GRANULATION OF ZIRCONIUM PHOSPHOBORATE

A

Thesis Submitted

In partial fulfillment of requirements for the

Degree of

Master of Science in Chemistry

Submitted By
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Contents

Items **Page No.**

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Rahul Sharma

Date: 15 July 2011

Regards

Place: Patiala

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CANDIDATE'S DECLARATION

I hereby declare that the work presented in this thesis entitled, **"Grannulation of Zirconium phosphoborate"** in partial fulfilment of the requirement for the award of Degree of **Master of Science in Chemistry**, submitted in **the School of Chemistry and Biochemistry, Thapar University, Patiala**, is an authentic record of my own work carried out under the supervision and guidance of **Dr.Susheel Mittal**, Senior Professor in chemistry, Head, School of Chemistry and Biochemistry and **Dr. Rajeev Mehta**, Associate Professor in Chemical Engineering, Thapar University, Patiala and refers other researcher's work which are duly listed in the reference section.

The matter embodied in this thesis has not formed the basis for the award of any other degree of this or any other university.

Date: July, 2011

Place: Patiala

Rahul Sharma.
(Rahul sharma)

This is to certify that the above declaration made by the student concerned is correct and true to the best of my knowledge.

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CERTIFICATE

This is to certify that the thesis entitled **"Granulation of Zirconium Phosphoborate"** being submitted in partial fulfillment of requirements for the award of degree of **Master of Science in Chemistry**, submitted in **the School of Chemistry and Biochemistry, Thapar University, Patiala** is a bonafide work carried out under the supervision of **Dr. Susheel Mittal,** Senior Professor in chemistry , Head School of Chemistry and Biochemistry and **Dr Rajeev Mehta** Associate Professor in Chemical Engineering in Thapar University, Patiala and that no part of this dissertation has been submitted for the award of any other degree.

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Abstract

Zirconium Phosphoborate was prepared by the reported method and was converted into granular form by combining the material with polymers like Nylon-66 and EPDM in ratios of 7:3 and 7:1. The resulting material was characterised by SEM, XRD and ion exchange properties. Many other methods like use of spray drier was also tried to get the granular form which was not successful but granules may be achieved by this method by using concurrent nozzle in the spray drier for importing the slurry. From the different methods used for preparing the ZrPB it was clear that equilibration with HCl does not affect the ion exchange capacity of ZrPB and the ratios used for the granulation confirmed that the granulation with Nylon-66 as binder is better with ratio 7:1 than 7:3 and it improves the properties of ion exchanger.

Chapter-1

INTRODUCTION

1.1 What are ion exchangers ?

Ion exchange materials are insoluble substances containing loosely held ions, which are to be exchanged with other ions present in the solutions, which come in contact with them. Ion exchange is the process through which ions in solution are transferred to a solid matrix which, in turn releases ions of a different type but of the same polarity. In other words the ions in solutions are replaced by different ions originally present in the solid. The exact definition of the ion exchange may be defined as follows:

"A reversible chemical reaction between an insoluble solid and a solution during which ions may be interchanged, used in water softening and in the separation of radioactive isotopes."

Synthetic ion exchange materials based on coal and and phenolic resins were first introduced for the industrial use during the year 1930's. A few years later resins consisting of or polystyrene with sulphonate groupss to form cation exchanger which were developed. These two kind of resins are still the most commonly used resins today. Along with all these there are many inorganic exchanger which may be used in sevral types of of the processes. These are explained to most probable extent in the following sceam.

1.2 TYPES OF ION EXCHANG MATERIALS

Ion exchangers prepared for the isolation or separation of cations must have negatively charged functional groups incorporated into the polymer backbone. The most common groups are sulfonic and carboxylic acids. Sulfonic acid groups are introduced by reacting the polymer beads with fuming sulfuric acid or a similar reagent. Similarly, carboxylic acid gro- ups can be introduced by a number of common chemical reactions or by hydrolysis of the ester group or oxidation of hydroxyalkyl groups in methyl methacrylate or hydroxyalkyl methacrylate polymers,respectively. Other common functional groups used in cation exchangers include phosphoric acid and phenol and, to a lesser extent, phosphinic, arsonic, and selenonic acids.

A common approach for the preparation of anion exchangers is to react the styrene-divinylbenzene polymer with chloromethylmethyl ether in the presence of a catalyst, which adds the side chain, CH_2Cl ; then this chloro-methylated product is treated with an amine to introduce the charged functional group. A tertiary amine produces a quaternary ammonium group, while primary and secondary amines give products that are charged only in contact with solutions of low pH. As well as simple alkyl and benzyl amines, hydroxyalkyl amines are used to intro duce functional groups of the type $[CH_2N(CH_3)_2C_2H_4OH]^+$.

