Synthesis and Characterisation of Zirconium Phosphate Ion exchanger and its Composites

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Submitted by
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UNDER THE SUPERVISION OF

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Certificate

This is to certify that the thesis entitled **"Synthesis and Characterisation of Zirconium Phosphate ion exchanger and its composites"**, being submitted by **Ms. Sheenam Sharma** in partial fulfilment of the requirements for the award of degree of Master of Science in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under the supervision of **Dr. Susheel Mittal** and that no part of this thesis has been submitted for the award of any other degree.

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Candidate's declaration

I hereby declare that the work being presented in the thesis entitled **"Synthesis and Characterisation of Zirconium Phosphate ion exchanger and its composites"**, in partial fulfilment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry, Thapar university, Patiala, is my own work during the period of January 2018 to June 2018, under the supervision of Dr. Susheel Mittal, Senior Professor, Thapar University, Patiala. I have not submitted the matter embodied in this thesis for the award of any other degree.

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

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ABSTRACT

Zirconium Phosphate (ZrP) as an ion exchanger was synthesized and modified with CNTs and incorporated in the framework of ZrP. The CNTs were used in modification of ion exchanger. The ion exchange capacity was determined in each ion exchanger and the ion exchange capacity of modified ZrP was much higher than ZrP. Moreover, characterization of both the ion exchangers were studied such as, X-Ray Diffraction, Scanning electron microsope, Solubility, Kinetics. The X-Ray diffraction results show the amorphous character of both the samples. The chemical stability was observed in various solvents and found that ZrP-CNT has good chemical stability in acids, salt solutionsand in various bases. Ion exchangers have a good kinetic behavior with the three different metals, with CNT as comparative to without CNT zirconium phosphate. The size, shape and morphology were studied using scanning electron microscope. The ion exchange capacity of modified ion exchanger was improved by 36% than that of its classical analogue.

CHAPTER 1 INTRODUCTION

Ion exchange is a process, whereby trade of ions either between two electrolytes and a complex solution. In this process, during a chemical reaction a non-reactive substance removes an ion (cations) or (anions) from an electrolyte solution and releases another ion from reactive charge into the solution in an equivalent manner.

The processes of “purification, separation, and decontamination of aqueous and supplementary ion-containing solutions with solid polymeric” are done by the use of ion exchangers. Zeolites, montmorillonite, clay are commonly used ion exchangers or resins. Exchange of ions mostly dependent on the “size of the ions, their charge, or their structure”, due to this reason some of exchangers are able to replace both cations and anions simultaneously during a chemical reaction [1].

ION EXCHANGER:

A resin or polymer that plays a role as medium for ion exchange is known as an ion exchange resin or polymer. These have a diameter of about 0.6 mm, are very small plastic bead .These contain “humidity” or “moisture content” due to porosity in which invisible water is present. The formation of the resin is a polymer on which an unchanging ion has been permanently attached. The fixed ion cannot be removed, seeing that it is a component of composition.

TYPES OF ION EXCHANGERS:

a) Organic Ion-Exchangers: These are long chain polymers, which are insoluble and crosslinked having micro structures. Though, these have high stability as well as ion exchange ability, the ion exchange occurs due to presence of functional group attached to chain.

b) Inorganic Ion-Exchangers: Such polymers have great influence on market, for example; zeolites, aluminosilicates. These polymers operate application in high radiation fields as like nuclear industries and also at high pH conditions where the organic ion exchangers have only limiting effects.

c) Hybrid Ion-Exchangers: It contains both organic as well as inorganic so that to increase the selectivity, and chemical stability.

In contrast with organic ion exchangers, inorganic ion exchangers have high stability at high temperatures and radiation fields. Though, they are virtually insoluble at a wide range of pH range. They show rapid sorption and elution behaviour [3].

1.1 TYPES OF INORGANIC ION EXCHANGERS

1.1 Oxides: These are applicable for nuclear waste treatment, wastewater treatment, though these can be both simple as well layered. The synthesis of metal oxides in exchangers is done by sol-gel method. By this method, the resultant is granulated form; used compounds are inexpensive as like metals, mineral acids and alkali in contrast from expensive alkoxy compounds [10, 11].

The studies have been done on various oxides as like for water treatment, alkali metal oxides as well as hydroxides and nuclear treatment.

For nuclear treatment ,derivatives of layered manganese oxide with cation that are similar in structure with the Birnessite ore have been discussed as their uses in separating the $^{57,60}Co$, ^{110}Ag, $^{134,137}Cs$ and also for ^{125}Sb from nuclear waste[26]. This shows that under less acidic conditions, exchangers were much better [26]. Further, Titanium and antimony were designed in such way to exhibit the rutile, pyrochlore or mopungite structure mixtures, the final structures were dependent on the Ti: Sb ratio, the pH, the temperature of the reaction and the order of metal hydrolysis [27]. The higher phase was rutile for ^{134}Cs and ^{57}Co than pyrochlore phase , yet for ^{85}Sr have higher selectivity as demonstrated by pyrochlore and the mopugnite phases[27].Further, the discussion proceeds under inert conditions, as a function of pH values; 1, 3, 5, 7, and 10, the adsorption of radioactive cobalt from aqueous solution of the ^{60}Co solution [28]. The adsorption was seen on MnO_2, TiO_2, MgO and SnO for direct exchanging of hydrogen ions from structural water on the surface of oxides [28].

For Alkali metal ion exchangers, lithium ion mobility for battery applications, framework oxides, rock salt structures, peroskite oxides and other closed packed oxides have been included [29]. The authors found that while schematic lithium ion-exchange does not automatically commit a high ionic selectivity or conductivity of lithium, thus provide important insight in structural and bonding needs for lithium mobility in solid. Further, preparation of niobium (V) oxide hydrate was done, by precipitating it in homogenous solution, leads to increase in size of particles of the material for later use in ion-exchange column and also improve the ion-exchange ability [30].It was done by Tagliaferro and his co-workers.

