



A new electron exchange material Ti(IV) iodovanadate: Synthesis, characterization and analytical applications

Syed Asfaq Nabi^a, Mu. Naushad^{b,*}

^a Analytical Research Laboratory, Department of Chemistry, Faculty of Science, Aligarh Muslim University, Aligarh 202002, India

^b Chemistry Laboratory, Department of Applied Sciences & Humanities, Faculty of Engineering and Technology, SRM University, Modinagar 201204, India

ARTICLE INFO

Article history:

Received 1 July 2009

Received in revised form 7 December 2009

Accepted 8 December 2009

Keywords:

Synthesis

Inorganic cation exchange material

Electron exchange material

Ti(IV) iodovanadate

Metal ion separation

H₂O₂ decomposition

ABSTRACT

A new inorganic cation exchange material Ti(IV) iodovanadate has been synthesized under a variety of conditions. The experimental parameters such as mixing volume ratio, order of mixing and pH established for the synthesis of the material. The most stable sample has been prepared by adding aqueous mixture of 0.1 M potassium iodate and 0.1 M sodium vanadate into 0.1 M solution (CCl₄ medium) of titanium chloride at pH 1. The material is characterized using various analytical techniques like XRD, FTIR, TGA–DTA and SEM. A tentative structural formula has been proposed on the basis of chemical composition, pH titration, FTIR and thermogravimetric analysis. The ion exchange capacity and distribution coefficients of various metal ions have been determined to understand the cation exchange behavior of the material. On the basis of distribution studies, the material was found to be selective for Pb²⁺ ion. Its selectivity has been examined by achieving some important and analytically difficult binary separations, viz. Cr³⁺–Pb²⁺, Fe³⁺–Pb²⁺, Zn²⁺–Pb²⁺, Cd²⁺–Pb²⁺, etc. The material has been also used as an electron exchange material. The oxidation of Fe(II) to Fe(III) has been achieved by batch–equilibrium technique successfully. The decomposition of hydrogen peroxide by the material has also been studied. The practical utility of Ti(IV) iodovanadate has been demonstrated by separating metal ions quantitatively from a synthetic mixture using the packed column of Ti(IV) iodovanadate.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The present considerable status of inorganic ion exchange materials is due to their growing applications in the area of analytical chemistry, electrochemistry, environmental chemistry, biochemistry and radiochemistry. Due to the high radiation stability and high selectivity, inorganic ion exchange materials are often preferred to organic resins in the treatment of nuclear waste effluents [1]. Moreover, they often exhibit specificity towards certain metal ions. It is for these reasons, there has been a revolutionary growth in the field of synthetic ion exchange materials [2]. Many studies have been done for their preparation, properties and analytical applications but most ion exchange materials show poor ion exchange capacity and selectivity for metal ions and low thermal and chemical stability [3–9]. Acidic salts of tetravalent metal ions with the general formula M(IV) (HXO₄)₂·nH₂O [where M represents Zr(IV), Ti(IV), Sn(IV), etc. and X represents P, W, Si, Mo, Se, As, etc.] have been most extensively studied. Both single and double salts have been synthesized but double salts have better ion exchange capacity, thermal stability, chemical stability, high resistance towards

chemical attack, heat treatment and good regeneration power as compared to single salts [10]. Ti(IV) based ion exchange materials are known to be stable chemically and thermally in a comparative study under identical conditions of synthesis [11]. Ti(IV) tungstate has unusual and interesting feature [12]. It has negligible adsorption of trivalent ions such as Fe³⁺, Al³⁺ and In³⁺ as compared to Zr(IV) tungstate, uranium tungstate and stannic tungstate which show complete adsorption [13]. A literature survey shows that a number of synthetic inorganic ion exchange materials have been found to act as electron exchange material [14,15]. Redox ion exchange materials have selectivity due to the built in functional exponents, which can be reversibly oxidized and reduced. The most important advantage of synthetic ion exchange materials as electron exchange materials over the conventional methods of oxidation and reduction is their insolubility in reaction medium and the interference caused by the untreated redox substances can be easily separated from the substance with which they are treated. Another advantage is that, they are readily regenerated after the use.

The present work describes the synthesis, characterization, ion exchange behavior of a new cation exchange material Ti(IV) iodovanadate. The material played a role as an electron exchange material for the oxidation of Fe(II) to Fe(III). The decomposition of hydrogen peroxide by the material has also been studied. The

* Corresponding author. Tel.: +91 9897830017.

E-mail address: shad81@rediffmail.com (Mu. Naushad).

Table 1
Condition of synthesis of different samples of Ti(IV) iodovanadate.

Sample no.	Mixing volume ratios of reagents (v/v)			Total volume (mL)	pH	Appearance of beads in H ⁺ form after drying at 40 ± 2 °C	Yield (g)	IEC for Na ⁺ ion (mequiv. g ⁻¹) exchanger
	TiCl ₄ (0.1 M)	KIO ₃ (0.1 M)	NaVO ₃ (0.1 M)					
S-1	1	1	1	300	0.7	Yellow	2.90	0.80
S-2	1	1	1	300	1.0	Yellow	3.00	0.92
S-3	1	1	1	300	1.2	Yellow	3.00	0.90
S-4	1	2	1	400	1.0	Brown	3.90	1.70
S-5	2	1	1	400	1.0	Brown	3.40	0.92
S-6	1	1	2	400	1.0	Brown	3.80	1.68

practical utility of Ti(IV) iodovanadate was also demonstrated by separating metal ions quantitatively from a synthetic mixture by using the packed column of the material.

2. Experimental

2.1. Reagents and instrumentation

Titanium chloride (99%, Riedael-de Haen, Germany), potassium iodate (Otto Chemie, Bombay, India), sodium vanadate (Otto Chemie, Bombay, India). All other chemicals and reagents used were of analytical reagent grade.

A single electrode pH meter (Toshniwal, India), FTIR spectrophotometer (Perkin-Elmer Spectrum-BX, USA), an automatic thermal analyzer (V2.2A Du Pont 9900), a PW 1148/89 based X-ray diffractometer (Phillips, Holland), an electron microscope (LEO 435 VP, Australia) with attached imaging device, a UV-vis spectrophotometer (Elico EI 301E, India) and a water bath incubator shaker were used.

