect of pH on selectivity factors (α): Systematic studies on R_f values of metal ions (except Fe(III) and Zr(IV)) at the range of pH 5.0-5.75 have been made. The Selectivity factors (α) (separation efficiency) with respect to titanium (IV) have been computed and it was 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.

3.14 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 in “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 (α ≥1.5)) [11] have been made. Then from these important mixtures, viz., Zr(IV), V(IV), Al(III), Ti(IV); Fe(III), Cr(III), Ti(IV) etc. (Table 4) metal ions have effectively been separated. The binary and ternary separations from diverse metal ions were achieved either by exploiting the differences in pH for extraction or by using suitable eluting agent utilizing the selectivity factors (α ≥1.5) [9] (Table: 3; Table 4) (separation procedure is given as supplementary file (f. 1)). After recovery, diverse ions were determined complexometrically [9]. In almost all the cases fairly good reproducibility with respect to quantitative extraction, separation and recovery have been achieved.

3.15 Application of the method of extraction in alloy sample of Titanium: Titanium, Ti6Al-4V alloy (V, Al, Ti & Fe) sample was treated [15] with 10 mL 1:1 nitric acid and 10 mL of 70 per cent perchloric acid. The analyte solution (80 mL) was evaporated to dryness. The mass was dissolved in 25 mL distilled water. Any residue left was filtered (whatman.No.42) and diluted to 100 mL with distilled water and extracted at pH 2.5, when Fe(III) was extracted and eluted with 0.5 M H_2SO_4. The

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effluent containing V, Al and Ti was passed through the column at pH 5.75 and sequentially eluted by the developed method (Table: 4). The recovery was quantitative (Table 5).

3.16 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). Preconcentration process gave slightly lower recovery with respect to 98.8% probably because of the loss of analyte in both extraction and elution steps during its recovery and were found to be all about 4.0 ± 0.5 % lower than AAS.

Separation of titanium (IV) and Cr(III) in water (pond and well water) samples were 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 have 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).

4. CONCLUSIONS

The DFT optimized structure 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 stabilized by 0.286 eV over the *syn* isomer due to intra-molecular hydrogen bonding. DFT optimized extracted complex turns out as anatase. The loading of titanium (IV) on to SSG-V 10 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 value of ΔH (0.048 kJ mol^{-1}) and ΔS (5 J K^{-1} mol^{-1}) and negative value of ΔG ((-1. 48 kJ

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mol^{-1}) indicated that the interaction process is endothermic, entropy gaining and spontaneous in nature. 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 factors ($\alpha \geq 1.24$) 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 multicomponent mixtures containing cations (Table 4) present in the acidic waste in "chloride process for titania production" (Ti(IV), Fe(III), Cr(III), V(V), Al(III)) and also in Gr III in 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. But, the present method does not face any such inconvenience as the interfering ions are already separated. The developed ion-exchange material is chemically stable (up to 6 M HNO_3, 4 M CH_3COOH, 4 M HCl and 2 M H_2SO_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.

5. ACKNOWLEDGEMENT

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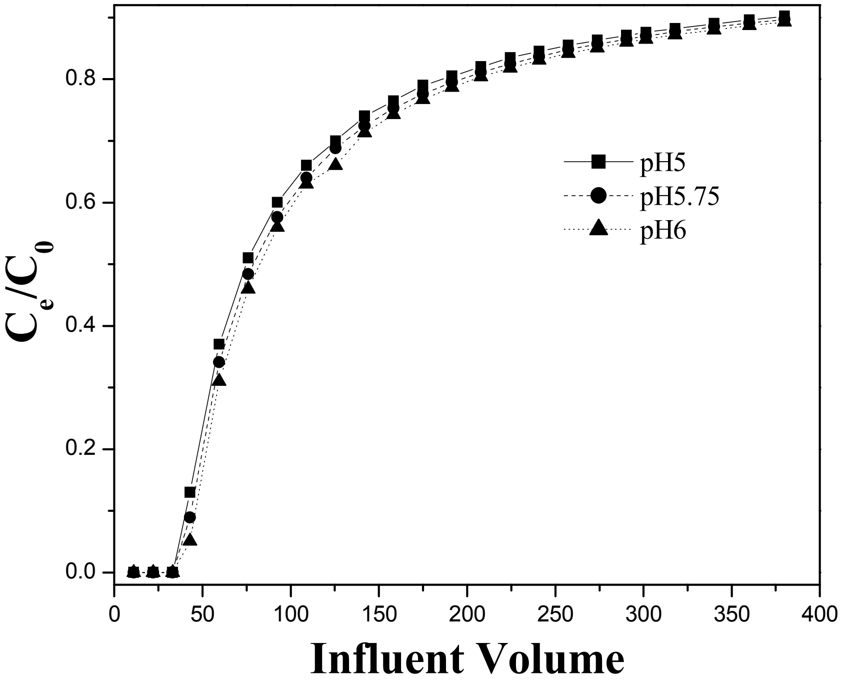

Fig. 1: Break through curve (■ =pH 5; ● = pH 5.75 and ▲= pH 6)