1.3 WHAT ARE ION EXCHANGE RESINS ?

An ion exchange resin is a polymer with electrically charged sites at which one ion may replace another. Natural soils contain solids with charged sites that exchange ions, and certain minerals called zeolites are quite good exchangers. Ion exchange also takes place in living materials because cell walls, cell membranes, and other structures have charges. In natural waters and in wastewaters, there are often undesirable ions and some of them may be worth recovering. For example, cadmium ion is dangerous to health but is not present usually at concentrations that would justify recovery. On the other hand, silver ion in photographic wastes is not a serious hazard, but its value is quite high. In either case, it makes sense to substitute an ion such as sodium for the ion in the wastewater.

Synthetic ion exchange resins are usually cast as porous beads with considerable external and pore surface where ions can attach. Whenever there is a great surface area, adsorption plays a role. If a substance is adsorbed to an ion exchange resin, no ion is liberated. Testing for ions in the effluent will distinguish between removal by adsorption and removal by ion exchange. Of course, both mechanisms may be significant in certain cases, and mass balances comparing moles removed with moles of ions liberated will quantify the amounts of adsorption and ion exchange.

1.4 HOW DOES AN ION EXCHANGE RESIN WORK ?

The resins are prepared as spherical beads 0.5 to 1.0 mm in diameter. These appear solid even under the microscope, but on a molecular scale the structure is quite open. This means that a solution passed down a resin bed can flow through the crosslinked polymer, bringing it into intimate contact with the exchange sites.

Suppose a resin has greater affinity for ion B than for ion A. If the resin contains ion A and ion B is dissolved in the water passing through it, then the following exchange takes place, the reaction proceeding to the right (R represents the resin):

$$\mathbf{AR + B^{n\pm} \rightleftharpoons BR + A^{n\pm}}$$

When the resin exchange capacity nears exhaustion, it will mostly be in the BR form.

A mass action relationship applies where the bracketed entities represent concentrations:

$$\frac{[BR]\,[A]}{[AR]\,[B]} = Q$$

Q is the equilibrium quotient, and is a constant specific for the pair of ions and type of resin. This expression indicates that if a concentrated solution containing ion A is now passed through the exhausted bed, the resin will regenerate into the AR form ready for re-use, whilst ion B will be eluted into the water. All large scale applications for ion exchange resins involved such exhaustion and regeneration cycles.

1.5 BASIC PRINCIPLE

Ion-exchange chromatography retains analyte molecules on the column based on coulombic (ionic) interactions. The stationary phase surface displays ionic functional groups (R-X) that interact with analyte ions of opposite charge. This type of chromatography is further subdivided into cation exchange chromatography and anion exchange chromatography. The ionic compound consisting of the cationic species M^+ and the anionic species B^+ can be retained by the stationary phase.

Cation exchange chromatography retains positively charged cations because the stationary phase displays a negatively charged functional group:

$$\mathbf{RX^-C^+ + M^+B^- \rightleftharpoons RX^-M^+ + C^+ + B^-}$$

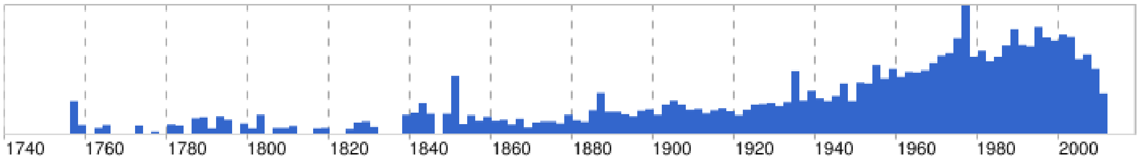
Anion exchange chromatography retains anions using positively charged functional group:

$$\mathbf{RX^+A^- + M^+B^- \rightleftharpoons RX^+B^- + M^+ + A^-}$$

Here the strength of either C+ or A- in the mobile phase can be adjusted to shift the equilibrium position and thus retention time.