2.2. Preparation of reagents and synthesis of ion exchange material

0.1 M solution of Ti (IV) chloride was prepared in CCl₄ and the solutions of 0.1 M sodium vanadate and 0.1 M potassium iodate were prepared in demineralized water.

A number of samples of Ti(IV) iodovanadate were prepared by mixing a mixture of aqueous solutions of 0.1 M sodium vanadate and 0.1 M potassium iodate with 0.1 M solution of Ti(IV) chloride (CCl₄ medium) in different reaction conditions. The pH 1.0 was adjusted by adding either dilute hydrochloric acid solution or ammonia solution in the precipitate. The gelatinous precipitates, so formed were allowed to stand for 24 h in the mother liquor. The supernatant liquid was removed and the precipitates were washed with demineralized water several times to remove excess reagents. The products were dried at 40 ± 2 °C in an oven. The dried products were then kept in demineralized water for cracking and to obtain the particle of the size range ~125 μm. These were converted to H⁺ form by placing them in 1.0 M HNO₃ solution and washed with demineralized water to remove excess acid and finally dried at 40 ± 2 °C. Hence, a number of samples were prepared, and on the basis of ion exchange capacity, percentage yield, sample S-4 was selected for detailed studies (Table 1).

2.3. Ion exchange capacity studies

To determine the ion exchange capacity of the sample, 1.0 g (dry mass) of the ion exchange material in H⁺ form was placed in a glass column with a glass wool support at the bottom. It was washed with demineralized water to remove any excess of acid remained sticking on the particles. The hydrogen ions eluted with 1.0 M solution of different alkali and alkaline earth salts. The flow rate was kept 0.5 mL min⁻¹. The collected effluent was titrated against a standard solution of sodium hydroxide using phenolph-

thalein as an indicator. The hydrogen ions released were then calculated.

To determine the regeneration of ion exchange capacity, exhausted exchange material Ti(IV) iodovanadate was regenerated by keeping it in 1.0 M nitric acid for 24 h. It was then washed with demineralized water, till neutral. The exchange capacity was determined and this procedure was repeated three times.

To see the effect of heating temperature on ion exchange capacity of the material, 1.0 g sample of the cation exchange material (S-4) in H⁺ form was heated at different temperatures in a muffle furnace for 1 h and Na⁺ ion exchange capacity was determined after cooling them at room temperature by standard column process as described above.

2.4. Effect of eluent concentration and elution behavior

To find out the optimum concentration of the eluent for complete elution of H⁺ ions, a fixed volume (250 mL) of NaNO₃ solution of different concentration were passed through the columns, containing 1.0 g of the exchange material in H⁺ form with a flow rate of 0.5 mL min⁻¹. The effluents were titrated against a standard solution of 0.1 M NaOH to find the H⁺ ions eluted out.

For the elution behavior, NaNO₃ solution of optimum concentration was passed for complete elution of H⁺ ions through a column containing 1.0 g of the cation exchange material (H⁺ form) with a flow rate of 0.5 mL min⁻¹. The effluent was collected in 10 mL fractions and each fraction was titrated against a standard alkali solution as described above.

2.5. Chemical stability and chemical composition

0.5 g of the exchange material was treated with 50 mL concerned solvent and kept for 24 h with occasional shaking. The amount of titanium, vanadate, and iodate released in the solution was determined spectrophotometrically [16,17].

To find the chemical composition, a 0.5 g of the sample was dissolved in 10 mL concentrated HCl. The solution was diluted to 50 mL. The amount of titanium, vanadate, and iodate contents of the solution was determined spectrophotometrically.

2.6. pH titration

0.5 g of cation exchange material (H⁺ form) was placed in each 250 mL conical flask, followed by the addition of 0.1 M solutions of alkali or alkaline earth metal chlorides and their hydroxides in different volume ratios [18]. The total volume was kept 50 mL to maintain the ionic strength constant. The pH of each solution was determined after equilibration and plotted against milliequivalents of OH⁻ ions added.

2.7. FTIR studies and X-ray analysis

10 mg of the material (H⁺ form) was mixed with 100 mg (dry mass) of KBr and ground to a very fine powder. A transparent

disc was formed by applying a pressure of 80,000 p.s.i. (1 p.s.i. 56,894.76 Pa). The IR absorption pattern was recorded between 400 and 4000 cm^{-1} using Nicolet Fourier transform spectrometer.

For X-ray diffraction analysis, manganese filtered $\text{CuK}\alpha$ radiation wavelength (150.1542 nm) at 298 K was used. The instrument was equipped with graphite monochromator and operating at 40 kV and 30 mA.

2.8. SEM and TGA–DTA studies

Scanning electron microscopy (SEM) was performed on ground materials (as prepared) by an electron microscope.

Simultaneous thermogravimetric analysis–differential thermal analysis (TGA–DTA) studies of the sample were carried out at a heating rate of $10^\circ\text{C min}^{-1}$ up to 900°C in the air atmosphere.

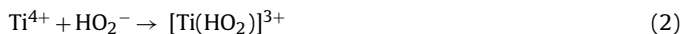
2.9. Oxidation of Fe(II) to Fe(III) and decomposition of H_2O_2 by Ti(IV) iodovanadate

Oxidation of Fe(II) to Fe(III) was accompanied by treating 0.5 g exchange material with the 0.0001 M ferrous nitrate solution for 40 min, the time in which maximum oxidation takes place. The substrate was determined by standard method [19] and the total amount oxidized by the exchange material was evaluated.

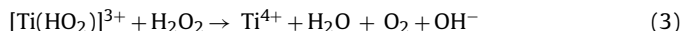
For the H_2O_2 decomposition study, 1.0 g Ti(IV) iodovanadate was treated with 20 mL of H_2O_2 (30%). The colour of Ti(IV) iodovanadate changes from yellow to brown. This could be due to the formation of redox species [19]. On the basis of above observations, the following reaction mechanism can be suggested which has been already proposed by Shivaneekar and Chudasama [20,21].