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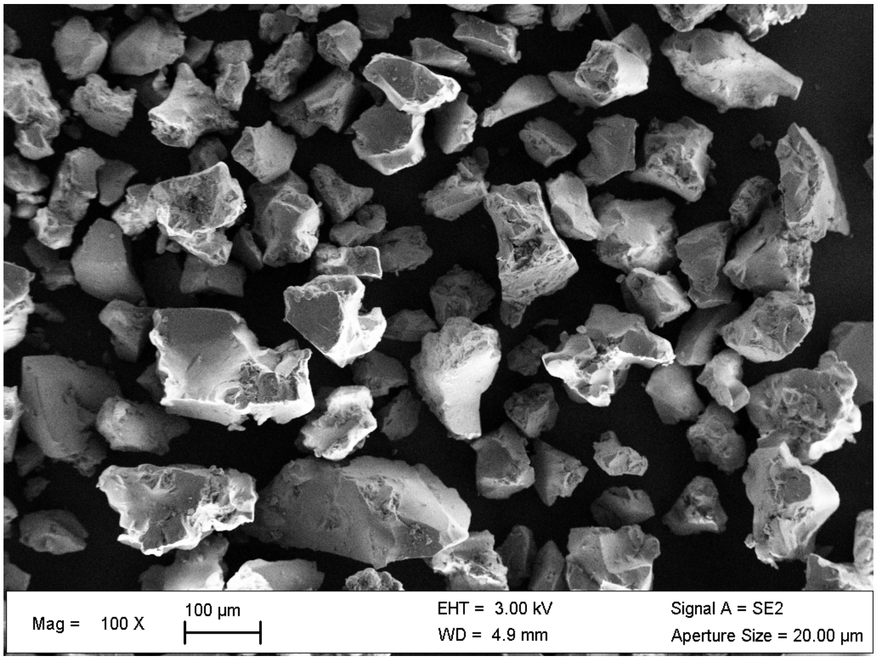

Fig.2: SEM image of SSG-V 10

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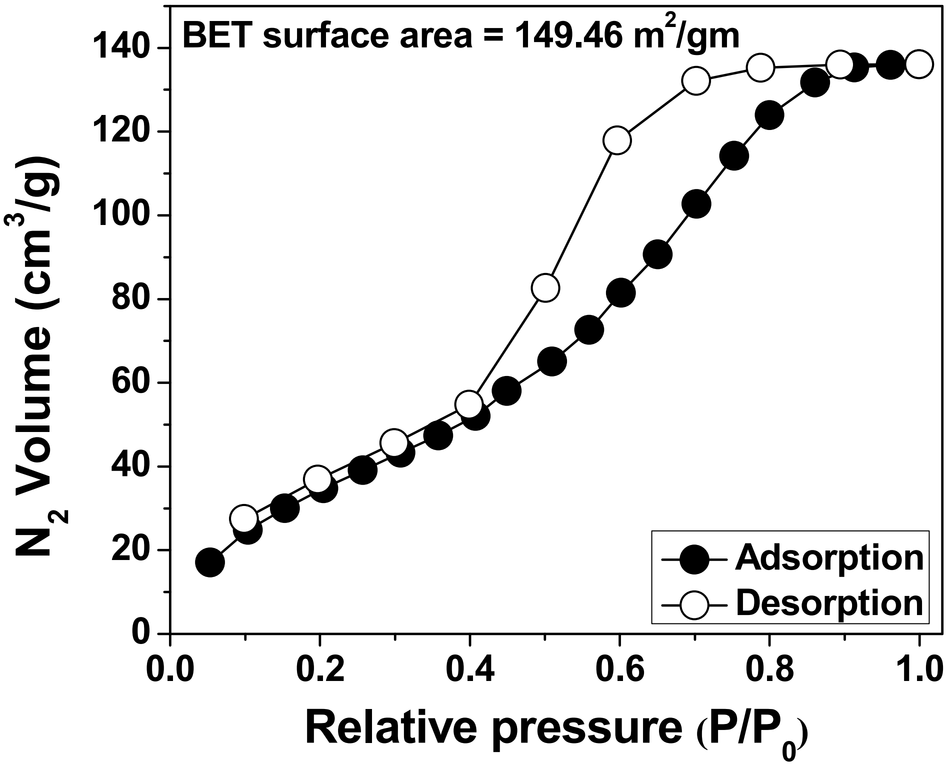

(a)