For water purification, that is eutrophication(due to presence of phosphate) in lakes and slow moving water, done by preparation of hydroxides of zirconium, aluminium ,iron which are available from raw materials for the purpose to removal of phosphate.[31]

1.2 Hydroxides: These are of two types, known as particle hydrates and framework hydrates. The formation of framework hydrates by metals in group 5 and 15 are higher in their oxidation states. There is formation of amorphous product, when there is rapid precipitation of antimony (V) oxide. These have poor crystalline hydrous oxides, so to improve it, refluxing is done in acidic medium or by hydrothermal treatment. Most of group 3, 4, 13, 14 metals form the particle hydrates having a bulk structure, having similarities with their ceramic oxides. Many of layered double hydroxides exist. Generally formula for layered double hydroxides is $[M^{II}_{(1-x)} M^{III}_{x} (OH)_2][A^{y-}_{x/y}]\cdot nH_2O$ or $[M^{I}M^{III} (OH)_6][A^{y-}_{1/y}]\cdot nH_2O$ which exhibits cations as mono-, di-, and trivalent and anions as interlayer charge-compensating.

1.3 Phosphates and Phosphonates: The metal acids usually known as synthetic tetravalent metal acids salt ion-exchangers are of heed due to their stability towards heat, selectivity toward a variety of different metal ions. Generally, these metals have formula $M^{IV} (HXO_4)_2\cdot nH_2O$, where M^{IV} = Zr, Ti, Th, Ce, Sn, etc. and X = P, Mo, As, W, Sb, etc. The resulting ion exchanging behaviour was due to the presence of hydroxyl protons [32].

1.4 Silicates: Such ion exchangers used for removal of metal ions from wastewater and are very effective in softening of water for example; zeolites which are aliminosilicates. These are also used for removing radioisotopes of cesium and strontium from acidic (neutral and moderately) wastewaters, but not in highly basic medium as like that present in consequence nuclear materials production[3].

1.2 NANOCOMPOSITE BASED ION EXCHANGERS:

Nanocomposites are synthesized to solve the flaws of macrocomposites and microcomposites materials.The recent research had shown the synthesis, properties and developing applications of polymer-layered silicate nanocomposites [33]. The nanocomposites have their one phase with dimensions in nanometer range (1 nm = 10^{-9} m) [23]. Carbon nanotubes is also an example of nanocomposite in which two dimensions are in same nanometer range and the third one is in elongated manner .There is the third most type, which includes only one dimension and fills in the form of sheets with few nanometer range thickness. Nanocomposites are classified as:

a) Polymer Matrix Nanocomposites
b) Ceramic Matrix Nanocomposites
c) Metal Matrix Nanocomposites

Nanocomposits CNT's were discovered in 1991.CNT's can be filled in variety of materials due to their hollow nature which leads to new applications[5].Though, the synthesis of nanocomposites have their control over properties if the materials as like melting temperature, charge capacity, colour change without changing its chemical composition and their magnetic properties[34].

Nanocomposites enhance the properties like electrical conductivity, chemical resistance, thermal stability, flame retardancy, barrier and membrane separations. These also improve the mechanical properties as dimensional ability, strength and modulus. Though, nanocomposites have many advantages over heavy materials too. This difference is appropriate to having high surface to volume proportion. Nanocomposites also have their applications in drugs, also used as anti-corrosion for barrier coatings, lubricants, for making lightweight sensor, preparing electronics and nanoelectronics devices. Due to their hydrophobicity and controlled functionality, it gives applications in organic chemistry, analytical chemistry, hydrometallurgy, separation of radioactive isotopes, antibiotic, purification, treating wastewater and pollution. Recently, new application is found as photo catalysts for the degradation of dyes by nanocomposites ion exchangers.

1.3 ATTRIBUTIONS OF ION EXCHANGER

a. Chemically and mechanically, good resistivity
b. Homogenous size of particles and effective surface area
c. Higher chemical stability
d. Function rapidly i.e., equilibrium operation is rapidly reached
e. Ion exchange capacity is effective and controlled
f. A hydrophobic gel structure of reproducible and regular form

One of the major hindrances to utilize of inorganic particle exchangers is the reality that they are not accessible in granular shape reasonable for column use. However, we have been collaborating with staff at Allied-Signal Enterprise to cure this situation. Finally, it may be specified that carbon based inorganic exchangers have been arranged within the previous Soviet Union for verbal organization to animals and people for the reason of sequestering ingested radioactive species. We have touched on as it were a number of the compound types that display particle traded behavior. One can envision a comparative accomplishment within the next two decades as we turn our consideration to the inorganic resources. The field is really expansive, and modern items are found routinely [2]. Crystalline (c-SnSbAs) and undefined (a-SnSbAs) tests of tin (IV) antimonoarsenate were arranged at diverse pH values from to 5. Crystalline and undefined tests, arranged at pH 1 having particle trade capability of 1.00 meq/g and 0.90 meq/g individually, were chosen for assist studies. Some quantitative parallel divisions for example, Mg^{2+}–Mn^{2+}, Cd^{2+}–Mn^{2+}, Ba^{2+}–Mn^{2+} and Ni^{2+}–Cu^{2+} were accomplished on a-SnSbAs and particle specific anodes arranged from c-SnSbAs are reported. Distribution coefficients (K_d values) for 22 metal particles have been decided in demineralised water [2].

ZrPB ion exchanger was synthesized by using the method of sol-gel, followed by incorporation of CNTs by sonication. It’s membrane at low concentration (up to 0.045 M) shows better characteristics, at such a low concentration no appreciable change is noticed in the membrane. Also being in smaller size (2–5 nm) as showed by TEM images and SEM images showed ,the ZrPB particles is spherical and agglomerated and also shows homogenous distribution of CNTs. ZrPB, being in the range of nanocomposite ion exchanger shows interesting properties. Under the UV-radiation exposure ZrPB completely degraded the dye, and it widely used as photo catalyst for water purification, water splitting, solar cells in electronics, and as antimicrobial agent [6].

In 2001, Ferragina and colleagues appeared that octadecyltrimethylammonium given uncommon development of the interlayer dispersing in α- and γ -zirconium dihydrogen phosphates in expansion to γ -titanium phosphate [13]. The resultant was seen an interlayer separate increment by a figure of 4.5 and 2.7 for α- and γ -zirconium dihydrogen phosphates, respectively [13]. Extension of the zirconium structure through intercalation with expansive surfactant atoms, as with titanium phosphates, permits for catalytic metals such as Pd^{2+} and Rh^{3+} to trade into the structure for conceivable utilize as heterogeneous catalysts [13]. Ferragina et al., proceeding a ponder of zirconium phosphates intercalated by diverse long chain alkylammonium cationic surfactants, watched that the altered ZrP was steady towards surfactant misfortune to 220ºC [14].

