Synthesis, Characterisation and Applications of Zirconium Phosphate Nanocomposite Ion Exchange Material

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Dissertation submitted in
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Submitted by

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Certificate

This is to certify that the dissertation entitled **"Synthesis, Characterisation and Applications of Zirconium Phosphate Nanocomposite Ion Exchange Material"**, being submitted by Miss Neeraj in the partial fulfillment of the requirements for the award of the degree of Master of Science in Chemistry in the School of Chemistry and Biochemistry at Thapar University, Patiala, is a bonafide work carried out under the supervision of Dr. Susheel Mittal and no part of this project has been submitted for the award of any other degree.

Susheel Mittal 13.7.17

(Supervisor)

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Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled **"Synthesis, Characterisation and Applications of Zirconium Phosphate Nanocomposite Ion Exchange Material"**, in partial fulfilment of the requirements for the award of the degree of Master of Science in Chemistry at School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of January 2017 to July 2017, under the supervision of **Dr. Susheel Mittal.** My dissertation has not previously formed the basis for the award of any degree, or other similar title or recognition.

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Patiala
Date: 13/7/17

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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List of Content

Abstract

Zirconium Phosphate (ZrP) based ion exchangers were prepared and modified with CNTs in different proportions (ZrP-CNT). Different amounts of CNT ranging from 0.01% to 0.1% were incorporated in the framework of ZrP. Ion exchange capacity of each of the prepared ion exchanger was tested and found that CNT (0.1%) based Zirconium Phosphate nanocomposite had better ion exchange characteristics. Further, thermal stability and chemical stability studies were also performed. It was found that ZrP-CNT material retains its structure even at higher temperature, i.e., at 400° C and has good chemical stability in strong acids, salt solutions and organic solvents except in NaOH solution. Potentiometric titration of ZrP and ZrP-CNT nanocomposites suggests that they are weakly acidic and monofunctional in nature. With the incorporation of CNTs during synthesis of the ZrP material, the ion exchange capacity improved by about 40%.

Chapter 1 Introduction

Ion exchangers are the water insoluble solid substances containing loosely held ions that can exchange positive or negative charged ions in an electrolyte solution. Ion exchangers can be classified as anion exchangers or cation exchanger depending upon whether the exchangeable counter ion is anion or cation. Another type of ion exchangers, which can exchange both positively and negatively, charged ions are known as amphoteric ion exchangers. There are large numbers of inorganic compounds, which show the property of ion exchange such as clays, zeolite, cellulose, proteins that play important role in the nature functionality. Many phosphates, titanates, heteropolyacid salts and layered double hydroxides possess the properties of ion exchangers [1].

Ion exchangers involve inorganic, organic and synthetic ion exchangers. Inorganic ion exchangers have high selectivity for particular ions resulting in much larger separation factors than those of organic resins [2]. Inorganic ion exchangers have rigid structure and during ion exchange reaction, they do not undergo appreciable dimensional change. The rigid structure of ion exchangers leads to its unusual and specific selectivity. Ion exchange materials have been widely used for the remediation of environmental pollution [3].

1.1 Classification of inorganic ion exchangers

Clearfield [4] broadly classified inorganic ion exchangers into three categories:

1.1.1 Hydrous oxides: The hydrous oxides are divided into two main types called as particle hydrates and framework hydrates. Particle hydrates are formed by most of the group 3, 4, 13, and 14 metals. They are having a bulk structure, which is similar to one of their ceramic oxides. The surface of this group is mostly covered with hydroxyl groups. Most of groups 5 and 15 metals in their higher oxidation states form framework hydrates. Amorphous product is formed when hydrous antimony (V) oxide is precipitated. Framework hydrates are mostly poor crystalline hydrous oxides. The crystallinity can be improved by refluxing in acid media or by hydrothermal treatment. The improvement in the crystallinity of these hydrous oxides results in more accurate determination of elemental content, some variation in selectivity and better regular titration curves [5].

1.1.2 Layered ion exchangers: Layered ion exchangers consist of

(a) *Oxides*: The ternary oxides can be usually determined from single crystal analysis due to their highly crystalline structure. The interlayer distance is small and many of them have a limited range of swelling capacity.

(b) *Phosphates of group 4 and 14*: Ion exchangers of these elements were firstly prepared as amorphous gels. Phosphated hydrous oxides have layered structure with composition Zr-$(HPO_4)_2.xH_2O$. The metal atoms in these ion exchangers are bridged by phosphate groups, which are located above and below the mean plane. Three oxygen atoms of phosphate group are bonded to Zr atom and the fourth one bonds to a proton. The staggered layer structure of this ion exchanger resembles the hexagonally shaped cavity. The water molecules stay in pocket cavity formed by three P-OH groups. The Vander waal forces hold the layers together and the water molecules are bonded to P-OH groups by hydrogen bonding on the top side of one cavity or bottom side of the adjacent layer. The phosphates of group 4 and 14 are most widely studied.

(c) *Double layer hydroxides*: These is an interesting class of layered compounds and their general composition can be represented as $M^{II}_n.M^{III}(OH)_{2n+2}X$, where n = 2-5 and X is charge balancing anion.

1.1.3 Exchangers with tunnel structure

Exchangers with tunnel structure were reported by Clearfield in 1988 [6]. Ion exchangers with octahedral tunnel dimensions are suitable for exchange of hydrated Mg^{2+} ions. These compounds are readily converted into H^+ form and have remarkable selectivity. A titanium silicate of ideal formula $Na_2Ti_2O_3(SiO_4).2H_2O$ is an example of this group and highly selective for Cs^+ and Sr^{2+} ions. It has a tetragonal unit cell with approximate cell dimensions of a=b=7.8 Å and c= 12.0 Å [5]. TiO_6 octahedra and SiO_4 tetrahedra formed the structure of the titanium silicate. Cations are resides in the tunnels of this structure and it is easier to exchange the ion within the tunnel rather than in framework.