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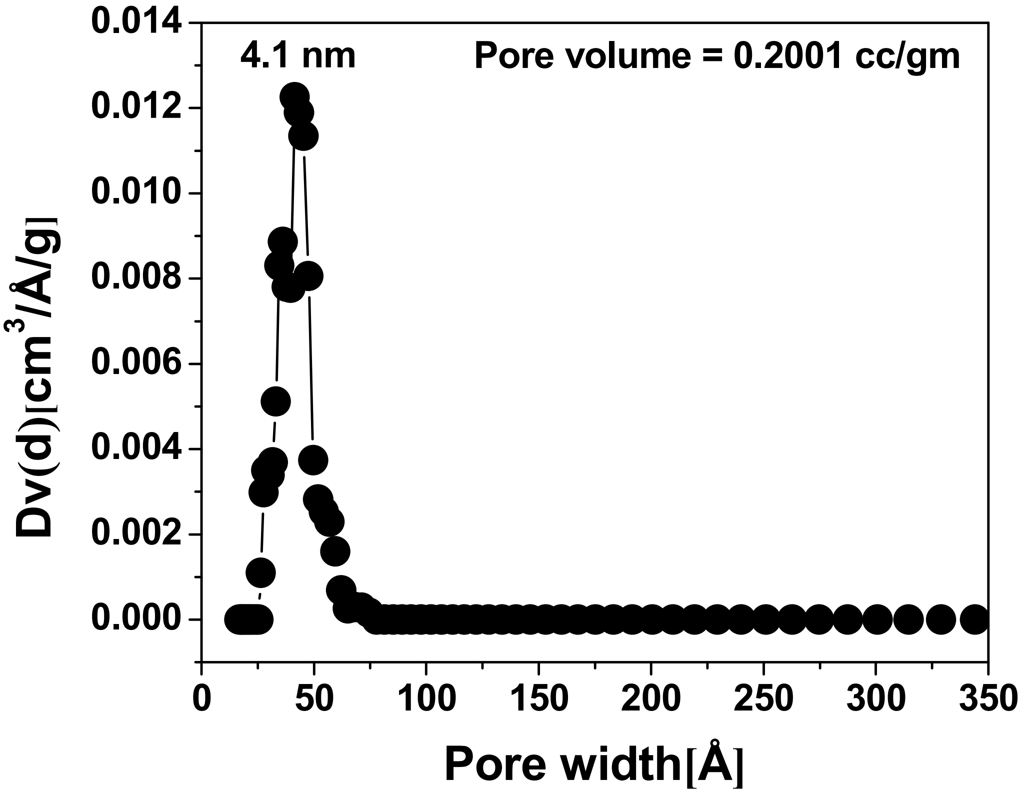

(b)

Fig 3: BET surface properties of SSG-V 10 a) BET surface area (149.46 m^2 gm^{-1}); b) Pore volume (0.2001 cc gm^{-1})

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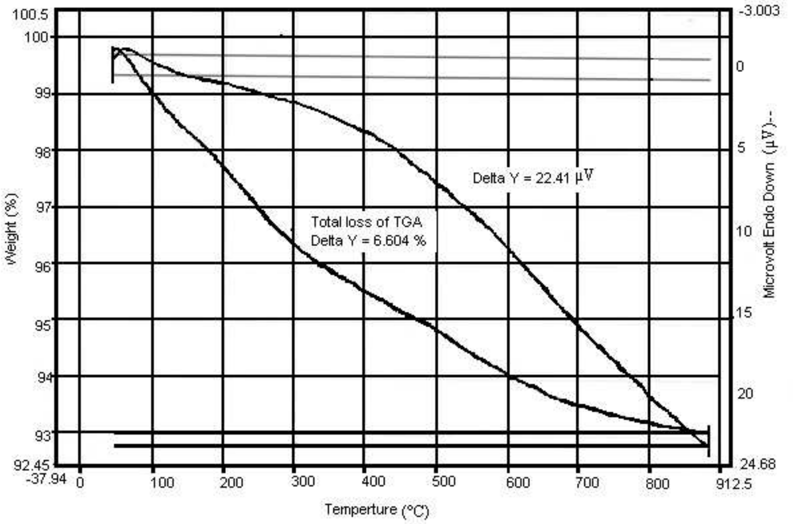

Fig. 4: TGA-DTA of Versatic-10; Flow-rate of Nitrogen: 20 mL/min; Temperature increment: 25 °C/min.

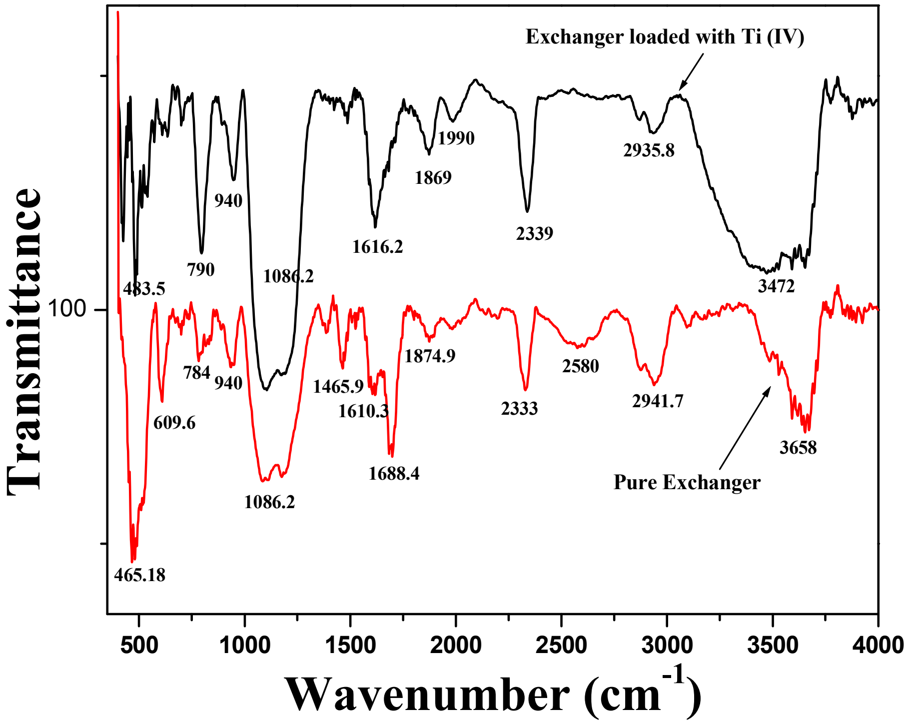

Fig. 5: FT-IR spectra of a) the ion exchanger and b) Titanium (IV) loaded ion exchanger