Intercalation of α-zirconium phosphate by the proteins, Met hemoglobin and lysosome, has been found feasible [8]. Isothermal titration calorimetric thinks about appear that authoritative of hemoglobin to α-ZrP at 25ºC is emphatically exothermic with a diminish in entropy whereas a demonstrate framework such as Mg (II) authoritative to α-ZrP was endothermic. The contrasts within the authoritative thermodynamics of the two visitors were translated to demonstrate that a straightforward electrostatic demonstrate for the official handle isn't satisfactory to clarify Hb official to α-ZrP [8]. Immobilization of chemicals on α-zirconium phosphate strong back has potential applications in biosensors, biomedical gadgets, biocatalysts, etc.

A careful audit in 2004 by Curini et al. give understanding into the flexibility of zirconium phosphates and phosphonates as heterogeneous catalysts.[9] . The attemptation to produce new heterogeneous catalyst was synthesized by exchanging γ-zirconium phosphate though Zn^{2+} and Cd^{2+} [10].

ZrP featured to condensation of structural hydroxyl groups, as the ion- exchange capacity of zinc phosphate decreases when there is increase in calcination temperature, and decreases more rapidly beyond 300°C [11]. During the intercalation between ferrocenium ion and zirconium phosphate, lead to the formation of redox material which is used as an electron acceptor for oxidation of ferro-cytochrome c and the excited state of tris(2,2'-bipyridine)ruthenium(II) [12].

In the analogues, it has been reported that zirconium phosphate as well as Cu^{2+} and Li^{+} zirconium phosphate transport the protons [13]. ZrP has the ability to sorb dyes also can exchange metal ions, and its conductivity decreases with increases thrice at 120ºC temperature, and also at this point it was observed in LiZrP [13]. At pH = 1 and pH = 3, respectively ZrP is used for the removal of medicinal dyes acriflavin (AF) and brilliant green (BG) from the water waste [14].

The done experiment results that ion exchange capacity of the ion exchanger decreases with the increase in the radii of hydrated metal ions. By enhanced Donnan exclusion at low electrolyte concentration the transport numbers increase with increase in average concentration of the electrolyte and by excessive polarization phenomenon transport number decreases at high concentration of electrolyte [18].

Min-Kyu Song et.al. (2003) prepared structurally stable organic-inorganic hybrid ionomer membrane in which nano-sized solid proton conductors were uniformly dispersed in an ion exchange polymer matrix. Due to the highly accessible adsorption sites and the short intraparticle diffusion distance of CNTs, adsorption kinetics is mainly fast. Fe and cerium oxide (CeO_2) with CNTs have been reported to remove heavy metal ions. The incorporation of a polymer material into an inorganic ion-exchanger provides a high class of hybrid ion-exchangers with enhanced ion-exchange properties, high reproducibility, high stability, and good selectivity for heavy metals [19].

An advanced organic-inorganic composite-polypyrrole zirconium titanium phosphate has been synthesized using zirconium titanium phosphate. The sol-gel strategy was used to synthsize organic-inorganic nanocomposite cation-exchanger polyaniline Zr (IV) sulphosalicylate. Physiochemical properties such as ion-exchange capacity, chemical and thermal stability of composite material have also been determined. The nanocomposite material exhibits improved thermal stability, higher ion-exchange capacity and better selectivity for toxic heavy metals. Thus, found result was proof for the cation exchanger that it was selective for Pb (II), Hg (II) and Zr (IV) ions. The analysis and recovery of heavy metal ions in environment was practically accepted by utilisation of polyaniline Zr (IV) sulphosalicylate cation exchanger [35].

Sandeep Kaushal et. al., synthesized zirconium phosphoborate ion exchange membranes to study electrical characteristics like transport numbers, permselectivity & fixed charged density of the material. As there is increase in concentration of the electrolytes, due to this there is increase of membrane potentials, transport numbers and permselectivity values increased [36].

A sol-gel strategy was used to study a prepared nano-composite cation exchanger sodium dodecyl sulfate acrylamide Zr (IV) selenite (SDS-AZS). The physico-chemical properties were considered utilizing FTIR, TGA, XRD, SEM, EDX, TEM and natural investigations. The fabric was successfully utilized for the evacuation of Pb^{2+} which is a critical natural poison. Group tests were performed as a work of different test parameters such as impact of pH between 2-10, contact time (5–60 min), SDS-AZS dosage (0.1–1.0 g), starting Pb^{2+} concentration and temperature. The take-up rate of Pb^{2+} onto SDS-AZS was quick and harmony built up inside 40 min. Active considers appeared way better appropriateness for pseudo-first-order show. The appropriateness of Langmuir, Freundlich and Temkin isotherm models was examined and the Freundlich isotherm displayed the finest fit with the test information. The thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were computed from the Van [15].

The arrangement of Crystalline (c-SnSbAs) and nebulous (a-SnSbAs) tests of tin (IV) antimonoarsenate at diverse pH values. The samples arranged at pH 1 having particle trade capacities of 1.00 meq/g and 0.90 meq/g separately, were chosen for advance considers. The materials appear tall warm and chemical solidness. Dissemination coefficients (K_d values) for 22 metal particles have been decided in demineralised water. Basic ponders based on IR, XRD, TGA, DTA are examined. A few quantitative double divisions such as Mg^{2+} -Mn^{2+}, Cd^{2+}-Mn^{2+}, Ba^{2+} -Mn^{2+} and Ni^{2+}-Cu^{2+} were accomplished on a-SnSbAs and particle specific cathodes arranged from c-SnSbAs are detailed [16].

Lactic acid (ZrP (IV)) nanocomposite was characterised by diverse methods. SEM clearly declares the arrangement of nanocomposite with a few morphological changes. The nanorange size was depicted by TEM photo with measure 50 nm. The observation made for ion exchange capacity was higher in LA/ZPNC than that of inorganic portion. The pH ponders delineate the bifunctional nature of nanocomposite [18].