1.6 HISTORY

Ion exchange methods have been in use since 1850, when H. Thompson and J. T. Way, researchers in England, treated various clays with ammonium sulfate or carbonate in solution to extract the ammonia and release calcium. In 1927, the first zeolite mineral column was used to remove interfering calcium and magnesium ions from solution to determine the sulfate content of water. The modern version of IEC was developed during the wartime Manhattan Project. A technique was required to separate and concentrate the radioactive elements needed to make the atom bomb. Researchers chose adsorbents that would latch onto charged transuranium elements, which could then be differentially eluted. Ultimately, once declassified, these techniques would use new IE resins to develop the systems that are often used today for specific purification of biologicals and inorganics. In the early 1970s, ion chromatography was developed by Hamish Small and co-workers at Dow Chemical Company as a novel method of IEC usable in automated analysis. This later led to the formation of Dionex Corp (Dow -Ion Exchange). IC uses weaker ionic resins for its stationary phase and an additional neutralizing stripper, or suppressor, column to remove background eluent ions. It is a powerful technique for determining low concentrations of ions and is especially useful in environmental and water quality studies, among other applications.



1850

1850 - The first research observations on the ion-exchange properties of soil were made by two British agricultural chemists, Thompson and Way, in 1850. They observed that soil can remove potassium or ammonium salts from aqueous solution and release calcium salts.

1955

Feb 18, 1955 - The definitive experiments were performed in a memorable, all-night session, on February 18, 1955. To increase the number of events that might be observed at one time, three successive 3-h bombardments were made, and, in turn, their transmutation products were quickly and completely separated by the ion exchange method.

1970

The removal of ammonia from secondary effluent was demon- strated successfully on a laboratory and pilot scale with a selective ion exchange process. The significant results of this program are: 1. Greater than 99-percent ammonia removal was demonstrated in the laboratory with 2 zeolite columns in series and clarified secondary effluent containing 10 to 19 mg/1 ammonia.

1976

Oct 12, 1976 - A method for producing aluminosilicate ion exchange materials is disclosed in US Patent 3985669, Kummel, et al, issued October 12,1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula: $NaI_{2.}2[AlO_2I_2(SiO_2)I_2]$.

1985

Inorganic ion exchange has been used extensively at Sellafield to treat Magnox pond water and decanning liquors, mainly for the removal of caesium and strontium. In 1985, BNFL successfully commissioned the site ion exchange plant (SIXEP) which used a naturally occurring inorganic exchange medium (clinoptilolite). This plant has met its design targets and significantly exceeded its planned availability, permitting the treatment ofadditional volumes of effluents.

1986

Apr 1986 - Plating and Surface Finishing, April 1986 Subject.Precipitation Chemical recovery Resource recovery Copper Nickel Chrome Chromic acid Effluent Pollution prevention Waste reduction Sludge Waste disposal Canada Metal pla... (2514 bytes) 0.90 Recovery of fluoboric acid from waste copper fluoborate - fluoboric acidsolutions by ion exchange Recovery of fluoboric acid from waste copper fluoborate - fluoboric acidsolutions by ion exchange.

1989

Mar 1, 1989 - ION EXCHANGE USING HYDROUS URANIUM DIOXIDE: Patented by David A. White and Paul Donson on March 1, 1989. Abstract: Ion exchange performed by contacting a solution containing ions to be absorbed with a hydrous oxide of uranium.

1992

Apr 6, 1992 - Introducing and removing ion-exchange and other particulates rom an assembled electrodeionization stack: Patented by Edgardo J. Parsi, Keith J. Sims, Irving D . Elyanow and Thomas A. Prato on April 6, 1992. Abstract: Apparatus and method for introducing ion-exchange and other particulates into certain compartments of an assembled electrodeionization stack comprising flowing a slurry of said particulates into the compartments while employing strainers for particulate .

1998

Jul 1998 - Over the years, Nature's Best has continued to grow through opening new markets. In July 1998, Nature's Best revolutionized the meal replacement supplement industry with the introduction of Isopure. Isopure is the first meal replacement /after workout supplement to have 50 grams of only 100% Pure Ion Exchange Whey Protein Isolate. All of the impurities such as fat and lactose are removed to provide the athlete with the cleanest tasting and most refreshing product.

2002

Aug 2002 - Microprofiles of nitrate were determined only in August 2002, using a Liquid Ion eXchange-type (LIX) electrode (see reference 9) with a calomel reference electrode (Radiometer Copenhagen) and calibrated at the in situ temperature (25° C) and salinity (0‰). Linear two-point calibration of the oxygen and nitrous oxide microsensors was performed with river water from the sampling site. The microelectrodes were mounted on a micromanipulator driven by a computer- controlled motor .