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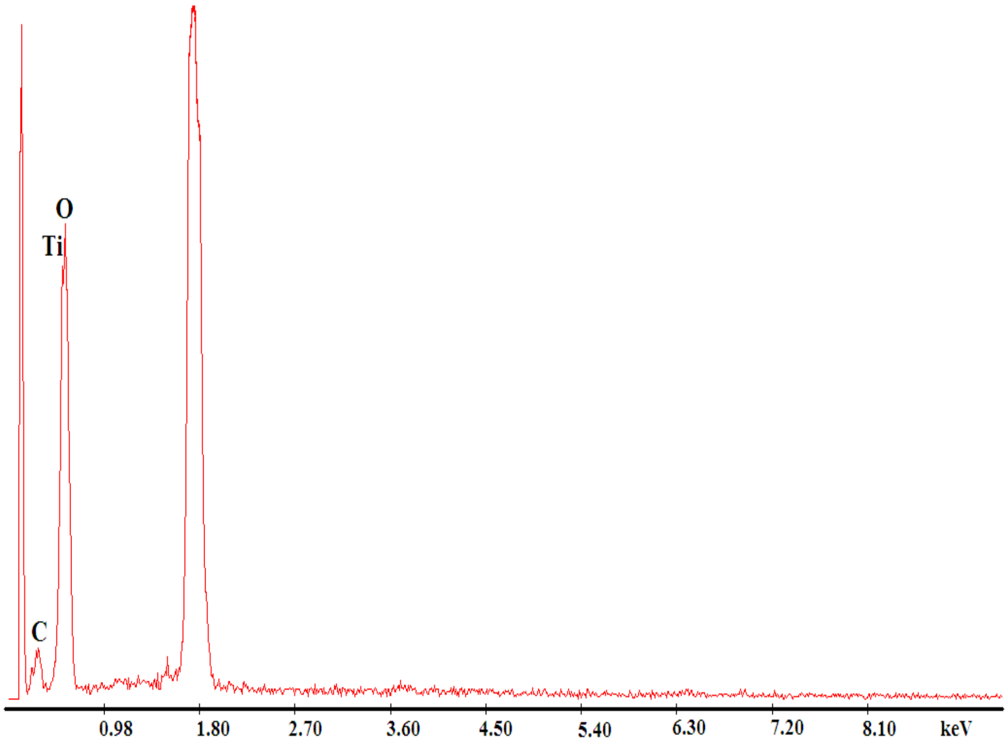
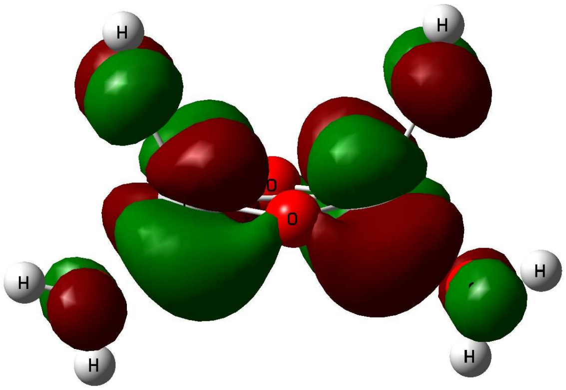
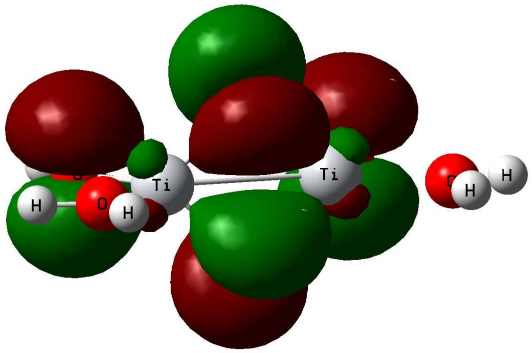


Fig. 6: EDX spectra of Versatic-10 loaded with Titanium (IV)



LUMO of Ti (μ-O_2) Ti (-12.8711 eV)

(a)



HOMO of Ti (μ-O_2) Ti (-16.7623 eV)

(b)

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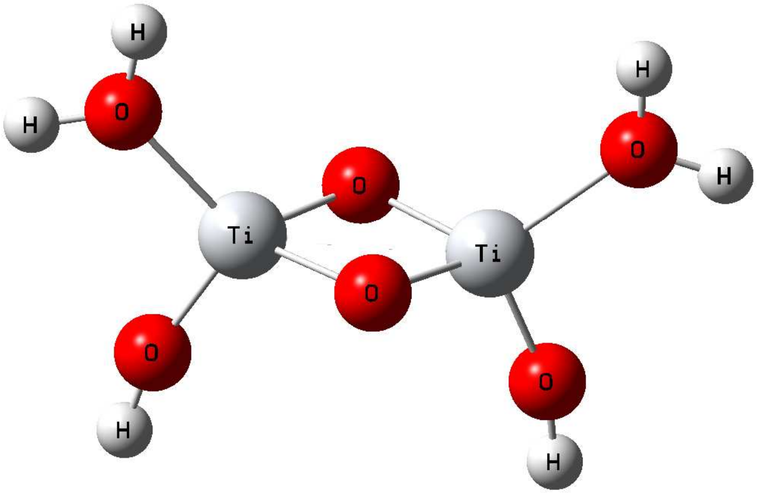