After that, metal ion (Ti^{4+}) interact with HO_2^- ions to form an intermediate complex as



A second molecule of H_2O_2 may then interact with the intermediate complex to give the products



During the decomposition of hydrogen peroxide, the increase in pH confirms the liberation of OH^- ions as per suggested mechanism.

2.10. Sorption studies

In order to get an idea of partition behavior of the exchange material towards the separation of metal ions of analytical interest, distribution coefficients (K_d) were determined in several solvent systems. A 0.4 g exchange material in H^+ form was treated with 40 mL solution of metal ions in required solvent medium in a 100 mL Erlenmeyer flask. The mixture was shaken for 6 h at $25 \pm 2^\circ\text{C}$ in a temperature controlled incubator shaker. The amount of metal ions before and after adsorption was determined by titration against a standard solution of 0.01 M di-sodium salt of EDTA. The K_d values may be expressed as follows.

$$K_d = \frac{\text{milli-equivalent of metal ions/g of ion-exchanger}}{\text{milli-equivalent of metal ions/mL of solution}} \quad (4)$$

$$K_d = \frac{I - F}{F} \times \frac{V}{M} \text{ mL g}^{-1}$$

where I is the initial amount of the metal ion in the solution phase, F is the final amount of metal ion in the solution phase after treatment with the exchange material, V is the volume of the solution (mL) and M is the amount of ion exchange material taken (g).

2.11. Quantitative separation of metal ions in binary synthetic mixtures

Quantitative separations of some important metal ions of analytical utility were achieved on Ti(IV) iodovanadate columns. 1.5 g of exchange material in H^+ form was packed in a glass column of 0.9 cm internal diameter with a glass wool support at the end. The column was washed thoroughly with demineralized water and the mixture of two metal ions having initial concentration 0.1 M of each with different volume ratios, was loaded on it and allowed to pass through the column at a flow rate of 0.20 mL min^{-1} till the solution level was just above the surface of the material. The column was then rinsed with demineralized water so that the metal ions, which were not exchanged, could be removed. Individual metal ions adsorbed on the exchange material, were then eluted using the appropriate eluting reagents. The flow rate of the eluent was maintained 0.5 mL min^{-1} throughout the elution process. The effluent was collected in 10 mL fractions and was titrated against the standard solution of 0.01 M di-sodium salt of EDTA.

3. Results and discussion

The samples of Ti(IV) iodovanadate have been synthesized under varying conditions. It is evident from Table 1 that the mixing ratios of the reactants and pH also affect the physical appearance and ion exchange capacity of the material. It is found that anionic part contributes towards ion exchange capacity as the replaceable groups are attached to this group. On the basis of better yield, ion exchange capacity and chemical stability as compared to others, sample S-4 has been selected for detailed studies. Ti(IV) iodovanadate has higher ion exchange capacity than other titanium based inorganic ion exchange materials which are prepared under similar conditions (Table 2). Ion exchange capacities for mono- and bivalent metal ions have been studied (Table 3). The affinity sequence for alkali metal ions are $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ and for alkaline earth metal ions are $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. This sequence is in accordance with the hydrated ionic radii. The ion exchange capacity should increase with decreasing hydrated radii and increases with electrode potential [22]. The ions with smaller hydrated radii easily enter the pores of exchange material, resulting in higher adsorption [23]. The similar results were observed in the case of Zr(IV) iodovanadate, stannic(IV) selenosilicate, stannic(IV) silicomolybdate and stannic(IV) selenoiodate [14,22,24]. The material can be regenerated by keeping it in 1.0 M nitric acid and used over and over again. Even after three regeneration, Ti(IV) iodovanadate loses only 8% of its original ion exchange capacity. The effect of heating on ion exchange capacity of Ti(IV) iodovanadate has been compared with Zr(IV) iodovanadate, Zr(IV) iodomolybdate and tin(IV) iodophosphate. It is apparent from Fig. 1, that Ti(IV) iodovanadate can withstand higher temperature as compared to other cation exchange materials as it retains significant ion exchange capacity even after drying the material up to 800°C . Ti(IV) iodovanadate is therefore superior to other inorganic ion exchange materials. It is observed that, for complete elution of H^+ ions, the concentration of the eluent also plays an important role. The optimum concentration of NaNO_3 as eluent is 1.2 M for maximum release of H^+ ions from 1.0 g of the cation exchange material as shown in Fig. 2. The elution behavior (Fig. 3) depicts that the exchange is quite fast at the beginning and maximum H^+ ions are eluted out in the first 150 mL by using 1.2 M NaNO_3 solution.

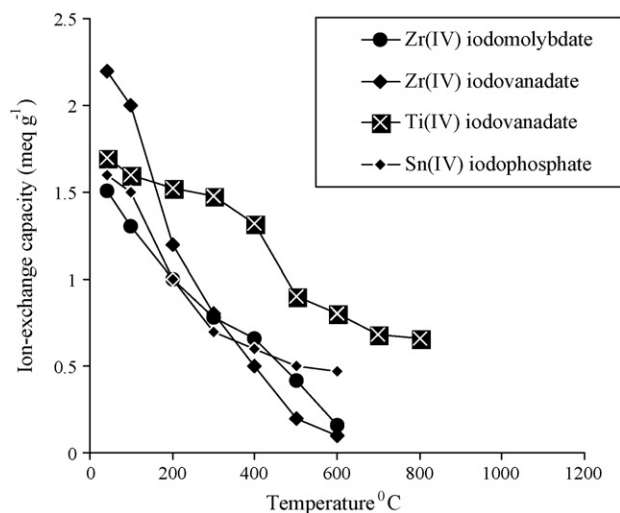
Ti(IV) iodovanadate is quite stable in common acids and bases of moderate concentration and also in organic solvents like dimethyl sulphoxide (DMSO), acetic acid and formic acid (Table 4). The chemical stability of the material may be due to strong covalent bonding, which would have prevented the dissolution of constituent ele-

Table 2

Comparison of the preparation and properties of titanium(IV) iodovanadate with those of other cation exchangers.