1.2 Characteristics of an ideal ion exchanger

1. Effective and controlled ion exchange capacity
2. A hydrophilic gel structure of reproducible and regular form
3. Good resistance, both in chemical and mechanical respects

4. Higher chemical stability
5. Operate rapidly i.e., equilibrium is rapidly reached
6. Consistent particle size and effective surface area

1.3 Nanocomposites ion exchange materials

Nanocomposites are composites in which at least one of the phases show dimensions in the nanometer range (1 nm = 10^{-9} m) [7]. There are three types of nanocomposites, depending on how many dimensions of the dispersed particles are in the nanometer range [8]. Isodimensional nanoparticles are those, which have their three dimensions in nanometer range such as spherical silica nanoparticles obtained by sol-gel methods or by polymerization. It also includes semiconductor nanoclusters. Carbon nanotubes is example of those nanocomposites in which two dimensions are in the nanometer range and the third one is larger leading to the formation of an elongated structure. These types of nanocomposites are mostly studied as reinforcing nanofillers yielding materials with different properties. The nanocomposites of third type includes only one dimension in the nanometer range and filler is present in the form of sheets of one to a few nanometer thick from hundreds to thousands nanometers long [8].

Nanocomposites are the materials synthesized to overcome limitations of the macrocomposite and microcomposite materials. Nanocomposite materials are classified as:

1. Ceramic Matrix Nanocomposites
2. Metal Matrix Nanocomposites
3. Polymer Matrix Nanocomposites

The nanoparticles can act as matrix reinforcement and interactions at phase interfaces leads to enhance properties of the base materials [7]. In order to study the structure-property relationships of nanocomposite materials, surface area/volume ratio of reinforcement materials plays an important role. Nanocomposite plastics were synthesized in 1970's by using sol-gel method and it form homogenous dispersion of small inorganic particles. Nanocomposite CNTs were discovered in 1991. CNTs have hollow nature due to which they can be filled by variety of materials, which leads to new

applications [9]. They improve the electrical and thermal conductivity. Properties of the nanocomposite materials depend upon both the properties of individual parents and also on the interfacial characteristics and morphology [10]. Nanoparticles synthesis put control on the properties of the materials like their magnetic properties, melting temperature, charge capacity and color without any change in its chemical composition [10]. Covalently functionalized nanotubes give better transfer of stress between the polymer matrix and the nanofiller [11].

Nanocomposites enhance the properties like:

1) Thermal stability
2) Chemical resistance
3) Mechanical properties like strength, modulus and dimensional stability
4) Flame retardancy
5) Electrical conductivity
7) Barrier and membrane separations

1.4 Advantages of nanocomposite over the bulk materials

Nanocomposites have difference from bulk materials because they have high surface to volume ratio, which leads to many application of nanocomposite materials over bulk materials. Nanocomposite synthesis that have controlled functionality and hydrophobicity gives application in the organic chemistry, analytical chemistry, organic host guest chemistry, hydrometallurgy, antibiotic purification, separation of radioactive isotopes, water treatment and pollution [10]. Nanocomposites are used in drug delivery systems, anti-corrosion barrier coatings, lubricants and scratch free paints, new fire retardant materials, superior strength fibers and films, environmental remediation, making lightweight sensors, preparation of electronics and nanoelectronics devices. In recent years, nanocomposite ion exchangers are used as photocatalysts for the degradation of dyes.

Clearfield (1995) classified inorganic ion exchangers into the three different categories i.e., hydrous oxides, layered compounds and exchangers with tunnel structures. Many of these inorganic ion exchangers can be used in hot organic solvents or in corrosive media due to their high selectivity. Clearfield reported that removal of the traces of metals for effective separation was too difficult to achieve with organic resins as compared to inorganic ion exchangers [4]. Insoluble ion exchange materials were synthesized by precipitation from metal salt solution with Na_2S, H_2S and their ion exchange properties were investigated. Generally, amorphous and crystalline forms of metal acid salts having general formula M(IV) $(HXO_4)_2.nH_2O$, where M may be Sn(IV), Zr(IV), Ti(IV) etc. and X may be P, W, Si, Sb, Se etc. were called single salts [12]. Many single salts based ion exchangers like Zirconium (IV) antimonate [13], Zirconium (IV) phosphate [14], Tin (IV) antimonate [15] etc. were characterized. The study about mixed salts showed that they had better ion exchange properties than single salts. Double salts of Tin and Zirconium had showed the better ion exchange properties [12, 16]. However, it was found that single insoluble salts of the metals have many limitations. Heteropolyacid salts were also synthesized to overcome the limitations of single salt ion exchangers [17]. Heteropolyacid salts were prepared by condensing two or more different types of anions. Ammonium phosphotungstate and ammonium molybdophosphate were first materials prepared of this type [18].

A new organic-inorganic hybrid material i.e., polyaniline Zr (IV) tungstoiodophosphate was synthesized by sol-gel method by Mispa *et al.,* (2013). The organic polymeric part of the nanocomposite material reinforced mechanical and chemical stability, whereas, inorganic part enhances the thermal stability, electrical conductivity and ion-exchange behavior. The reported nanocomposite was selective for Pb^{2+} metal ion and can be used in the formation of Pb^{2+} ion selective membrane electrode. Nanocomposite material showed antimicrobial activity against E.coli and proteus vulgaris [19].

Naushad (2014) synthesized nanocomposite cation exchanger sodium dodecyl sulfate acrylamide Zr(IV) selenite (SDS-AZS) by sol–gel method. The reported nanocomposite

cation exchange material SDS-AZS was a potential material selective for Pb^{2+} from aqueous solution and which adsorbed >90% Pb^{2+} metal ions within 40 min. Freundlich model was the best fit model studied by adsorption isotherm. Kinetic studies showed that pseudo-first order model was applicable. The studied show that by using 0.01 M HNO_3 solution Pb^{2+} ion was recovered and regenerated SDS-AZS nanocomposite material was used up to 4 consecutives cycles without any loss in absorption of Pb^{2+} [20].