Fig. 7: DFT optimized structure of $[(H_2O)(OH)Ti(\mu\text{-}O)_2Ti(H_2O)(OH)]^{+2}$($\eta$ = 3.8912 eV); Ti-Ti:(bond distance) 265.99 pm; Bond distance (Ti-O: 179.0 pm (bridge); Ti-O: 200.78 pm (terminal)); ∠Ti-O-Ti: 96.24°; ∠O-Ti-O: 106.4°; dipole moment: 4.2980 debye

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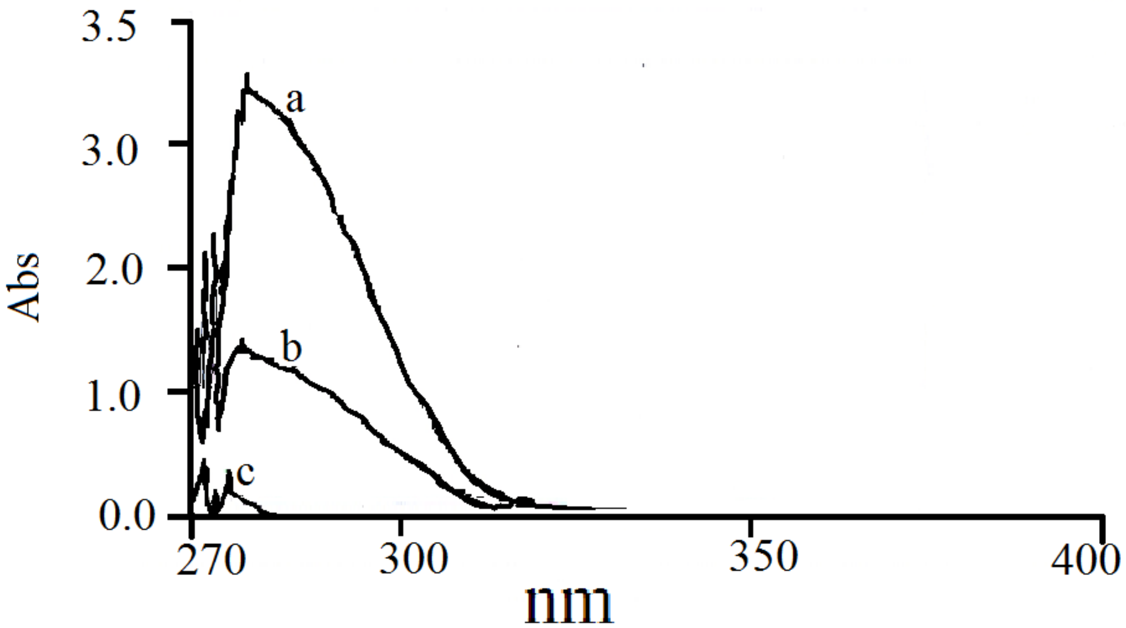

Fig. 8: UV-Visible spectra of organic phase (ligand **:** Titanium (IV) (a) 1: 1 (b) 1:2 (c) 1:3)

a) LUMO (-1.714331 eV)

b) HOMO (-6.85732 eV)