2003

May 2003 - The highest concentration of perchlorate detected at the Base was 160000 parts per billion (ppb). In May 2003, EPA initiated an ion exchange treatability study that is expected to run for two years. EPA hopes that this study will not only demonstrate the technology's effectiveness, but also achieve cleanup to levels safe to human health and the environment.

2007

Oct 2007 - The article reports on the expansion of Rohm and Haas ion exchange resin facility in China in October 2007. The expansion aims to strengthen its global exchange resins supply network and will complement various developments in the US Rohm and Haas has also invested significant resources in different countries to reflect the company's continued strength in its core markets. Quality will also be duplicated in all Rohm and Haas ion exchange resin manufacturing facilities made .

Chapter-2

LITERATURE REVIEW

The first commercially available ion exchangers were amorphous aluminosilicate gels[13,14]. These gels later were known as permutites but their instability towards acid solutions and their variability of behavior led chemists to seek alternatives. This search eventually led to the synthesis of organic ion exchange resins[15]. These resins soon dominated the field because of their uniformity, chemical stability and the ability to control resin properties by synthetic procedures. The advent of the nuclear technology initiated a search for ion exchange materials that would remain stable above 150^0C and in high radiation fields. Early attention was focused on hydrous oxides since it was known that they sorbed coprecipitated many ions. It was soon discovered that hydrous oxides such as phosphate,vanadates,molybdates and antimonates produced superior exchangers[16-19]. Much attention paid to the synthesis of ziorconium phosphate which actually had been discovered earlier[20]. These materials are amorphous in nature and not resistant to alkaline hydrolysis.

Various scientists have worked to improve the strength of inorganic ion exchangers. Some of these have been given below:

- Under the normal circumstances, ammonium salts of hetropolyacids may be prepared only in the form of very small crystals. A procedure for preparing larger particles described by Smith[21] consist of contracting molybdophosphoric acid with a concentrated solution of ammonium nitrate. Relatively strong agglomerates of ammonium salt resulted.
- Zinc or nickel hexacyanoferrate(ii)[22,23] crystals have also been prepared by slow growth method. In this method local growth occurs on sodium or potassium ferrocyanide crystals placed in concentrated zinc or nickel solution to produce hollow spheres. Particles of 0.1 to 0.5 mm could easily be prepared. The chemical stability for zinc ferrocyanide in solutions from pH 1 to 10 and for nickel ferrocyanide from pH 0 to 12.
- The various granulated hydrous oxides were prepared by freez thaw method. e.g;

SnO_2, SiO_2, MnO_2, TiO_2, ZrO_2 and mixed absorbed[24]- nickel hexacyanoferrate + $Ni(OH)_2$,PBS + $Pb(OH)_2$, NiS + $Ni(OH)_2$. The freeze thaw method is used to produce granules from inorganic ion exchangers yielding amorphous precipitate that settled and filtered poorly. The method make use of the fact that water is irreversibly separated when a gel is frozen and the absorber become granular. After thawing, the granules are separated from the solution and air dried at ambient or elevated temperature.

- The use of sol gel method to prepare spherical particles of inorganic ion exchangers is a significant contribution to developing procedures for modifying their granulometric and mechanical properties. This method making use of converting a sol dispersed in an Orgainc solvent to hydroxide gel[25-27]. From the principle of the method followed, that it is possible to prepare uniform spheres of hydroxide gel from only polyvalent hydrolysable cation, e.g, Al^{3+}, Fe^{3+}, Cr^{3+} , Si^{4+} , Ti^{4+} , Zr^{4+} , or their mixtures. The conversion of sol gel into a gel may be accomplished by either internal or external gelation[25-27]. Internal gelation is generally used to prepare intrinsic absorbers. Sols may be dispersed in media that are immiscible with water (paraffin or silicon oils, kerosene etc.) in chemical reactors equipped with good stirring capability , or in continuous gelation column by dripping from capillaries [27]. The disadvantage of sol gel method is the great shrinkage of the particles after drying of hydrogels , or their conversion to xerogels. The procedure is not universal because it is not possible to prepare zinc or nickel hexacyanoferrates by sol gel method[27].
- Caletka et al[9-11] used silica gel as the support for depositing several hexacyanoferrates on different types of silica gel[9] of suitable grain size. The simplest way to prepare supported sorbents is to either mix the fine grained or precipitates of the ion exchanger with an inert support material or induce it to precipitate directly on a suitable support. The main disadvantage of this method is a considerable increase in the volume and problems in loading the large columns.
- Porous stainless steel membrane[28] were used for the support of hydrous titanium and Zirconium oxides. TiO_2 and ZrO_2 were precipitated within the porous metal

matrix using tetraisopropyl orthotitnate or zirconium propoxide and LiOH solution. Such stainless steel might be impregnated with TiO_2 upto 7% of their weight. Impregnated steel membrane is used as a means of removing radionuclides from the primary coolant used in pressurized water reactors.