ALOthman *et al.,* (2015) synthesized a conducting polymeric-inorganic nanocomposite i.e., polyaniline Sn(IV) tungstomolybdate (PSTM) by sol-gel method. The PSTM nanocomposite showed effective ion exchange properties and thermal activated behavior from temperature range 30 to 200 ^oC. The electroactive material PSTM was used for formation of ion selective membrane electrode, which was selective for Pb^{2+} ions [21].

Pectin@zirconium(IV) silicophosphate (Pc/ZSPNC) nanocomposite ion exchange material synthesized by using simple sol–gel method by Pathania *et al.,* (2015). The ion exchange capacity of Pc/ZSPNC was higher (1.01 meq/g) than its inorganic counterpart (0.56 meq/g) and thermal study showed that it was more stable and exhibited 59% ion exchange capacity at 400^oC. Pc/ZSPNC used for photocatalytic activity to degrade the methylene blue dye and 97.02% of methylene blue dye was degraded within 60 min and kinetically pseudo-first- order was followed. Pc/ZSPNC nanocomposite material showed antimicrobial activity by inhibiting the growth of Escherichia coli and Staphylococcus aureus bacteria [22].

A conducting polymer-based polyaniline Zirconium(IV) selenotungstophosphate (PANI/ZSWP) nanocomposite ion exchange material synthesized by sol-gel method (Sharma *et al.,* 2015). The nanocomposite ion exchanger had high ion exchange capacity (1.20 meq g^{-1}) than its inorganic counterpart ZSWP. DC conductivity of reported nanocomposite was selective for Cu^{2+} and Ca^{2+} metal ions from synthetic mixture [23].

Kaushal *et al.,* (2016) prepared poly-o-toluidine-zirconium phosphoborate (PTD-ZrPB) by sol-gel method. PTD-ZrPB was utilized as electro-active material for fabrication of ion-selective membrane electrode for Hg(II) ions. Composite membrane was found to be selective for Hg^{2+} ions with detection limit 0.014 ppm, response time of 6 seconds and 6

months lifetime. The Hg^{2+} ions were estimated in the tap water, thermometer unit waste, CFL unit waste water by potentiometric titrations [24].

Silbernagel *et al.,* (2016) synthesized layered metal phosphonate-phosphate hybrid with general formula $Zr\text{-}(O_6P_2C_6H_4)_{1-x/2}(O_3POH)_x.nH_2O$ by varying the value of X i.e., X = 0.5, 0.8, 1.33, 1.6. Composite material has high preference for highly charged ions (+3) as compared to low charged ions (+1 and +2). Reported composite material altered the selectivity by the addition of large excess amount of phosphate and these materials were used to remove all ions from solution without any concern of charge [25].

Kaushal *et al.,* (2016) prepared new form of nanocomposite ion exchanger Zirconium phosphoborate (ZrPB) by incorporating multiwalled carbon nanotubes (CNTs) through sol-gel method. SEM images showed that ion exchanger particles have spherical shape and TEM images confirmed the size of ion exchanger was 2-5 nm. The reported nanocomposite material show decrease in ion exchange capacity by additive loading of CNTs and degrade the methylene blue dye completely under UV-radiations. ZrPB-CNTs used as photocatalyst for water purification, solar cell in electronics, water splitting and as antimicrobial agent [26].

Jiang *et al.,* (2016) used photoactive cation N, N$^{'}$-Dimenthyl-9, 9$^{'}$-bisarcridinium nitrate (BNMA) with exfoliated layered α-ZrP by an electrostatic layer-by-layer assembly method. The reported nanocomposite materials lifetime prolonged by 16-fold because of isolation effect of nanosheets and migration of hydrogen ions between the interlayers. α-ZrP used for designing new optical devices and chemical sensors [27].

Lee *et al.,* (2016) studied the identification of best column material as an absorbent for the $^{68}Ge/\ ^{68}Ga$ generator system. Four different type of zirconium phosphates were prepared having pore size 55 -190 Å, particle size 200-800 nm and surface area 0.72-268 $m^2\ g^{-1}$. Amorphous zirconium (ZrP-1) which was synthesized by mixing 50 mL of a zirconium (IV) propoxide 3M solution and 100 mL of 5 wt% H_3PO_4. Study showed that from four different Zirconium phosphates, ZrP-1 showed the more chemical stability, surface area and thermal stability. Most interesting feature shown by ZrP is that ability

for absorption and desorption of ^{68}Gawith very low ^{68}Ge breakthrough and used as a column material with high potential for a ^{68}Ge/ ^{68}Ga generator system [28].

Sharma *et al.,* (2017) synthesized sodium dodecyl sulphate-ironsilicophosphate (SDS-FeSP) nanocomposite by co-precipitation method. The ion exchange capacity of SDS-FeSP was 1.45 meq/g i.e., higher than its inorganic counterpart FeSP (0.40 meq/g). SDS-FeSP was highly selective for Zn^{2+} and Mg^{2+} metal ions [29].

Pathania *et al.,* (2017) synthesized Lactic acid-Zr(IV) phosphate nanocomposite (LA/ZPNC) by sol-gel method. It was reported that LA/ZPNC has higher value of ion exchange capacity as compared to its inorganic part. Nanocomposite has bifunctional nature studied by pH titrations and highly selective for Al^{3+}. The results of photocatalytic studies showed that the nanocomposite degrade the 89.47% methylene blue dye in 4 hour illumination and used for binary separation [30].