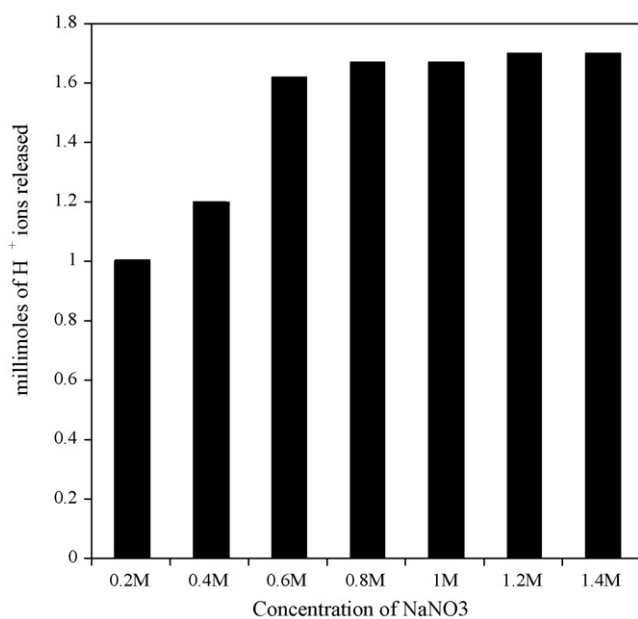
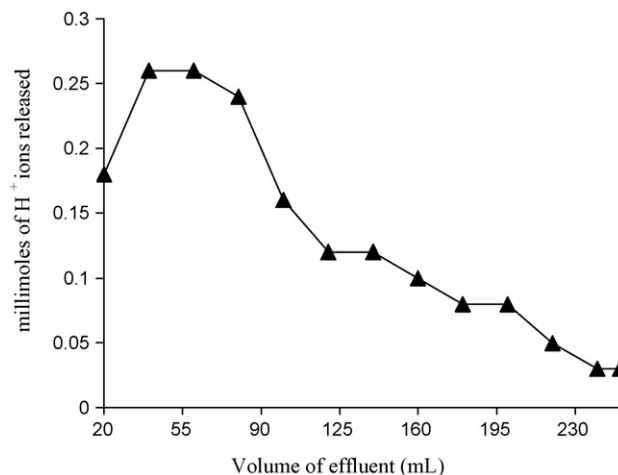
Ion exchange materials	Reagents	Mixing ratio	pH	Ion exchange capacity (mequiv. g ⁻¹) exchanger
Titanium(IV) iodovanadate (present study)	0.1 M T + 0.1 M PI + 0.1 SV	1:2:1	1.0	1.70
Titanium (IV) tungstosilicate [11]	0.1 M T + 0.1 M ST + 0.1 M SS	1:1:1	1.0	0.44
Titanium (IV) tungstophosphate [11]	0.1 M T + 0.1 M ST + 0.1 M OP	1:1:1	1.0	0.80
Titanium(IV) molybdosilicate [28]	0.25 M T + 0.25 M MB + 0.25 M SS	1:0.75:0.75	1.5	0.74
Titanium(IV) molybdophosphate ¹ [29]	0.1 M T + 0.05 M MB + 0.05 M OP	1:1:1	0.8	0.82
Titanium(IV) molybdophosphate ² [29]	0.1 M T + 0.05 M MB + 0.05 M OP	2:1:1	1.0	1.30

M, molar; T, titanium chloride; PI, potassium iodate; SV, sodium vanadate; ST, sodium tungstate; SS, sodium metasilicate; OP, orthophosphoric acid; MB, sodium molybdate.

**Fig. 1.** Comparison of the ion exchange capacity of different ion exchange materials after drying at different temperatures.

ments of the material into the solution. The composition of Ti(IV) iodovanadate was found in the ratio Ti:I:V::1:2:1.

The pH titration in the presence of Ti(IV) iodovanadate was performed for NaCl–NaOH, KCl–KOH, MgCl₂–Mg(OH)₂ and CaCl₂–Ca(OH)₂ systems. The pH titration curves (Fig. 4) show

**Fig. 2.** Effect of eluent concentration on ion exchange capacity of Ti(IV) iodovanadate cation exchanger.**Fig. 3.** Elution behavior of Ti(IV) iodovanadate cation exchanger.

that Ti(IV) iodovanadate releases H⁺ ions easily on addition of mono- and bivalent metal salt solutions. Moreover, Ti(IV) iodovanadate shows monofunctional behavior for monovalent systems and bifunctional behavior for bivalent systems.

The FTIR spectrum of the Ti(IV) iodovanadate (Fig. 5) contains a strong and broad band in the region of 3500–3000 cm⁻¹ which may be due to interstitial water molecule and OH⁻ groups [25]. A sharp peak at 1629 cm⁻¹ corresponds to the deformation vibration of free water molecules. The peak in the region of 970–537 cm⁻¹ indicates the presence of iodate, vanadate groups [26,14] and metal oxide bond. Thus the FTIR spectrum establishes the presence of H₂O, –OH⁻, iodate, vanadate and Ti–O–H in Ti(IV) iodovanadate.

The weak X-ray diffraction intensities (Fig. 6) predict that the material is amorphous in nature.

SEM image of Ti(IV) iodovanadate (Fig. 7) shows that its particles have irregular form. Lack of clearly defined morphology speaks for its amorphous nature.

The TGA–DTA curves of Ti(IV) iodovanadate (Fig. 8) show that 12% weight loss up to 150 °C is due to the removal of external water molecules. Further weight loss from 150 to 390 °C may be

Table 3

Ion exchange capacity of Ti(IV) iodovanadate for various ions.