The half-exchanged phase takes up protons it forms an un- exchanged phase which is more highly hydrated than the original «-zirconium phosphate. The sodium ion-hydrogen ion, hydrogen ion-sodium ion exchange titration curves of «-zirconium phosphate crystals, $Zr\ (HPO_4)_2 \cdot H_2O$ exhibit a hysteresis loop. The interconversion of the half and fully exchanged phases is reversible. They are the unexchanged -zirconium phosphate and a half-exchanged phase whose formula is $Zr\ (NaPO_4)_2(HPO_4)\ \cdot 5H_2O$. The two phases are the half-exchanged crystals and a fully exchanged phase of composition $Zr\ (NaP0_4)_2.3H_2O$. When the crystals are titrated with sodium hydroxide two solid phases are present up to 50% of exchange [19].

Chemical composition, ion-exchange capacity for antacid and soluble soil metal particles, dispersion coefficients for a number of metal particles, impact of warm treatment on ion-exchange capacity are detailed for the ion-exchangers. The synthesis of inorganic ion-exchangers zirconium antimonophosphate (ZrSbP) and zirconium phosphotungstate (ZrPW) was done and characterisation was found as feebly acidic particle exchangers by potentiometric titrations against soluble base metal hydroxides. The exchanger ZrSbP loses as it were 30% of its ion-exchange capacity upto 200°C. [20].

Being biologically welcoming, applications of nanocomposites offer advanced development and commerce openings for some divisions of the flying, car and biotechnology industries Nanocomposites, a tall execution texture appear anomalous property combinations and one of a kind arrange possibilities. In this bound together chart the three sorts of grid nanocomposites are shown underlining the require for these materials, their dealing with techniques and a number of afterward comes almost on structure, properties and potential applications, perspectives tallying require for such materials in future space mission and other inquisitively applications at the side exhibit and security angles. [22].

This inquires about presents a definition of nanocomposites, its beginning, classification, properties, benefits, as well as its future. The tall warm resistance and moo combustibility of a few nanocomposites to make them great choices to utilize as insulin and wire covers. The definition of nanocomposites has broadened basically to envelop a huge collection of frameworks such as one - dimensional, - dimensional, 3 - dimensional and nebulous materials manufactured from unmistakably divergent components and mixed at the nanometer scale. Within the building plastics field, mechanical components can be considered, making utilize of lightweight, affect, scratch - safe and higher warm distortion performance characteristics. With the correct choice of compatibilizing chemistries, the nanometer - measured clay platelets associated with polymers in special ways. In plastics the focal points of nanocomposites over customary ones don’t halt at quality [21].

3.1 Materials

Zirconium oxychloride octahydrate was purchased from LOBA Chemie, India with assay 98%.The another two acids, phosphoric acid (97% purity) and hydrochloric acid (95-98% purity) was purchased from Merck, India. The multi-walled CNTs used in modification have dimensions as 10-30 nanometers in length, 1-10 milimeters in diameter, and >95% purity were obtained from NANOSHEL LLC (USA).These CNTs were determined by chemical vapour deposition process. The distilled water was used in preparation of all other solutions for analysis by setting up standardisations or by direct weighing the AR grade chemicals.

3.2 Methods

3.2.1 Synthesis of Zirconium Phosphate

The preparation of zirconium phosphate was done by the addition of zirconyl oxychloride (0.1M) solution, which was prepared in Hydrochloric acid (0.1M) into a phosphoric acid (0.1M), by persistently stirring it at constant temperature (60ºC) ,respectively having volume proportion 1:1. After 5-6 hours of stirring, solution is kept to rest for next 8-9 hours., white gelatine precipitates are found. The filtration of precipitates was done using distilled water, so as to remove acid and chloride, also noted the pH of gel. The filtered gel was kept in air oven at 40ºC for 24 hours. The dried precipitates are broken in small granules after adding water and are converted into H^+-form by keeping it in HCl (0.1M) solution for 24 hours. To remove excess acid, the residue was washed with distilled water and kept for drying at 40ºC. The dried material in H^+-form was kept in a air tight bottle for further characterisation.

3.2.2 Synthesis of modified Zirconium Phosphate

The sol-gel method can be used for the preparation of Zirconium Phosphate with CNTs by passing it through sonication with 0.05% of CNTs in zirconyl oxychloride (0.1M) solution into a continuously stirring phosphoric acid (0.1M) solution with volume ratio 1:1, respectively. The prepared precipitates are filtered, also washed and noted the pH, till they become acid and chloride free of the white gel. The gelatinous material was kept at 40ºC in air oven. The distilled water was added to the dried material and broken into small granules and kept in HCl (0.1M) solution to convert these precipitates in an H^+-

form for 24 hours. The excess acid was removed with distilled water and left to dry at 40ºC. The dried material in H^+-form was kept in a air tight bottle for further characterisation.

3.2.3 Ion Exchange Capacity

The ion exchange capacity of ZrP and modified ZrP was determined by using column method. The 0.5g of each ion exchangers were used in H^+-form with the support of glass wool in the column. From each, 200ml pf 0.5M $NaNO_3$ was passed with the rate of 10-12 drops in a minute through the column. The eluent in H^+-form was titrated against 0.01 M standardised NaOH solution.

$$\text{IEC} = N*V/W \text{ meq/g}$$

Where N = Normality of NaOH solution, V = volume of NaOH solution used and W = mass of ion exchanger (in grams).

3.2.4 Chemical stability

0.2g of both samples was kept in each 20ml of different solutions like water, HCl, H_2SO_4, HNO_3, NaCl, $NaNO_3$, Na_2SO_4, KNO_3, KCl, K_2SO_4, NaOH, LiOH, KOH, having strength of 0.1M for 24 hours and then filtered. The Phosphorous content was checked in the filtrate samples, by spectrophotometrically.

3.2.5 Kinetics stability

0.2g of ZrP and its modified sample was kept in each 20ml of different metal solutions like Cu^{2+}, Co^{2+}, Ni^{2+}. Among these three metal ions, the extent of reaction Co^{2+} have higher stability kinetically.

The extent of rate reaction was expressed as,

F= amount of absorbed content in m.eq per time\total absorbed concentration initially

3.2.6 Characterisations of ZrP ion exchanger

The use of XPERT-PRO diffractometer (Cu Kα, $\lambda = 0.15406$ nm, 40mA. 45Kv, step size =0.017º) was done for both ion exchanger to study powder X-Ray diffraction (XRD). The data was examined between the range 3º to 29º. The chemical composition was determined by the use of EDS (INCA x-act Oxford). The scanning electron microscope JEOL (JSM-6510LV) was used to determine the size, shape and morphology. The examined solubility content was done by using UV (Spectra 200) Spectroscopy. The kinetics was studied by atomic adsorption spectrophotometer (AAS) by using GBC 932 AA and running the standards of three metal ions Ni^{2+}, Co^{2+} and Cu^{2+} (each of 0.1M strength).