Zirconium tetraphenylporphyrin was encapsulated into dealuminated Y zeolite by template synthesis method. ZrTPP-DAZY nanocomposite has catalytic activity, which was observed in the oximation of aromatic and aliphatic aldehydes. It was reported that ZrTPP-DAZY was recycled and reused without any loss of its catalytic activity (Moosavifar *et al.,* 2017) [33].

Pathania *et al.,* (2017) synthesized alginate-Zr(IV) phosphate nanocomposite (AG/ZPNC) ion exchange material was synthesized by sol-gel method and highly selective for Al^{3+} metal ion. The nanocomposite material was found to degrade 94.45% of MB and 92.43% of FG in solar illumination of 5 hours and inhibit the growth of E.*coli* bacteria by binding with its outer membrane [34].

ZnS/C nanocomposite was synthesized by solvothermal process with carbonization treatmentby Du *et al.,* (2017). The reported ZnS/C nanocomposite was used as anode material with high specific capacity for Lithium ion batteries and exhibited high rate capability and cycling stability. ZnS/C showed good electrochemical performance, which led to describe its hierarchical structure [35].

Chapter 3 Materials and Methods

3.1 Materials

Zirconyl oxychloride and orthophosphoric acid were purchased from Loba Chemie, India and hydrochloric acid from Merck, India. Multi-walled carbon Nanotubes-COOH (MWCNT-COOH) with 10-30 nm diameter, 1 µM length and >95% purity were obtained from Nanoshel (USA) and used for the synthesis. All other solutions for analytical work were prepared in double distilled water by direct weighing of AR grade chemicals or by indirect standardization.

3.2 Methods

3.2.1 Synthesis of Zirconium Phosphate without CNTs

Zirconium phosphate was prepared by adding Zirconyl oxychloride (0.1 M) solution prepared in hydrochloric acid (0.1 M) to a continuously stirred solution of orthophosphoric acid (0.1 M) at 60º C in volume ratio 1:1. White gelatinous precipitates were obtained and noted pH of the gel. Precipitates were filtered and washed with distilled water till precipitates became chloride and acid free. The filtered gel was kept for drying at 40º C in air oven. The dried residue broke down into small granules after immersing in water. The material was then converted into H^+-form by keeping it in HCl (0.1 M) for 24 hours and washed with distilled water to remove the excess acid and then dried again at 40º C.

3.2.2 Synthesis of Zirconium Phosphate with CNTs

Zirconium phosphate with CNTs can be prepared by sol-gel method. Three samples were prepared by sonication of different amounts of CNTs (w/w, 0.01%, 0.05%, 0.1%) in zirconyl oxychloride (0.1 M) solution. Zirconyl oxychloride with different amount of CNTs was added to continuously stirred orthophosphoric (0.1 M) solution with volume ratio 1:1, respectively. The precipitates thus obtained were filtered and washed with distilled water till they become free from chloride and acids. The residue was kept at 40º C for drying and then immersed in distilled water. The residue broke down into small

granules, converted into H^+-form by keeping it in HCl (0.1 N) for 24 hours, washed with distilled water to remove excess acid, and dried again at 40º C.

3.2.3 Ion exchange capacity of monovalent and divalent cations

Column operation was used for the determining the ion exchange capacity of different samples of ZrP. 0.5 g of ion exchanger in H^+-form was taken in a glass column with the support of glass wool. 200 mL of each electrolyte solution was eluted through the glass column with the rate of 10-12 drops per minute. The protons were liberated in each different solution and then these solutions were titrated against the standardized NaOH solution. Ion exchange capacity of different monovalent and divalent cations was determined.

3.2.4 Regeneration of ion-exchangers

The used ZrP ion exchanger was regenerated by placing it in the hydrochloric acid (0.1 M) overnight. The exchanger material was washed with deionized water repeatedly to remove excess of the acid. Ion exchange capacity of the regenerated ion exchanger was noted again. This procedure was repeated 5 times to see regeneration capacity of the exchanger.

3.2.5 Thermal stability

1.5 g of ZrP ion exchangers were taken in two prewashed silica crucibles. These silica crucibles were placed in a muffle furnace maintained at 100º, 200º, 300°, 400º C, respectively. All the four samples were ignited separately for 2 hours at each selected temperature and after cooling to room temperature their weights were measured. Ion exchange capacity of each ignited sample was determined by above procedure. Ion exchange capacity was determined by above procedure for all the heated samples. Further, their conformational changes were determined by scanning electron microscopy and infrared spectroscopy techniques.

3.2.6 Chemical stability

0.2 g of ZrP ion exchangers were kept in 20 mL of different solvents, separately for 24 hours and then filtered. Phosphorous [34] was determined in the filtrate of above samples, spectrophotometrically.

3.2.7 Potentiometric titrations

The pH titrations of ZrP ion exchanger were carried out with sodium hydroxide (0.1 M) by the added salt method [35]. 0.2 g of ion exchanger was placed for 24 hours in contact with different volumes of salt solution and base and pH of the supernatant liquids were recorded.

3.2.8 Characterisation of ZrP ion exchanger

Powder X-ray diffraction (XRD) studies for four different ion exchanger samples of ZrP were determined by using an XPERT-PRO diffractometer (Cu Kα, λ = 0.15406 nm, 45 kV, 40 mA, step size = 0.013°). Data was examined between 5^o to 35^o. The size, shape and morphology was examined by using JEOL (JSM-6510LV) scanning electron microscope. For chemical composition of four different ion exchangers of ZrP, EDS (INCA x-act Oxford) instrument was used. Fourier transform infrared (FTIR) studies were determined by using Agilent Resolutions Pro (Cary 660) by preparing KBr pellets in volume ratio of 1:100 (sample:KBr).