Exchanging ions	Ionic radii (Å)	Hydrated radii (Å)	IEC (mequiv. dry g ⁻¹) exchanger
Li ⁺	0.68	10.0	0.85
Na ⁺	0.97	7.90	1.70
K ⁺	1.33	5.30	1.75
Mg ²⁺	0.78	10.80	0.76
Ca ²⁺	1.06	9.60	1.80
Sr ²⁺	1.27	9.40	1.94
Ba ²⁺	1.43	8.80	2.07

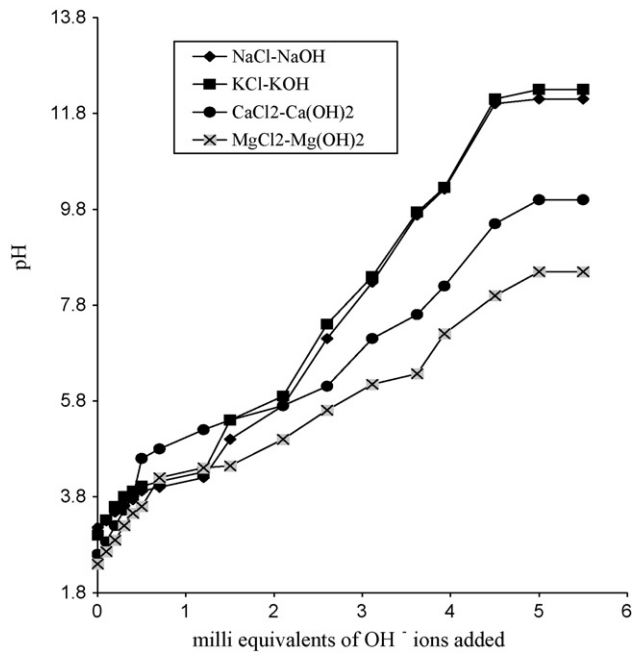


Fig. 4. pH titration curves for Ti(IV) iodovanadate cation exchanger with alkali and alkaline earth metal hydroxides.

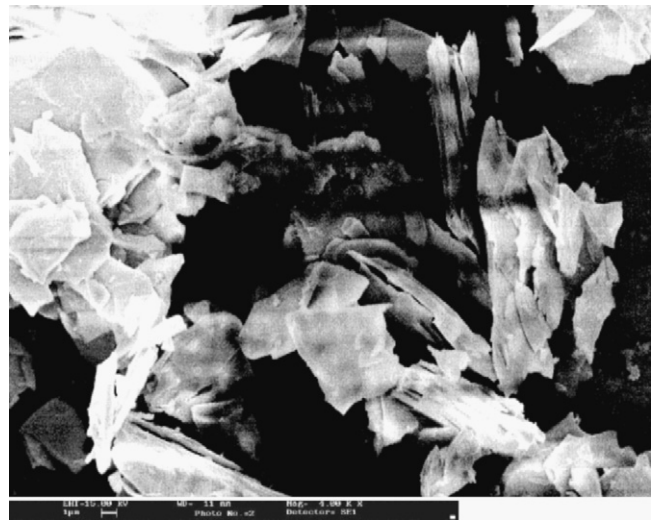


Fig. 7. Scanning electron microphotograph of chemically prepared Ti(IV) iodovanadate at 1.00k× magnification.

due to the removal of water molecule arising from the condensation of hydroxyl groups. There is a sharp weight loss in the region 390–440 °C indicates the volatilization of IO_3^- group [14]. These conclusions are also supported by DTA curve. Beyond 450 °C, the weight becomes almost constant due to the formation of mixed oxides of titanium, iodide and vanadium as final products. The number of external water molecules associated with the structure (per mole of the material) has been calculated by Alberti's equation [27]

$$\% \text{Weight loss} = \frac{18n \times 100}{M + 18n}$$

where $(M + 18)$ is the molecular weight of the material, and “n” is the number of water molecules per mole of the material. It gives the value of “n” as 4.30.

On the basis of chemical composition, FTIR and thermal analysis, a tentative structural formula for Ti(IV) iodovanadate may be assigned as $(\text{Ti})(\text{OH})_4(\text{HIO}_3)_2(\text{HVO}_3)_2 \cdot n\text{H}_2\text{O}$.

Ti(IV) iodovanadate acts as a cation exchange material as well as electron exchange material. In Ti(IV) iodovanadate, IO_3^-/I_2 group is responsible for oxidation process. It has been practically demonstrated that the material can be used for the oxidation of Fe(II) to Fe(III) because IO_3^-/I_2 couple has higher reduction potential than $\text{Fe}^{2+}/\text{Fe}^{3+}$. It is clear from Table 5 that only 40 min are required

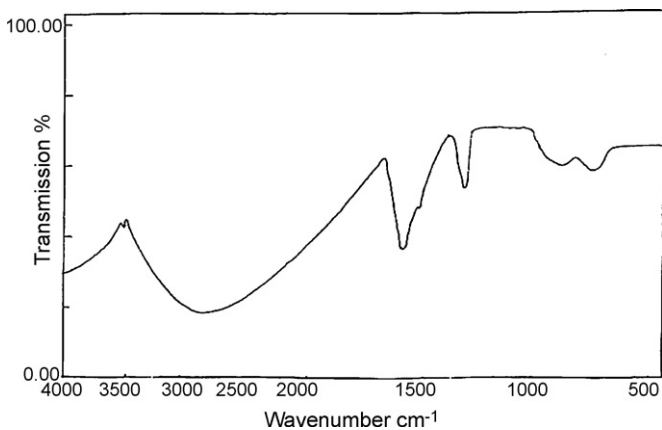


Fig. 5. FTIR spectra of Ti(IV) iodovanadate.

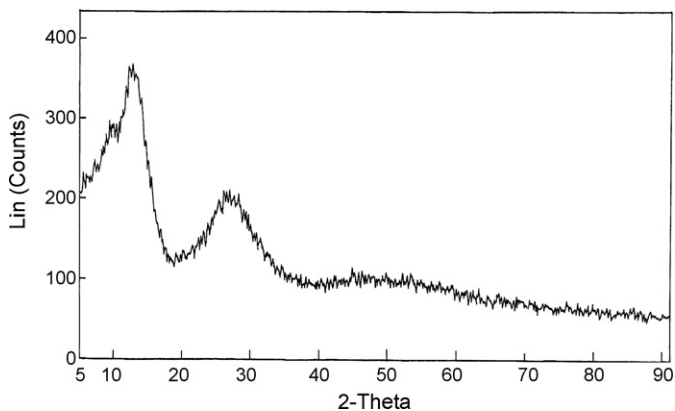


Fig. 6. Powder X-ray diffraction pattern of Ti(IV) iodovanadate.