The synthesis of zirconium phosphate was discovered by Clearfield et al., and further studies were done by many of other researchers in the last five decades [24].Thus, the results have been determined that zirconium phosphate have higher ion exchange capacity and is chemically stable [25]. In the present time, the examination was done so as to know that during the maintenance of its ion exchange character, whether the ion exchange capacity can be enhanced with incorporation of CNTs. The CNTs used were of 10-30nm in diameter, 1-10μm in length, and have -COOH functional group. The material of Zirconium phosphate (ZrP) was prepared without embodying CNTs. The prepared material in different batches was collected together in a single lot.

The comparable material was synthesized by using sol-gel method. An acidic solution Zirconium oxychloride and 0.05% of CNTs zirconyl oxychloride was prepared with addition of functionalised CNTs of appropriate amount i.e., 0.05% and were sonicated. The sonicated solution was added slowly to the continuously stirring phosphoric acid, maintaining the constant temperature at 60ºC. About 10 minutes were consumed for addition of half of the $ZrOCl_2$ solution. After, stirring to 5-6 hours and keep it constant at temperature 60ºC, white gel type material was obtained. The filtration and washing was done by using distilled water to remove the chloride and acids. The residue was kept to dry and broken into small granules, washed with water with crackling sounds and converted into H^+-form.

4 .1 Enhancements in ion exchange capacity

Ion exchange capacity of different material ZrP and ZrP-CNT were tested for 0.05% of CNT content used. Thus, as expected the resultant was enhancement in the ion exchange capacity of CNT sample. The increased amount is shown in Table 1, i.e., the ZrP-CNT is increased by 36% than ZrP.

Table 4.1: Ion exchange capacity for Zirconium Phosphate and modified Zirconium Phosphate

Sr.No.	Sample	CNT content (%)	Ion exchange capacity (meq/g)
1.	**ZrP**	**0.0**	**0.53**
2.	**ZrP-CNT**	**0.05**	**0.72**

4.2 Solubility of ion exchangers

Ion exchangers ZrP and ZrP-CNT show good chemical stability in salt solutions (NaCl, $NaNO_3$, Na_2SO_4, KNO_3, KCl, and KSO_4), acids (HCl, HNO_3, and H_2SO_4) each having 0.1 M solutions. The exceptional case is seen in bases (NaOH, LiOH, KOH), solubility was increased in highly basic solution. The difference in the chemical stability among strong acids and salt solutions is not noteworthy. Thus, both ZrP and ZrP-CNT can be used in strong acids and in salt solutions.

Table 4.2: Solubility of ZrP and modified ZrP in different solvent media

Sr.No.	Solvent Medium	Solubility	
		ZrP [µg/200mg]	ZrP-CNT [µg/200mg]
1.	Total	522.1	960
2.	Water	36	26
3.	HCl (0.1M)	27	11
4.	HNO_3 (0.1M)	52	40
5.	H_2SO_4 (0.1M)	35	12
6.	NaCl (0.1M)	54	50
7.	$NaNO_3$ (0.1M)	20	10
8.	Na_2SO_4 (0.1M)	45	29
9.	KNO_3 (0.1M)	48	24
10.	KCl (0.1M)	33	30
11.	K_2SO_4 (0.1M)	20	16
12.	NaOH (0.1M)	512	702
13.	KOH (0.1M)	248	712
14.	LiOH (0.1M)	406	610

4.3 Kinetics and mechanism of ZrP and ZrP-CNT

Ion exchanger shows the kinetically good behaviour with the different metal ions as depicted from Figure 1, 2 and 3 that ZrP with modification by incorporating CNTs was much better than that of Zirconium phosphate without nanocomposite.