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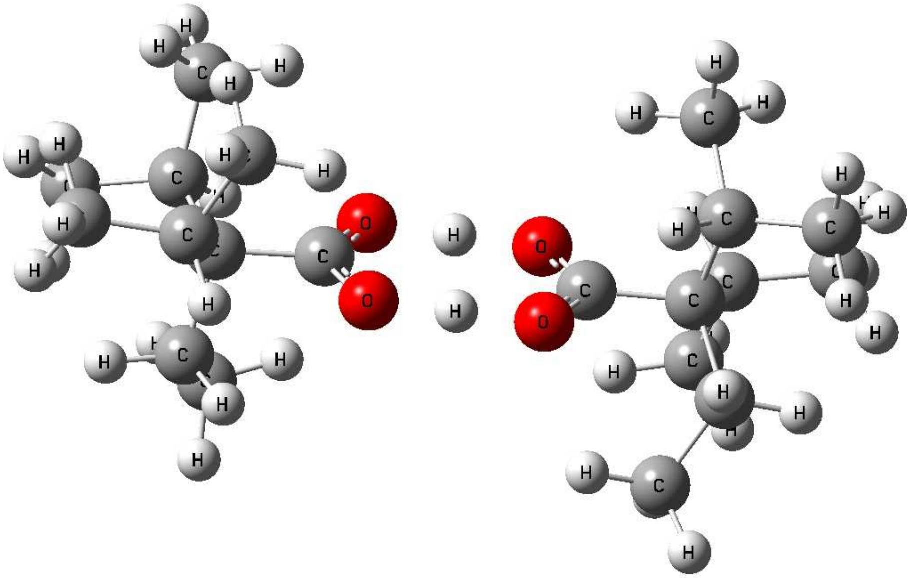
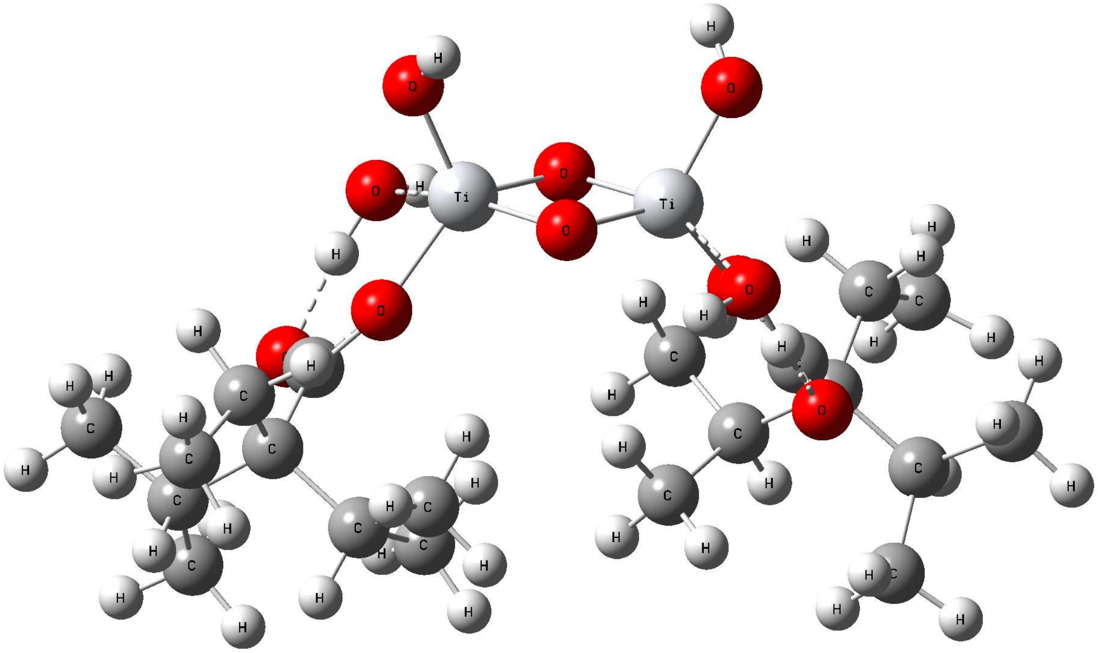


c)

Fig. 9: Hydrogen bonded dimer of Versatic-10 (η_{dimer} = 5.143 eV) a) LUMO b) HOMO and c) Optimized dimer



Syn-Side-View

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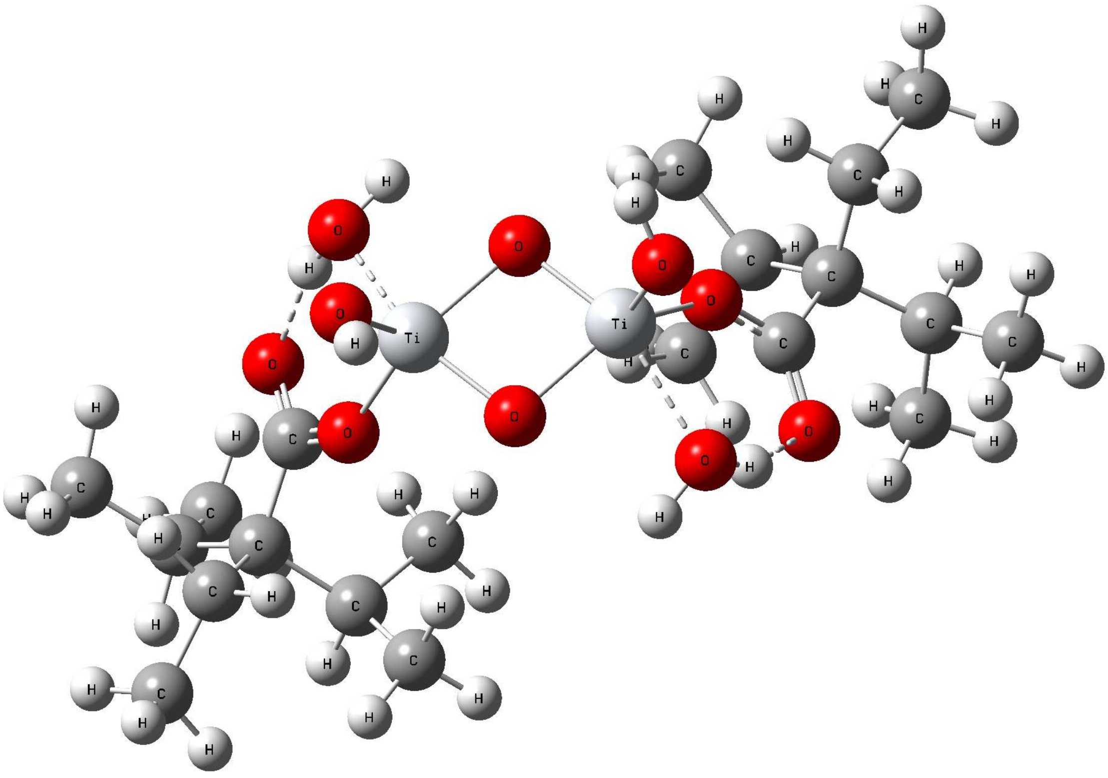