- Water et al.[29] used organic polymers as a support for inorganic ion exchangers[16]. They were the first to describe the preparation or copper hexacyanoferrate-loaded anion axchange resin. Harjula et. al. also studied possible applications of IRA-400 and IRA-904 anion exchange resins, chelex-100 chelating resin as supports for the potassium-cobalt hexacyanoferrates. A Harjula selected granular cobalt hexacyanoferrate for separating Cs form the concentrates at Lovissa NPP.
- Krishnaswami et. al.[31] used fibrous polymers as a support for inorganic ion exchangers. He edveloped the procedure for impregnating acrylic fibers with iron hydroxide. Iron treated fibers were used for the in situ extraction of various elements from the seawater.
- Powdered microcrystalline inorganic ion exchangers might also be converted into granular form by using suitable binding material. Both inorganic and organic materials may be used as binding materials for such composite sorbents. Possible inorganic binding materials includes e.g: clay minerals, which might be mixed with the powdered inorganic ion exchangers and water to form a paste of suitable consistency. This paste is thus used to form pallets, which are dried and calcined to improve their mechanical strength. Cement has also been used as a binding material for granulating nickelhexacyanoferrate[32]. At first a dry mixture of cement and hexacyanoferrate salt (3:2 or 4:1) was prepared and then mixed with water. The resulting dense grout was moulded into desired form. After 3-7 days of curing the product was crushed and sieved. Granules obtained from both of these mixtures exhibited sample long-term stability in contact with solution. A sol gel method was used for granulating the powdered inorganic ion exchangers into the matrix of SiO_2. Urea and hexamethylenetetramine are added to the sol of silicic acid and upto 70% (w/w) of exchanger. This mixture was mixed with the organic medium such as silicon oil at elevated temprature. A composite sorbent

containing ammonium molybdophosphate (AMP) perpared by this procedure[34].

- Spherically granulated[37] sodium aluminophosphatesilicate was prepared by sol gel method. According to this method H_3PO_4 solution, 1M $Na_2SiO_3.SiO_2$ solution and $NaAI(OH)_4.NaOH$ were mixed efficiently in a mixer. The reaction mixture obtained was dispersed in the organic solvent like alipthatic hydrocarbons. In the column the formation of spherical granules of hydrogel took place.
- Some new procedures for prepration of fibrous polystyrene thorium(IV) phosphate (PStThP)[38-39] are reported. The ion exchanger was characterized on the basis of scanning electron microscopy, X-ray diffraction analysis, IR, thermogravimetric analysis, and ion exchange studies. The ion exchange capacity[40] for Na^+ ion is found to be 4.52 mequiv/dry g basis.[41-42] Separation factors and K_d values for various cations at different concentrations have been determined, and a marked selectivity for Cd(II) has been found. The unusual selectivity for Cd(II) should lead to some useful practical applications.

- Many hydrophobic ionizable[43-44] organic compounds like aromatic sulphonates might be present in industrial waste water. These are present in the anionic form[45-46] and not easy to trapped by conventional methods. So a recyclable acrylic polymer (NDA-801) and inorganic salts (e.g: 5-10% Na_2So_4 in mass) from which the trapping molecule was sodium 2-napthalene sulfonate (2-NS) were synthesized for the removal of such compounds. As compared to a granular activated carbon GAC-1, NDA-801 exhibited much higher removal efficiency and capacity of 2-NS in fixed-bed adsorption. Moreover, the exhausted NDA-801[47] beads by 2-NS can be completely regenerated by water wash for repeated use, which is more economically desirable than by other regenerants, such as NaOH solution. Continuous column adsorption−regeneration cycles indicated negligible capacity loss of NDA-801 during operation and further validated its feasibility for potential application in associated wastewater treatment[47].