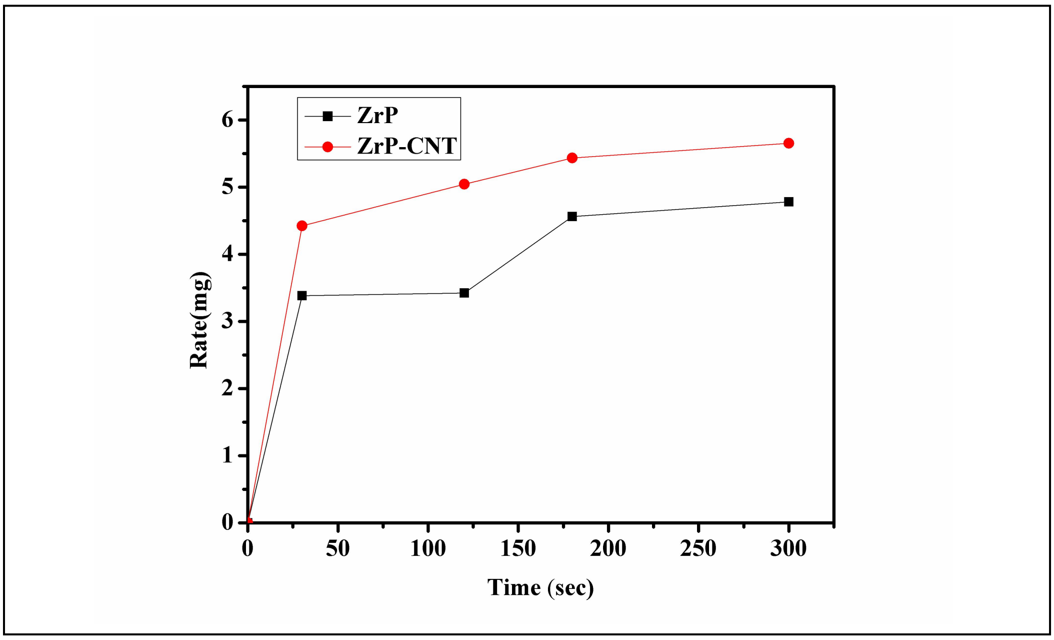


Figure 1: The kinetics with Cu^{2+} for ZrP and ZrP-CNT

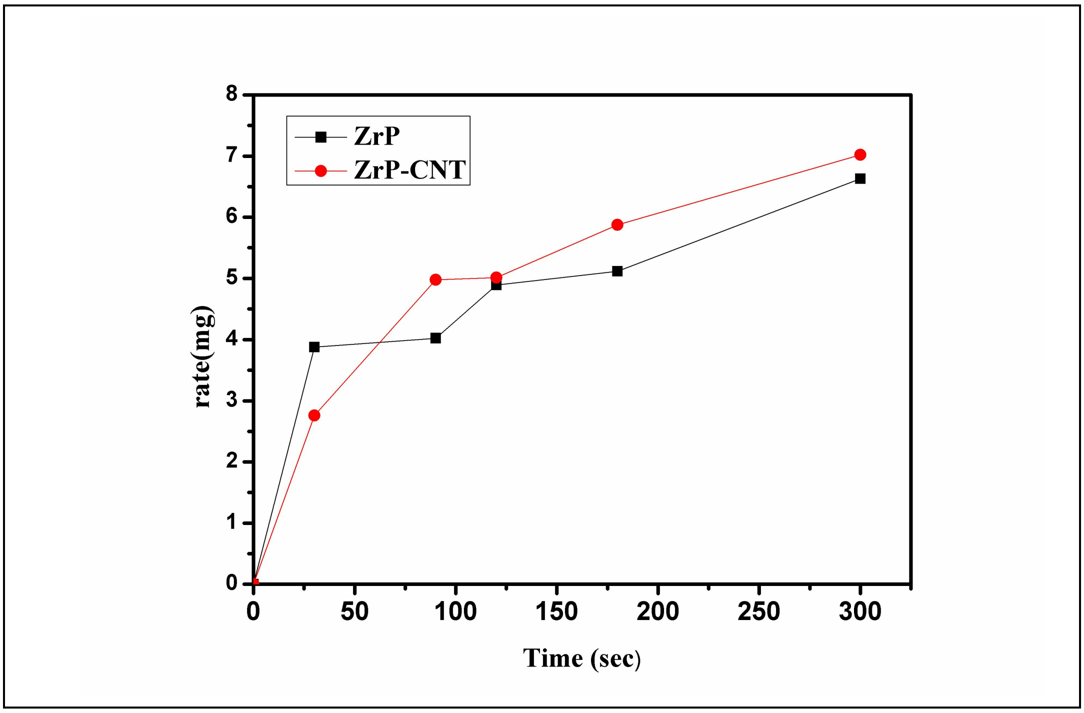


Figure 2: The kinetics with Co2 + for ZrP and ZrP-CNT

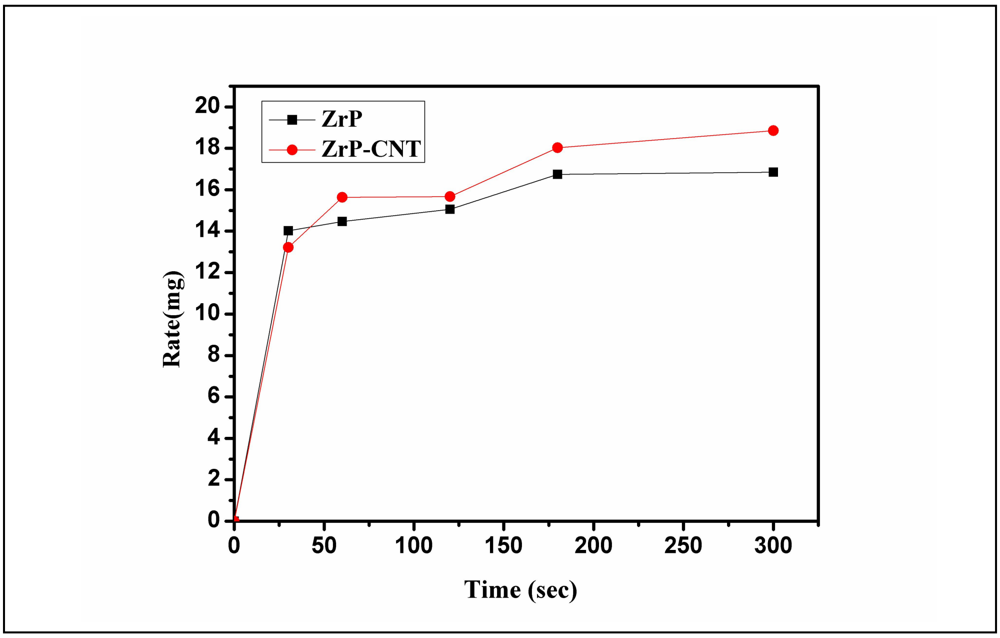


Figure 3: The kinetics with Ni^{2+} for ZrP and Zrp-CNT

The images of SEM of two different samples were seen at four different magnifications i.e., at 5000x, 10000x, 15000x and 20,000x. Consequentially, in 15000x for ZrP showed that there is presence of porosity, but not such seen for modified ZrP.