ZrP was first synthesized by Clearfield *et al.*, [36] and the material was studied extensively by many research workers over the last four decades. ZrP is reported to be a chemically and thermally stable ion exchanger with a high ion exchange capacity of (6.64 meq/g) [37]. The present investigation was done to see if ion exchange capacity of the material can be enhanced by incorporating CNTs while maintaining its ion exchanger character. CNTs of 10-30 nm diameter and 1 μm length and functionalized with COOH group were used in the three different ratios i.e., 0.01%, 0.05%, 0.1% (w/w) during synthesis of the material by sol-gel method. An acidic solution of $ZrOCl_2$ containing appropriate amounts of the functionalized CNTs were sonicated before its addition to the stirred solution of phosphoric acid with constant heating arrangement of 60º C. The addition of 250 mL of $ZrOCl_2$ solution was completed in 10 minutes. The gel so obtained was stirred at 60º C for an hour and allowed to settle. The supernatant liquid was decanted and precipitates were washed with double distilled water. The ZrP gel free of chloride and phosphate ions was filtered using Buchner funnel. The material was dried and converted to H^+ ions after addition of water to the dried material, which broke down into fine granules with a crackling sound.

An analogous material of ZrP was synthesized without incorporation of CNTs. The material was prepared in different batches and after checking ion exchange capacity of each batch, they were mixed to form one lot.

4.1 Enhancement in ion exchange capacity

Ion exchange capacity of different lots of the material ZrP and ZrP-CNT were tested for Na^+ ions. As expected, there was an enhancement in the ion exchange capacity of samples containing CNTs. Results of ion exchange capacity with increased amount of CNTs are shown in Table 1, where maximum ion exchange capacity (0.34 meq/g) is obtained for ZrP with CNTs content of 0.1%. Further increase in the CNT content did not improve the ion exchange capacity. Hence, all further studies were done with ZrP-CNT (0.1%).

The incorporation of CNTs during synthesis leads to an increase in ion exchange capacity of about 40% in its value. This increase is probably a result of better orientation of precipitating species leading to an effective increase in the number of ionogenic groups with exchangeable H^+ ions. Although, most of the characteristics of ZrP are preserved in the modified material, yet not all properties of original material (ZrP) are claimed. The synthesis protocols can be tuned further to achieve still better morphology, stability and ion exchange characteristics of the material.

Table 1: Ion exchange capacity of Zirconium Phosphate ion exchangers

Sr. No.	Sample	CNT content (%)	Ion exchange capacity (meq/g)
1.	ZrP	0.00	0.24
2.	ZrP-CNT 1	0.01	0.25
3.	ZrP-CNT 2	0.05	0.30
4.	ZrP-CNT 3	0.10	0.34

4.2 Ion exchange capacity for monovalent and divalent cations

Ion exchange capacity was determined for different alkali and alkaline earth metal ions using ZrP and ZrP-CNT. There is an increase in the ion exchange capacity with increase in bare ion radii of alkali and alkaline earth metal ions. These are exchanged as their hydrated species from solution phase to the ion exchanger phase. The magnitude of the ion exchange capacity of ZrP-CNT for all the metal ions is higher by almost same proportion than that with ZrP (Table 2).

Table 2: Ion exchange capacity of Zirconium Phosphate ion exchangers for monovalent and divalent cations

Sr. No.	Metal ion	Salt solution used	Ion exchange capacity (meq/g) (ZrP)	Ion exchange capacity (meq/g) (ZrP-CNT) (0.1%)
1.	Li^+	LiCl	0.13	0.25
2.	Na^+	$NaNO_3$	0.23	0.34
3.	K^+	KNO_3	0.47	0.60
4.	Ca^{2+}	$CaCl_2$	0.27	0.42
5.	Sr^{2+}	$SrCl_2$	0.32	0.45
6.	Ba^{2+}	$BaCl_2$	0.35	0.51

4.3 Regeneration of ion exchangers

Both types of ion exchangers, ZrP and ZrP-CNT can be regenerated and used repeatedly for this cation exchange capacity. ZrP and ZrP-CNT ion exchangers lose 53% and 50% of their ion exchange capacity after five-regeneration cycle.

4.4 Thermal stability

One of the advantages of inorganic ion exchange materials over their organic counter parts is their stability at high temperature. The materials are known to retain their structure and maintain their ion exchange capacity even at high temperature in the range from room temperature to 400° C, beyond which the functional groups collapsed and the exchanger is converted to a mixture of metal oxides. The selected sample of ZrP-CNT was heated respectively at 100° C, 200° C, 300° C and 400° C. Percentage lost in weight and ion exchange capacities of each of these heated materials are shown in Table 3. It can be seen that there is only a marginal decrease in ion exchange capacity from 0.34 meq/g at room temperature to 0.29 meq/g at 400^o C. FTIR and XRD of these samples were also recorded. A weak absorption band at 3730 cm^{-1} corresponds to the OH stretch of PO_4^{3-} group in the ion exchanger, whereas the band at 1630 cm^{-1} corresponds to the OH deformation mode. The presence of strong absorption band at 1000 cm^{-1} is due to the phosphate symmetrical stretching vibrations. It can be seen clearly (Figure 1) that the

absorption band at 1000 cm^{-1} tends to collapse [18] with increasing temperature due to merging of the phosphate groups. SEM images of the samples treated at different temperatures are shown in Figure 2. There is no significant difference observed in morphology of the samples on heating.