Syn-Top-View

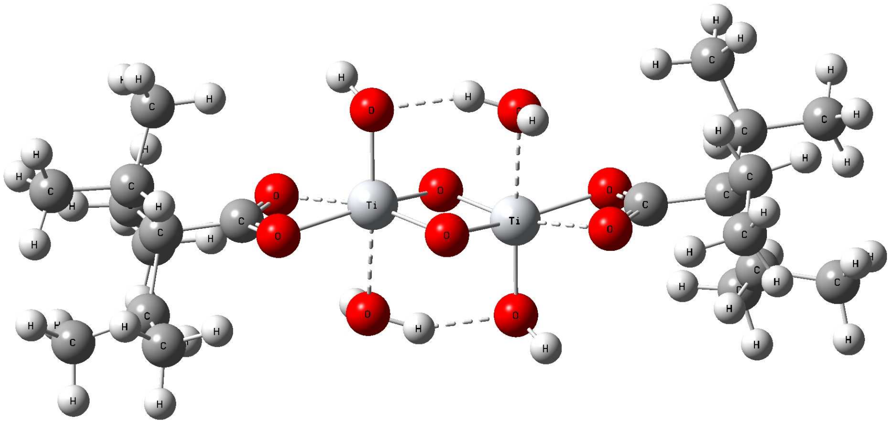

Fig. 10: Ti-Versatic-10 *anti*-complex complex: Bond distances (Ti-O: 179.0 pm (bridge); Ti-O: 260.05 pm (terminal)); Ti-O: 213.61 pm (axial)); ∠Ti-O-Ti: 94.56°; ∠O-Ti-O: 63.02°

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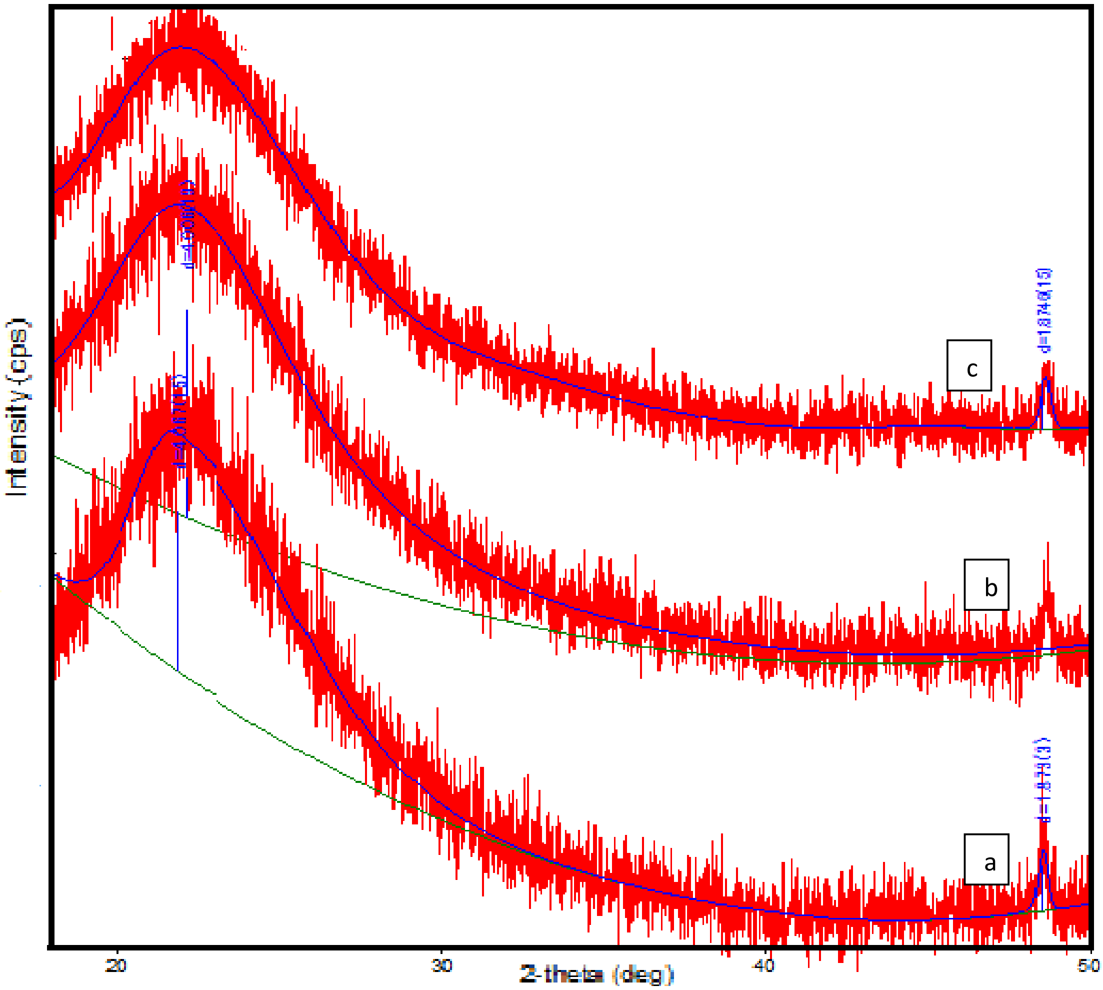

Fig.11: XRD pattern of a) SSG b) SSG V10 and c) SSG V10 Titanium (IV).