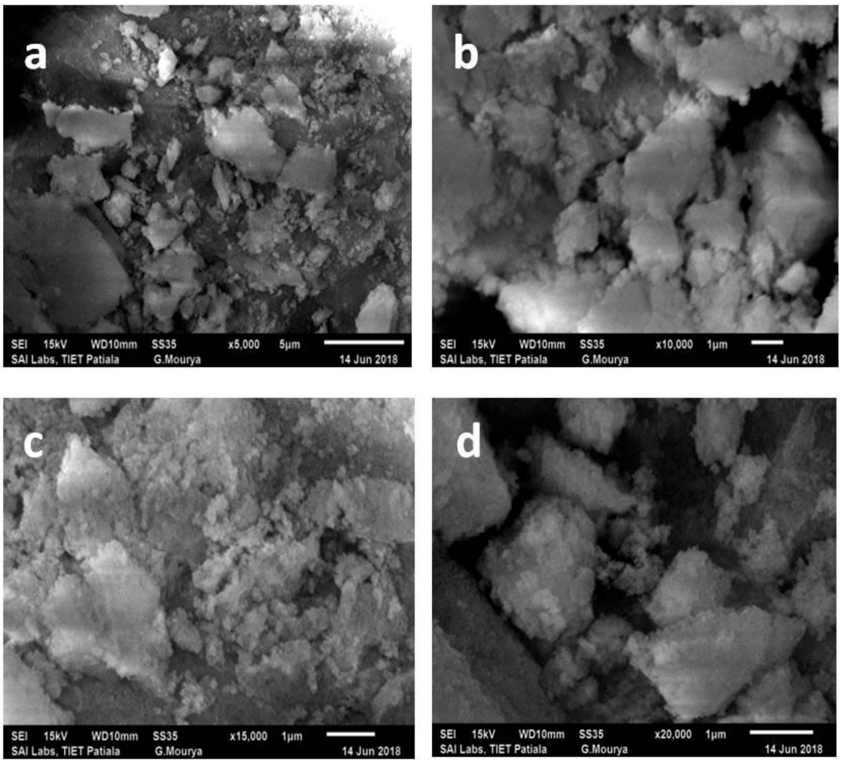


Figure 4: SEM images of Zirconium Phosphate (ZrP) at different magnifications

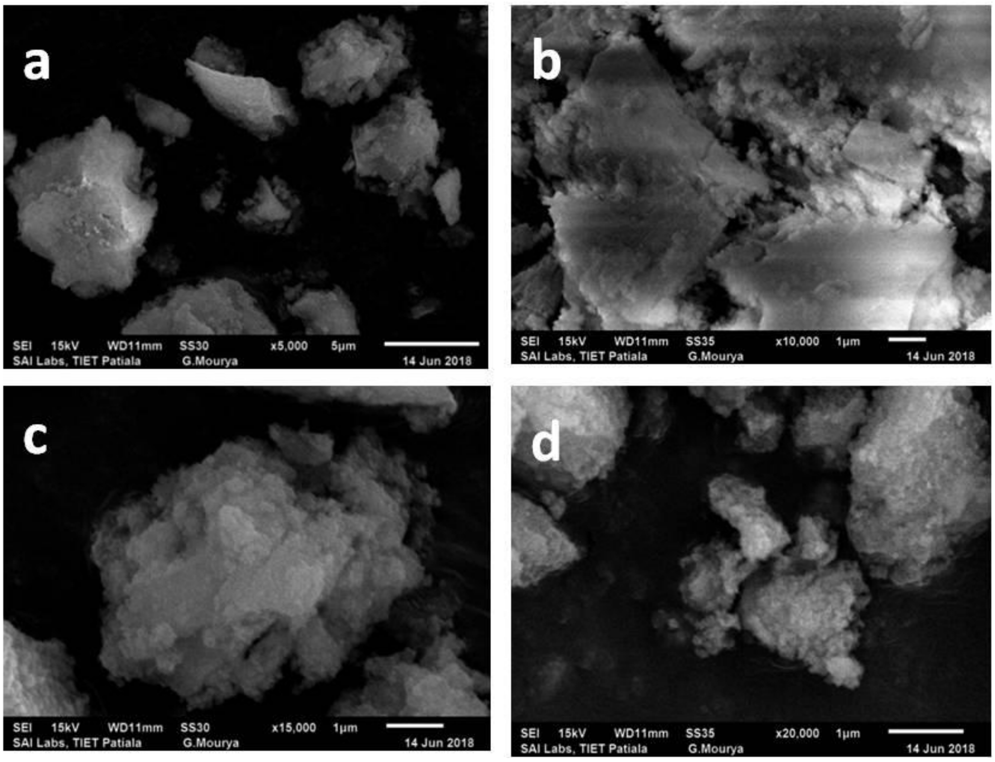
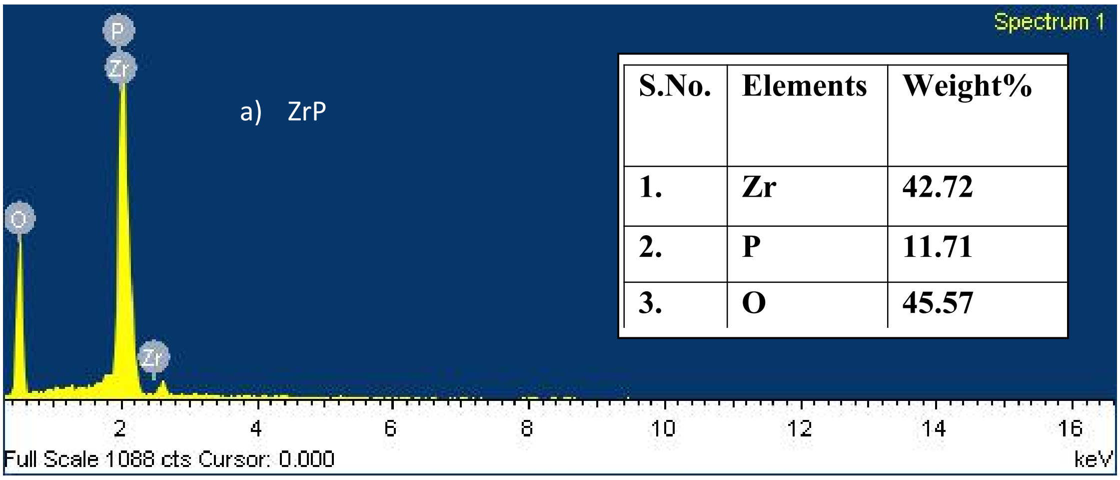


Figure 5: SEM images of modified Zirconium Phosphate (ZrP-CNT)

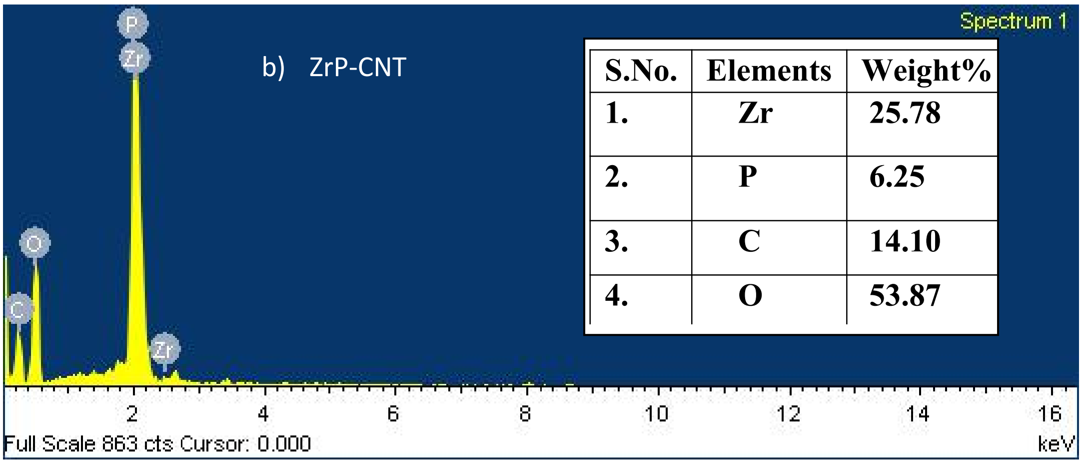
4.3 Energy dispersive X-Ray spectroscopy for SEM

The composition shows that in ZrP sample excess amount of zirconium and phosphate was found, but in modified CNT along with these two, traces of carbon was found about 24.06 % by weight.