Table 3: Effect of heating on ion exchange capacity of Zirconium Phosphate ion exchanger ZrP-CNT for sodium ions

Sr. No.	Temperature (°C)	Ion exchange capacity (meq/g)	Loss in weight (%)
1.	RT	0.34	0.0
2.	100	0.32	24.0
3.	200	0.30	24.0
4.	300	0.29	33.3
5.	400	0.29	33.3

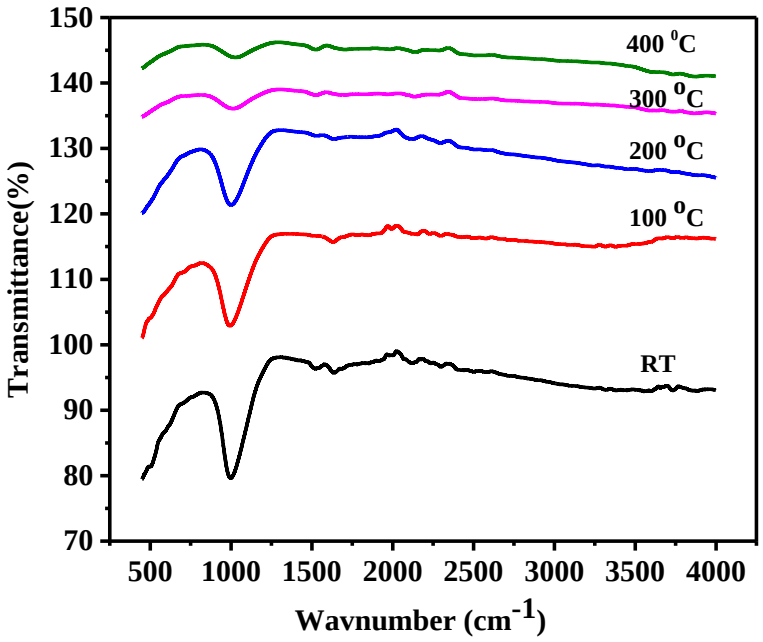

Figure 1: FTIR spectra of ZrP-CNT heated at different temperature (scale on y-axis shifted to overlay the spectra)

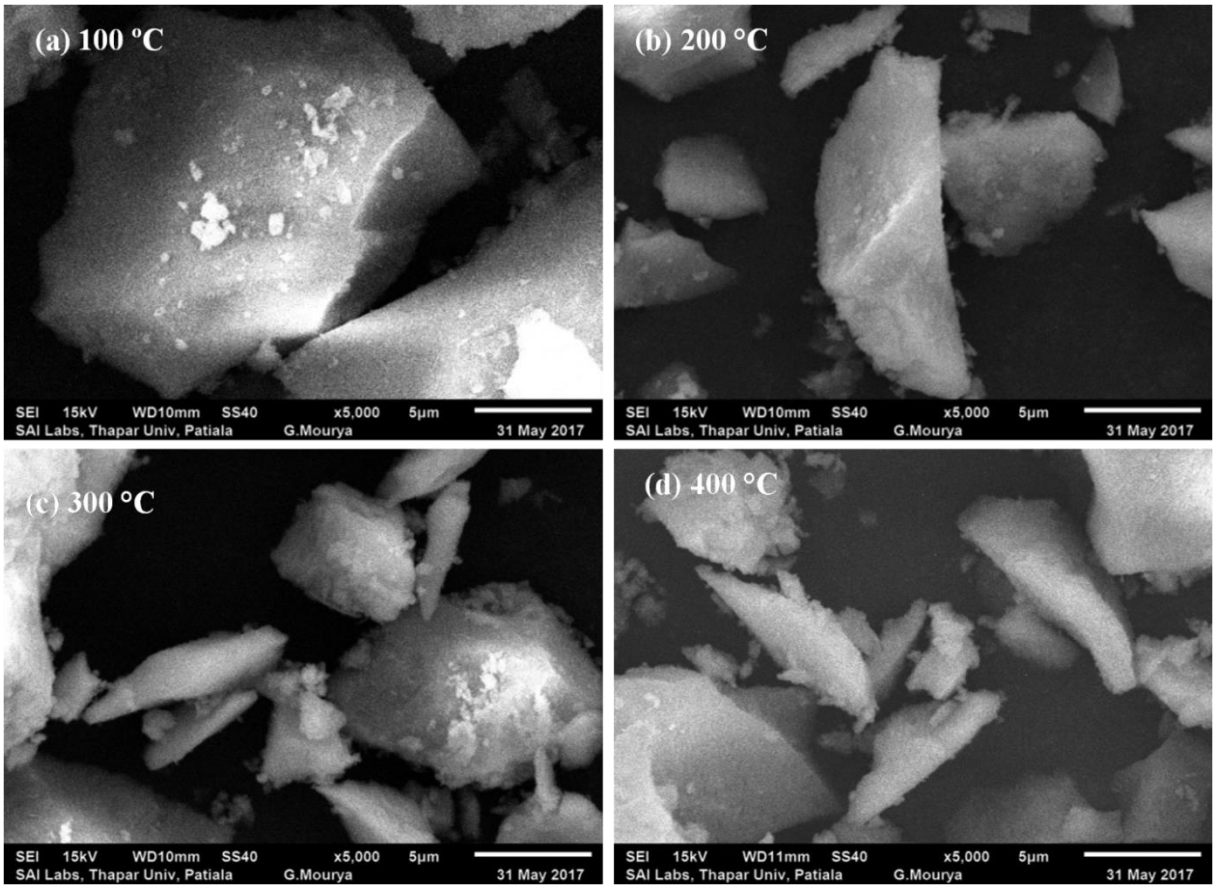

Figure 2: SEM images of ZrP-CNT heated at different temperatures

4.5 Chemical stability

Ion exchangers ZrP and ZrP-CNT show good chemical stability in strong acids, salt solutions, organic solvents and bases except in NaOH solution (Table 4). Both ion exchanger do not have any significant difference in their chemical stability. Hence, both the ion exchangers can be used in strong acids, salt solutions and organic solvents.