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Table 1: Effect of volume, sample concentration and pH on 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]

*p*H	Sample Conc. (C_s) (μg mL^{-1})	Sample volume, V_s (mL)	Amount of Ti(IV) (μg)		Effluent conc. (C_f) (μg mL^{-1})	[a]Recovery (%)	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	19160	18393.6	1226.2	96.0	51.2
		1000	23950	21674.7	1445.0	90.5	**60.3**
		1300	31135	21888.0	1459.2	70.3	**60.9**
		1561	37386	20487.5	1365.8	54.8	57.0
5.5	29.93	200	5986	5938.1	395.9	99.2	13.2
		400	11972	11684.6	778.9	97.6	26.0
		800	23944	23201.7	1546.8	96.9	51.7
		1000	29930	21595.5	1839.7	92.2	**61.4**
		1200	35916	27511.7	1834.1	76.6	**61.2**
		1306	39088	27010.0	1800.7	69.1	60.2
5.75	35.92	200	7184	7083.4	472.2	98.6	13.1
		400	14368	14080.6	938.7	98.0	26.1
		800	28736	27988.8	1865.9	97.4	51.9
		1000	35920	32759.0	2183.9	91.2	**60.8**
		1100	39512	32874.0	2191.6	83.2	**61.0**
		1133	40698	23884.0	2192.2	80.8	61.0

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

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Table 2: Effect of pH on R_f values and selectivity factors (α = $\left(R_f\right)_i \left(R_f\right)_{Ti(IV)}$) of different metal ions 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 Vlues	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

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Table 3: Separation of Titanium (IV) from synthetic metal ion mixtures
[Titanium (IV) taken: 2.2 mg mL^{-1}, column: 0.8×8cm., Flow rate: 1mL min^{-1}, pH-2.5*, 5.0; temp: 25^{0}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	0.1M HCl (30)
	Titanium (IV)	2.20	2.22	3.73	1 M HCl+H_2O_2 (15)
2	Th(IV)	1.8	1.88	3.80	2.5M HNO_3 (25)
	Titanium (IV)	2.20	2.16	1.53	1M HCl
3	Pb(II)	2.20	2.24	2.41	0.005M CH_3COOH (60)
	Titanium (IV)	2.15	2.17	3.22	1M HCl+H_2O_2 (15)
4	Ni(II)	2.15	2.12	1.50	Mobile Phase
	Titanium (IV)	2.20	2.24	2.41	1M HCl+H_2O_2 (15)
5	Zn(II)	2.63	2.62	2.17	Mobile Phase
	Titanium (IV)	2.20	2.22	3.73	1M HCl+H_2O_2 (15)
6	*Zr(IV)	2.08	2.06	2.12	4M HNO_3 (20)
	Titanium (IV)	2.20	2.21	3.48	1M HCl+H_2O_2 (15)
7	Cd(II)	1.80	1.83	3.87	Mobile Phase
	Titanium (IV)	2.20	2.22	3.73	1M HCl+H_2O_2 (15)

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Table 4: Separation of Titanium (IV) from synthetic metal ion mixtures

[Titanium (IV) taken: 2.2 mg mL^{-1}, column: 0.8×8cm., Flow rate: 1mL min^{-1}, pH-2.5*, 5.0; temp: 25^{0}C; RSD = Relative Standard Deviation]

Mixture	Cations	Added (mg mL^{-1})	Recovered (mg mL^{-1})	R.S.D.(%)	Eluent vol. (mL)
1	*Fe(III) Cr(III) Titanium (IV)	2.85 2.15 2.20	2.87 2.12 2.24	1.74 1.50 2.41	0.1M H_2SO_4 (20) Mobile Phase (25) 1M $HCl+H_2O_2$ (15)
2	U(VI) V(IV) Titanium (IV)	2.90 2.20 2.20	2.98 2.14 2.26	2.21 3.48 3.60	0.25M HNO_3 (30) 0.1M CH_3COOH (50) 1M $HCl+H_2O_2$ (15)
3	*Zr(IV) Cr(III) Titanium (IV)	2.98 2.15 2.20	3.04 2.20 2.18	2.45 1.66 2.13	4M HNO_3 (20) Mobile Phase (25) 1M $HCl+H_2O_2$ (15)
4.	*Zr(IV) V(IV) Titanium (IV)	2.98 2.20 2.20	3.02 2.15 2.26	1.68 1.68 2.54	4M HNO_3 (20) 0.1M HNO_3 (05) 1M $HCl+H_2O_2$ (15)
5.	*Zr(IV) U(VI) Titanium (IV)	2.98 2.90 2.20	3.08 2.96 2.12	3.12 1.98 2.78	4M HNO_3 (20) 0.25M HNO_3 (30) 1M $HCl+H_2O_2$ (15)
6.	*Zr(IV) V(IV) Al(III) Titanium (IV)	2.98 2.20 1.80 2.20	3.08 2.13 2.00 2.12	3.08 3.11 2.69 3.22	4M HNO_3 (20) 0.1M HNO_3 (05) 1M CH_3COOH (20) 1M $HCl+H_2O_2$ (15)

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

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

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)

Values in the parenthesis represent the relative errors (%)

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