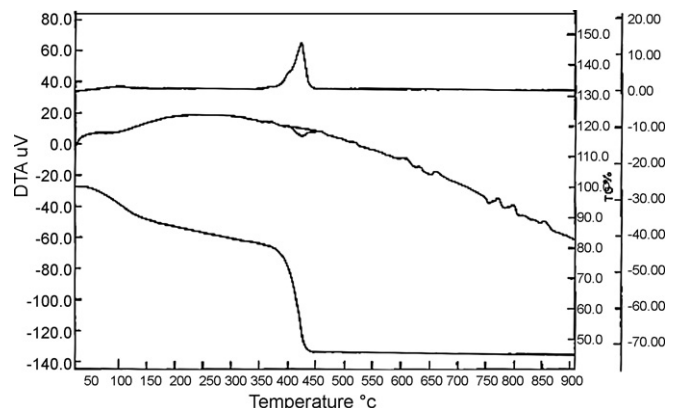


Fig. 8. Simultaneous TGA-DTA curves of Ti(IV) iodovanadate.

Table 4

Solubility of Ti(IV) iodovanadate in various solvents (500 mg of the material was initially taken for the treatment).

Solvents used	Amount released mg. 50 mL ⁻¹ of the solvent		
	Ti	IO ₃ ⁻	VO ₃ ⁻
DMW	0.00	0.00	0.00
0.05 M HCl	2.50	6.00	6.25
1.0 M HCl	4.00	6.70	7.50
0.05 M H ₂ SO ₄	2.15	4.40	5.00
1.0 M H ₂ SO ₄	3.20	5.00	6.50
0.05 M HNO ₃	1.00	1.80	1.75
1.0 M HNO ₃	2.00	2.80	4.25
0.1 M DMSO	0.20	2.00	5.00
0.1 M NaOH	1.50	6.00	3.75
0.1 M KOH	1.50	9.00	2.50
0.1 M CH ₃ COOH	0.30	3.00	7.00
0.1 M HCOOH	0.40	4.00	2.00

DMW, demineralized water.

Table 5

Effect of time for the oxidation of Fe(II) to Fe(III).

S. no.	Amount of ion exchanger ^a (mg)	Time (min)	Amount of Fe ²⁺ taken ^a (mg)	Amount of Fe ³⁺ found ^a (mg)
1	0.5	10	0.16	0.02
2	0.5	20	0.16	0.02
3	0.5	30	0.16	0.05
4	0.5	40	0.16	0.11
5	0.5	50	0.16	0.11
6	0.5	60	0.16	0.11

^a Average of three replicate determinations.

for the maximum conversion of Fe²⁺ to Fe³⁺ by batch process. The results in Table 6 show that Ti(IV) iodovanadate has a remarkable redox property. It was found that the material could not be used for the oxidation of Mn(II)/Mn(III) and Ce(III)/Ce(IV) because the reduction potential of these couples are higher than that of the IO₃⁻/I₂. Probably iodate group in Ti(IV) iodovanadate is bonded at a place which is available for electron exchange with IO₃⁻/I₂ couple and

Table 6

Oxidation of Fe(II) to Fe(III).

S. no.	Amount of ion exchanger ^a (mg)	Amount of Fe ²⁺ taken ^a (mg)	Amount of Fe ³⁺ found ^a (mg)
1	0.5	0.12	0.07
2	0.5	0.16	0.11
3	0.5	0.19	0.14
4	0.5	0.24	0.16

^a Average of three replicate determinations.

responsible for the oxidation of the substrate. The material has also been used for the decomposition of H₂O₂ as given in Section 2.9.

In order to explore the potentiality of this new inorganic cation exchange material in the separation of metal ions, sorption studies for metal ions have been performed in different solvent systems (Table 7). It has been observed that for all metals, *K_d* values decrease with the increase in acidic strength of solvents. It may be due to slower releasing rate of H⁺ ions from the exchange material in strong acidic medium. So less adsorption of metal ions took place by the exchange material. However, in DMSO system the *K_d* values for all metal ions (except Hg²⁺) increase with increasing concentration. The differential behavior of the exchange material for the uptake of metal ions in these solvent systems shows the separation possibilities of certain metal ions of analytical interest from a given mixture. The separation capability of the material has been demonstrated by achieving quantitative binary separations of some important metal ions, viz. Cr³⁺-Pb²⁺, Fe³⁺-Pb²⁺, Zn²⁺-Pb²⁺, Cd²⁺-Pb²⁺, Hg²⁺-Pb²⁺, Ni²⁺-Pb²⁺, Co²⁺-Pb²⁺ and Ce³⁺-Pb²⁺ (Table 8). The sequential elution of ions through column depends upon the metal-ligand stability. The weakly retained metal ions elute first and strongly retained at last. The order of elution and eluents used for binary separations are shown in Fig. 9. The separations are quite sharp and recovery was quantitative and reproducible. The practical utility of these separations was also demonstrated by separating metal ions quantitatively from a synthetic mixture of Pb²⁺, Fe³⁺, Zn²⁺, Cd²⁺, Hg²⁺, Ni²⁺, Co²⁺ and Ce³⁺ (Table 9).