S.No.	Elements	Weight%
1.	Zr	42.72
2.	P	11.71
3.	O	45.57

Figure 6: EDS of Zirconium Phosphate



S.No.	Elements	Weight%
1.	Zr	25.78
2.	P	6.25
3.	C	14.10
4.	O	53.87

Figure 7: EDS of Zirconium Phosphate with CNTs

4.4 X-Ray diffraction

Ion exchanger ZrP and modified zirconium phosphate (ZrP-CNT) was seen in the range of 2θ between 3º to 29º with the step size of 0.017º having continuous scan type at room temperature. The resultant for Zrp was amorphous shown in Figure 8with slight peaks showing little crystallinity character. Whereas, for ZrP-CNT peak varies with large deviation from 3º to 10º as shown in figure 9.

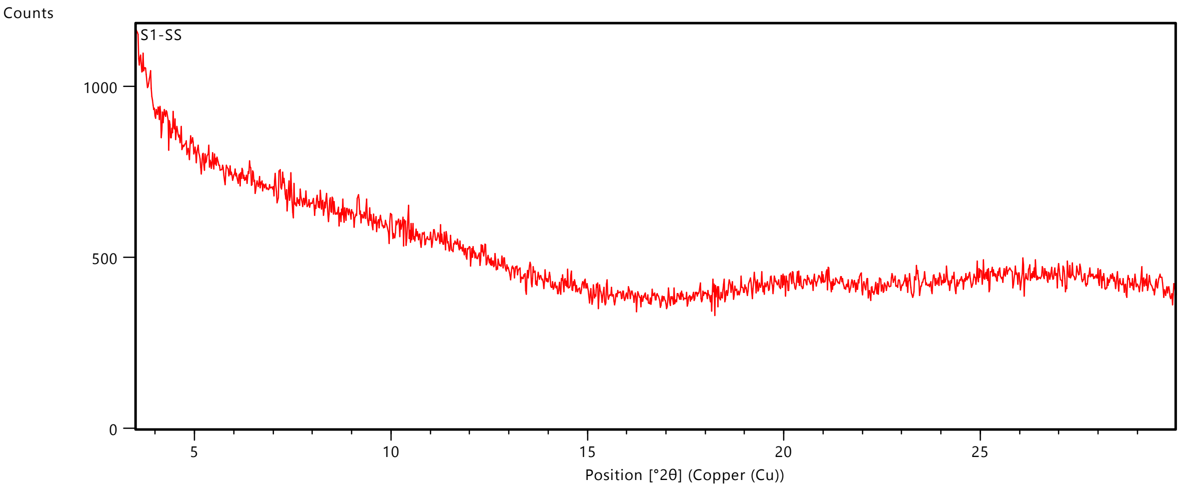


Figure 8: XRD pattern showing amorphous character for ZrP

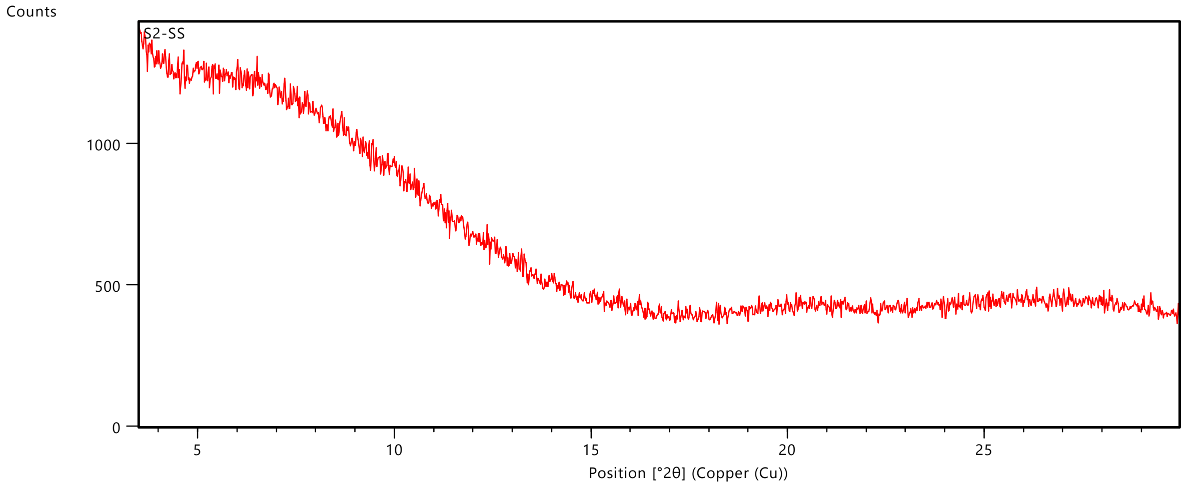


Figure 9: XRD pattern showing amorphous character of ZrP-CNT

CONCLUSION

The two different samples of ZrP were prepared, without and with incorporation of CNTs. Ion exchange capacity for modified with CNTs was found to be higher than that of analogous exchanger. The increment in ion exchange capacity was about 36%. Chemical stability showed that ZrP and ZrP-CNTs were stable in acidic and salt solutions, but not in basic solutions. The sample incorporated with CNTs have good absorbance of Cu^{2+}, Co^{2+} and Ni^{2+} metal ions in comparison to ZrP. The morphology, chemical composition and structural studies were done by XRD, SEM and EDS of prepared ion exchangers. The SEM images showed the porosity character of ZrP. The amorphous character was showed by using X-Ray diffraction.

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