Table 4: Solubility of ZrP and ZrP-CNT in different solvent media

Sr. No.	Solvent Medium	Solubility	
		ZrP [P (%)]	ZrP-CNT [P (%)]
1.	KNO_3 (0.1 M)	0.04	0.02
2.	CH_3COOH (0.1N)	0.03	0.02
3.	DMSO	0.1	0.01
4.	NaOH (0.1 N)	5.0	7.0
5.	CH_3CN	0.04	0.02
6.	HCl (0.1 N)	0.05	0.03
7.	$NaNO_3$ (0.1 M)	0.02	0.01
8.	H_2SO_4 (0.1 N)	0.03	0.0
9.	HNO_3 (0.1 N)	0.0	0.02
10.	NH_4NO_3 (0.1 M)	0.03	0.02

4.6 Potentiometric titrations

The degree of activity of ion exchangers is associated with the release of mobile protons and the types of conjugate base moieties present in the ion exchanger network. Potentiometric titration of the ZrP and ZrP-CNT samples were carried out by added salt method. As seen from the titration curves (Figure 3), both materials are monofunctional in nature and incorporation of CNTs in the polymeric matrix of the ZrP has not changed the acidic character of the material. Both material are weakly acidic in nature.

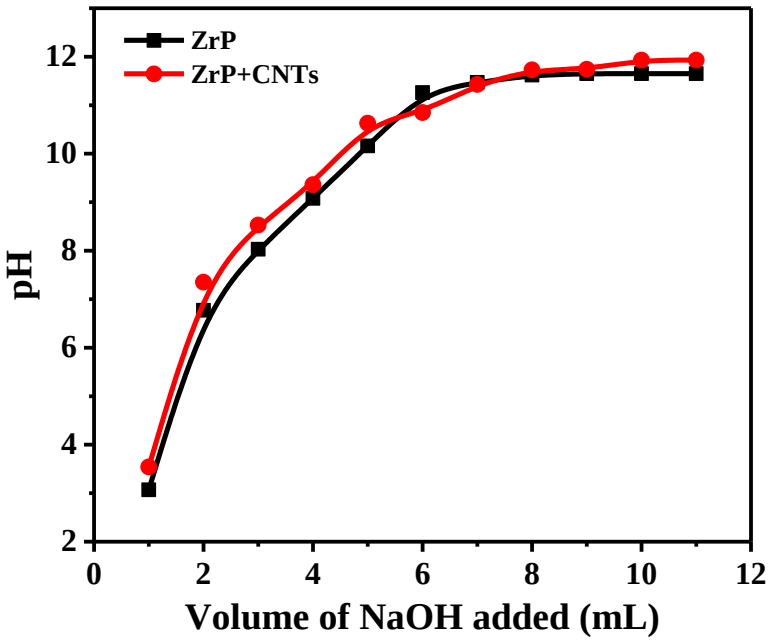

Figure 3: Potentiometric titration of NaOH solution by added salt method

4.7 Characterization of Zirconium Phosphate ion exchanger

The powder-XRD diffraction patterns of four samples of Zirconium Phosphate and their nano-composites with CNTs are shown in Figure 4. No sharp peaks were observed which suggests that the materials are amorphous in nature and do not indicate any tendency of crystallinity in the ion exchanger.

The surface morphology of ZrP and ZrP-CNT were studied by scanning electron microscopy (SEM). Figure 5 shows that there is no significant change in morphology of ZrP before and after the incorporation of CNT. Due to the large surface area of CNT roughness occurs in ZrP-CNT nanocomposite, which might be responsible for its enhanced ion-exchange capacity.

To investigate elemental composition of prepared samples of Zirconium Phosphate composites Energy Dispersive X-ray Spectroscopy (EDS) was done. It is clear from the EDS analysis (Figure 6) that all the samples are rich in Zr, P and O elements. Apart from that, carbon is absent in the ZrP ion exchanger whereas other three samples which are ZrP-CNT nanocomposite ion exchangers show presence of carbon content. Also, the percentage of carbon has been enhanced and amount of Zr, P and O decreased

simultaneous with the incremental addition of CNT in the ZrP sample for the preparation of different nano-composites.