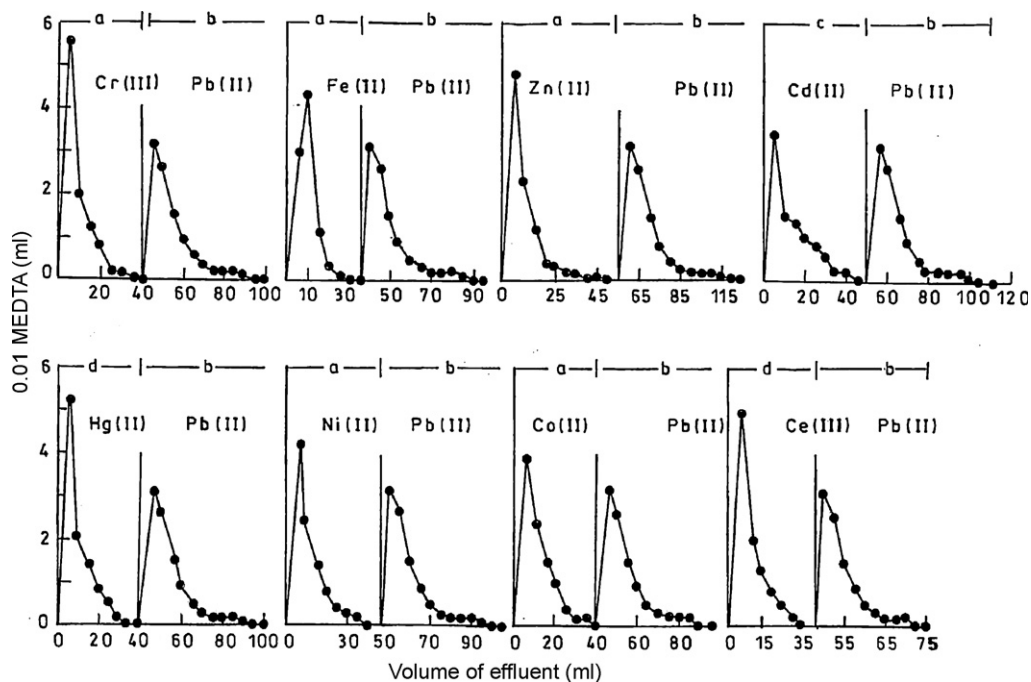


Fig. 9. Chromatograms of binary separations of metal ions on Ti(IV) iodovanadate column.

Table 7
Distribution coefficient (K_d) values of metal ions on Ti(IV) iodovanadate in different solvent systems.

Metal ions	0.1 M HClO ₄	0.1 M HCl	0.1 M HNO ₃	0.1 M HCOOH	0.1 M CH ₃ COOH	0.1 M DMSO	0.5 M DMSO
Cr ³⁺	90	103	263	330	380	63	220
Fe ³⁺	84	96	101	250	402	149	210
Co ²⁺	102	117	170	238	445	163	230
Ni ²⁺	118	129	168	180	554	177	180
Zn ²⁺	119	125	125	175	434	185	190
Cd ²⁺	160	160	192	242	285	172	180
Hg ²⁺	76	93	74	184	192	120	107
Pb ²⁺	1247	1250	1250	1833	1843	1647	1115
Al ³⁺	180	258	270	310	390	190	196
Ce ³⁺	120	132	160	160	610	113	188

Table 8
Quantitative separation of metal ions from a binary mixture using Ti(IV) iodovanadate column at room temperature.

S. no.	Metal ions separation	Amount loaded ^a (mg)	Amount found ^a (mg)	% Recovery	% Error	Volume of eluent used (mL)	Eluent used
1	Cr ³⁺	2.59	2.56	98.84	-1.16	70	0.1 M HClO ₄
	Pb ²⁺	10.36	10.30	99.42	-0.58	90	0.1 M DMSO
2	Fe ³⁺	2.79	2.53	90.68	-9.32	50	0.1 M HClO ₄
	Pb ²⁺	10.36	10.30	99.42	-0.58	90	0.1 M DMSO
3	Zn ²⁺	3.28	3.15	96.03	-0.397	70	0.1 M HClO ₄
	Pb ²⁺	10.36	10.30	99.42	-0.58	90	0.1 M DMSO
4	Cd ²⁺	5.62	5.56	98.93	-1.07	70	0.1 M HCl
	Pb ²⁺	10.36	10.30	99.42	-0.58	90	0.1 M DMSO
5	Hg ²⁺	10.02	9.82	98.09	-1.91	60	0.1 M HNO ₃
	Pb ²⁺	10.36	10.30	99.42	-0.58	90	0.1 M DMSO
6	Ni ²⁺	2.93	2.89	98.63	-1.37	60	0.1 M HClO ₄
	Pb ²⁺	10.36	10.30	99.42	-0.58	90	0.1 M DMSO
7	Co ²⁺	2.95	2.91	98.64	-1.36	60	0.1 M HClO ₄
	Pb ²⁺	10.36	10.30	99.42	-0.58	90	0.1 M DMSO
8	Ce ³⁺	14.01	13.98	99.78	-0.22	70	0.1 M HNO ₃
	Pb ²⁺	10.36	10.30	99.42	-0.58	90	0.1 M DMSO

^a Average of three replicate determinations.

Table 9
Selective separations of Pb²⁺ from a synthetic mixture of Pb²⁺ (8.28–14.50 mg), Fe³⁺ (2.79 mg), Zn²⁺ (3.27 mg), Cd²⁺ (5.62 mg), Hg²⁺ (10.03 mg), Ni²⁺ (2.93 mg), Co²⁺ (2.94 mg), and Ce³⁺ (7.00 mg) using Ti(IV) iodovanadate columns.

S. no.	Amount of Pb ²⁺ loaded ^a (mg)	Amount of Pb ²⁺ found ^a (mg)	% Recovery	% Error	Eluent used 0.1 M DMSO (mL)
1	8.28	8.22	99.27	-0.73	80
2	10.36	10.24	98.84	-1.16	90
3	12.42	12.16	97.90	-2.10	95
4	14.50	14.32	98.75	-1.25	100

^a Average of three replicate determinations.

4. Conclusion

The proposed exchange material Ti(IV) iodovanadate has good ion exchange capacity, chemical stability and selectivity for metal ions. The material has been used for the oxidation of Fe(II) to Fe(III) and for the decomposition of hydrogen peroxide. The practical utility of the material has also been demonstrated by separating metal ions quantitatively from a synthetic mixture using packed column of Ti(IV) iodovanadate.

Acknowledgement

One of the authors (Dr. Mu. Naushad) is thankful to the Chairman, A.M.U. Aligarh, India, for providing all necessary facilities.