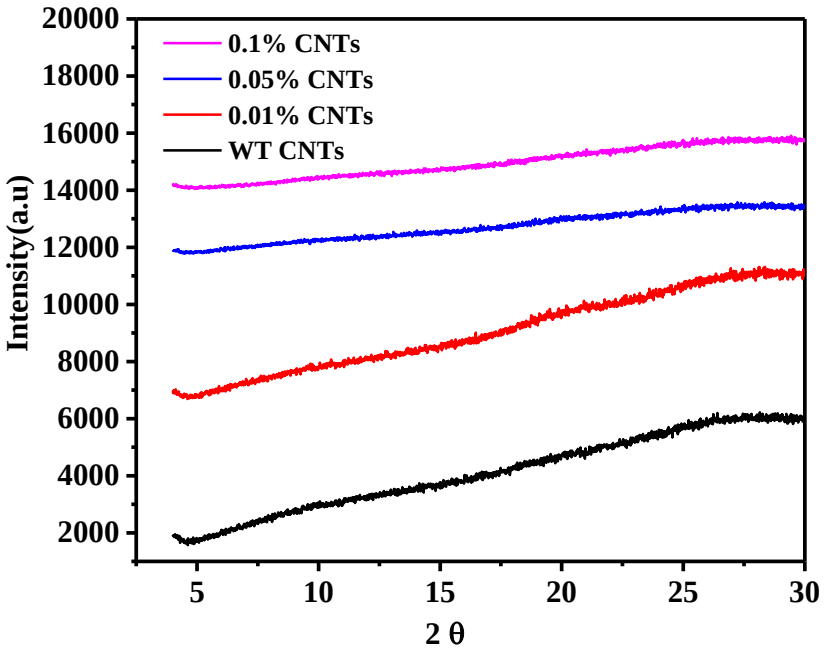

Figure 4: XRD pattern of different samples of Zirconium phosphates

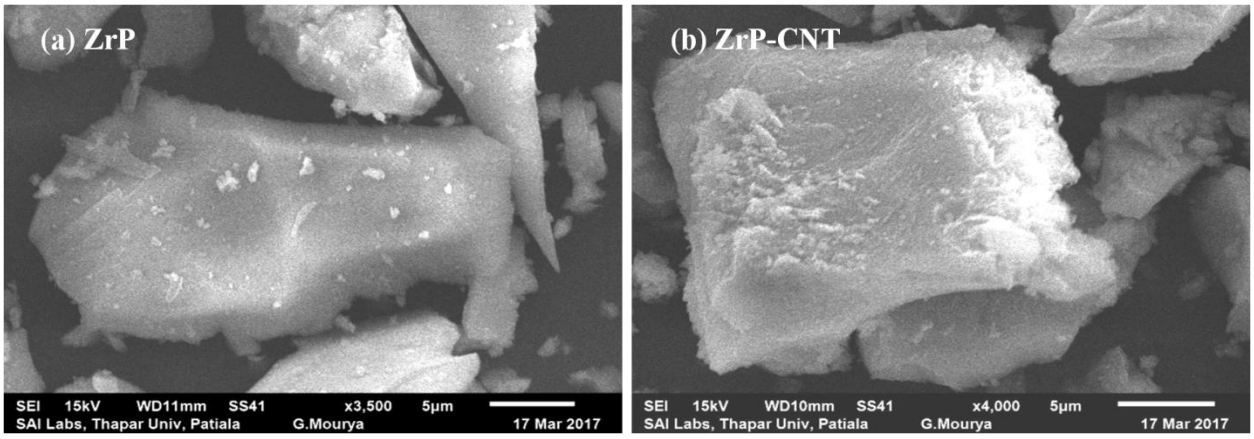

Figure 5: SEM images of ZrP and ZrP-CNT

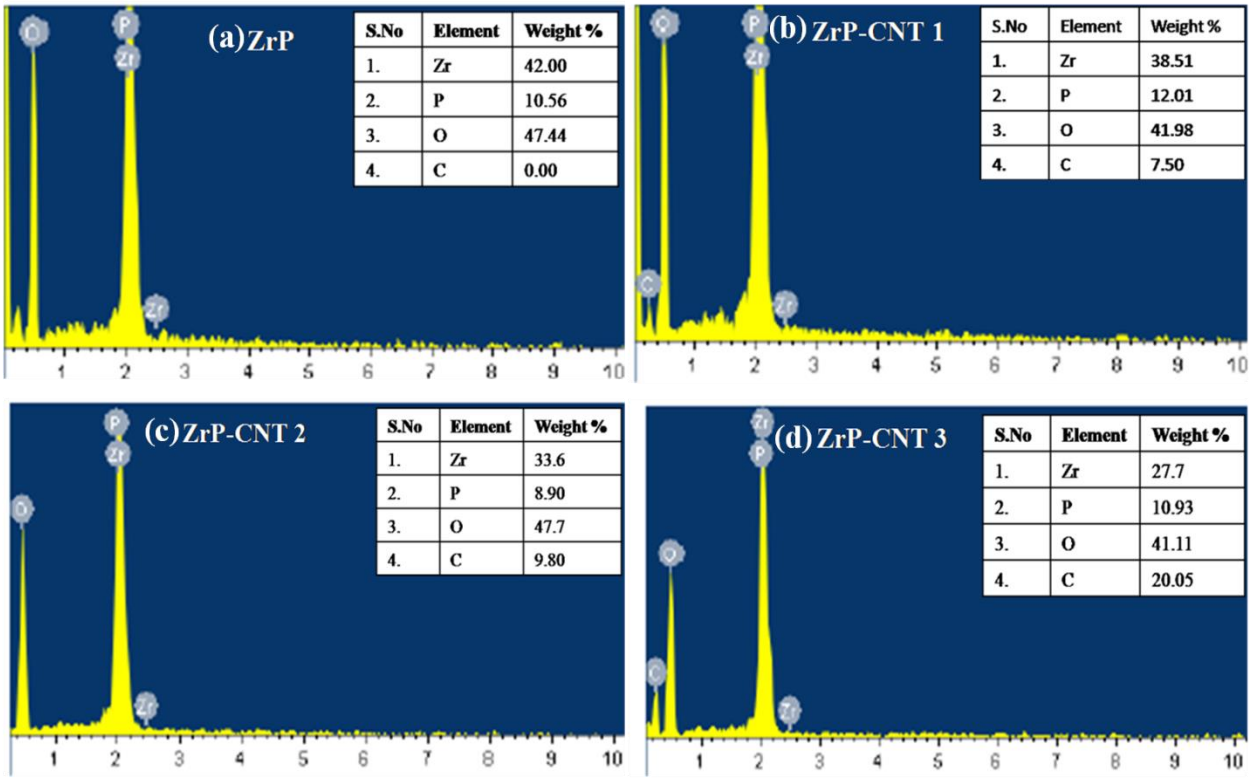

Figure 6: EDS of different samples of Zirconium Phosphate

Conclusions

Different samples of ZrP were prepared with and without the incorporation of CNT content i.e., 0.01%, 0.05% and 0.1%. Ion exchange capacity of ZrP-CNT (0.1%) show maximum value of 0.34 meq/g. There was an increase in ion exchange capacity value of ZrP-CNT nanocomposite for alkali and alkaline earth metal ions as compared to ZrP, which can be due to the incorporation of CNT. Both ZrP and ZrP-CNT can be regenerated. Thermal stability study showed that there was a marginal decrease in value of ion exchange capacity from 0.34 meq/g at room temperature to 0.29 meq/g at 400^{o} C. ZrP and ZrP-CNT are chemically stable towards organic solvents, acids, salt solutions except NaOH solution and were found to be weakly acidic in nature by potentiometric titrations. The structural, morphological and chemical composition studies of prepared ion exchangers were done by powder XRD, FTIR, SEM and EDS, respectively.

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