References

- [1] R. Harjula, J. Lehto, A. Paajanen, E. Tusa, P. Yarnell, Use inorganic ion exchange materials as precoat filters for nuclear waste effluent treatment, *React. Funct. Polym.* 60 (2004) 85.
- [2] G.I. Cathers, *Prog. Nucl. Energy* 3 (1965) 168; C.B. Amphlett, *Proceedings of 2nd Conference Peaceful uses of Atomic Energy*, Geneva, 1958, p. 2817.
- [3] M. Qureshi, K.G. Varshney, *Inorganic Ion Exchangers in Chemical Analysis*, CRC Press, Boca Raton, FL, USA, 1991.
- [4] K.G. Varshney, S.M. Maheshwari, Synthesis, characterization and ion exchange behavior of antimony(V) phosphate: selective adsorption of cadmium and mercury on its column, *Ecotoxicol. Environ. Saf.* 18 (1989) 1.
- [5] M. Qureshi, J.P. Gupta, H. Khan, A. Ahmad, Ion-exchange properties of niobium(V) materials. II. Synthesis and characterization of crystalline niobium(V) phosphate, *Bull. Chem. Soc. Jpn.* 61 (1988) 2181.
- [6] K.V.S. Nath, S.N. Tandon, Synthesis and characterization of a new crystalline tin(IV) arsenophosphate ion exchanger, *Can. J. Chem.* 68 (1990) 346.
- [7] A.P. Gupta, Renuka, Studies on araldite based zirconium tungstophosphate membrane—a lead(II) ion selective electrode, *Ind. J. Chem.* 36 (1997) 1073.
- [8] Z.R. Turel, S.S. Narkhade, Radiochromatographic separation of scandium(III) with inorganic ion exchanger zirconium phosphosilicate, *J. Ind. Chem. Soc.* 75 (1998) 172.
- [9] A. Shivaneekar, U. Chudasama, U. Gupta, K.G. Varshney, Synthesis, characterisation and catalytic activity of (Cu(NH₃)₄)²⁺ bound to zirconium arsenophosphate, *J. Ind. Chem. Soc.* 77 (2000) 5.
- [10] Z.M. Siddiqi, D. Pathania, Titanium(IV) tungstosilicate and titanium(IV) tungstophosphate: two new inorganic ion exchangers, *J. Chromatogr. A* 987 (2004) 147.

- [11] M. Qureshi, N. Zehra, S.A. Nabi, V. Kumar, Comparative study of titanium(IV)-based exchangers in aqueous and mixed solvent systems, *Talanta* 20 (1973) 609.
- [12] M. Qureshi, J.P. Gupta, Synthesis of a poorly crystalline titanium tungstate: separation of Hf^{4+} from Zr^{4+} and of La^{3+} from Ce^{3+} , Pr^{3+} , Nd^{3+} and Sm^{3+} , *J. Chromatogr.* 62 (1971) 439.
- [13] M. Qureshi, J.P. Gupta, V. Sharma, Comparison of the ion-exchange behaviour of zirconium, thorium, vanadium, uranium, stannic and titanium tungstates, *Talanta* 21 (1974) 102.
- [14] P.V. Singh, J.P. Rawat, N. Rahman, Synthesis and characterization of zirconium(IV) iodovanadate and its use as electron exchanger, *Talanta* 59 (2003) 443.
- [15] J.P. Rawat, M. Bhardwaj, Electron exchange studies on stannic molybdate, *J. Indian Chem. Soc.* 78 (2001) 13.
- [16] F.D. Snell, C.T. Snell, *Colorimetric Methods of Analysis*, vol. 11, D. van Nostrand, Princeton, NJ, 1949, p. 325.
- [17] F.D. Snell, C.T. Snell, *Colorimetric Methods of Analysis*, vol. 11, D. van Nostrand, Princeton, NJ, 1949, 741, p. 335.
- [18] S.A. Nabi, S.A. Ganai, Mu. Naushad, A new Pb^{2+} ion selective hybrid cation-exchanger-EDTA-zirconium iodate: synthesis, characterization and analytical applications, *AST* 26 (6) (2009) 1.
- [19] I.M. Kolthoff, R. Belcher, *Volumetric Analysis*, vol. 3, Interscience, New York, 1957.
- [20] B. Beena, A. Shivaneekar, U. Chudasama, Catalytic activity of Pd(II) sorbed on an inorganic ion exchanger-zirconium molybdate, *J. Mol. Catal.* 107 (1996) 347.
- [21] A. Shivaneekar, U. Chudasama, Catalytic behaviour of a Cu(II) complex sorbed on zirconium molybdate in the decomposition of hydrogen peroxide, *Trans. Met. Chem.* 15 (1990) 226.
- [22] S.A. Nabi, A.M. Khan, Synthesis, ion exchange properties and analytical applications of stannic silicomolybdate: effect of temperature on distribution coefficients of metal ions, *React. Funct. Polym.* 66 (2006) 495.
- [23] S.A. Nabi, Mu. Naushad, Synthesis, characterization and analytical applications of a new composite cation exchanger cellulose acetate-Zr(IV) molybdophosphate, *Colloids Surf. A: Physicochem. Eng. Aspects* 316 (2008) 217.
- [24] S.A. Nabi, A.M. Khan, Ion-exchange behavior of stannic seleniodate and stannic selenosilicate: analytical application of stannic seleniodate, *Anal. Bioanal. Chem.* 382 (2005) 1163.
- [25] M. Davis, *Infrared Spectroscopy and Molecular Structure*, Elsevier Publishing Co., Amsterdam, 1963, p. 318.
- [26] G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley, New York, 1980, p. 145.
- [27] G. Alberti, E. Torocca, A. Conte, Influence of thermal treatment on the rate of ion-exchange of zirconium phosphate, *J. Inorg. Nucl. Chem.* 28 (1966) 607.
- [28] S.A. Nabi, A.H. Shalla, A.M. Khan, S.A. Ganie, Synthesis, characterization and analytical applications of titanium(IV) molybdosilicate: A cation ion-exchanger, *Colloids Surf. A: Physicochem. Eng. Aspects* 302 (2007) 241.
- [29] R. Yavari, S.J. Ahmadi, Y.D. Huang, A.R. Khanchi, G. Bagheri, J.M. He, Synthesis, characterization and analytical application of a new inorganic cation exchanger-Titanium(IV) molybdophosphate, *Talanta* 77 (2009) 1179.