- A blend of polyaspartyl polymer and chitosan in the form of granules was prepared by the combination of polyaspartyl polymer and chitosan[48], a kind of novel environmentally friendly biomimetic blend material with peptide-polysaccharide-resembling structure was synthesized for heavy-metal removal. The resulting blend possesses diversified functional groups and was further modified by introducing a mercapto group through esterification between thioglycollic acid and hydroxyl group in the structure of chitosan[49-50]. The polyaspartyl polymer-chitosan blend with 2.2 wt % mercapto group content improves the adsorption of organic compounds of mercury and arsenic.

- A study was done for removing arsenic using a polymer supported hydrated Fe^{3+} in the university of Lehigh[51], In this case a hydrated exchanger was prepared using a three step process. In any polymeric cation exchanger, negatively charged sulfonic acid groups are covalently attached to the polymer chains. It is well-established that submicron or nanoscale hydrated iron(III) oxide (HFO) particles exhibit high sorption affinity toward both arsenates and arsenites. In this study, commercially available cation and anion exchangers were used as host materials for dispersing HFO nanoparticles within the polymer phase using a technique previously developed. The resulting polymeric/inorganic hybrid sorbent particles were subsequently used for arsenic removal in the laboratory[52-53]. The most significant finding of the study was that the anion exchanger as a substrate containing dispersed HFO offered substantially higher arsenate removal capacity as compared to the cation exchanger, all other conditions remaining identical. In fact, HFO nanoparticles dispersed within the gel-type cation exchanger were unable to remove arsenic.
- A method was presented for the preparation of zirconium titanate mixed oxides in bead form having hierarchical pore structure[54]. This method entailed the use of both preformed polyacrylonitrile (PAN) polymer beads and surfactants as templates[55]. The templates were removed by calcination at temperatures below about 500^0 C, resulting in mixed oxide beads with trimodal pore size distributions and interconnected pores. In this method, PAN beads were prepared using a home-built droplet generator assembly[56]. The PAN solution was placed in the reservoir of a pressure-driven solution feed system and was pumped to the nozzles

(constructed from modified 21 gauge hypodermic syringe needles) of the vibrating droplet generator head at a constant flow rate. The flow of the PAN solution through the vibrating nozzles produced laminar flow, breaking into a stream of droplets with uniform size. The free-falling droplets were solidified to form PAN polymer beads on contact with a stirred bath. The bath was prepared by dissolving 1 g of Triton-X100 surfactant in 5 L of deionized water. The precipitated PAN beads were washed with deionized water until all DMSO was removed and subsequently dried in air. The PAN beads were then used as templates for the preparation of mixed oxide inorganic beads[57-58].

- D001, a strongly acidic cation exchange resin in spherical form of sizes ranging from 0.3 to 0.85 mm were combined with the Polyethyleneimine (PEI) to remove Cu(ii) ions. The processes can be represented as the following steps: (1) The Na+-type D001 was first transformed to H^+-type by immersing the resin beads into 1 mol/L HCl for 24 h. After being filtered, the resin beads were flushing by D.I. water until neutral pH (6.8-7.2), and then vacuum-dried at 80 °C until reaching constant weight. (2) Five grams of D001 beads were introduced into a conical flask, followed by introducing 100 mL PEI solution (3.5% in mass). Then the flask was shaken continuously at 25 °C for 2 days. (3) After being filtered, the resin beads were rinsed with D.I. water and then immersed into 200 mL 0.1 mol/L $NaHCO_3$ solution at room temperature for 3 h. (4) The resulting beads were washed with D.I. water until the effluent pH approached to 7.1-7.3. After that they were vacuum-dried at 60 °C until reaching constant weight, and we obtained the PEI-immobilized hybrid adsorbent D001-PEI.
- Crystalline silicotitanate[59](CST) an inorganic ion exchange material used for selective cesium and strontium removal was converted to the granules using $Zr(OH)_4$ as binder[60-61]. As the binder is a hydroxide ,the material will suffer some degradation when used with acidic feed material[62].

Chapter-3

Materials and Methods

3.1 Apparatus

A digital pH-meter (Denver Instrument Co., U.S.A.) was used for pH measurements, a temperature controlled electric oven was used for drying the sample. A thermo gravimetric analyzer TGA (Shimadzu TGA-$5^0$0, Japan) were used for Thermal stability. X-ray Diffractometer of (PAN lytical's X' Pert Pro) for X-ray diffraction. For FTIR (Perkin Elmer FTIR spectrometer), scanning electron microscope (JEOL JSM 6510LV, Japan) and Muffle furnace (Carbolite, Aston Lane, England) for heating were used.

3.2 Synthesis of Zirconium Phosphoborate

3.2(a) Zirconium phosphoborate washed with distilled water , without H^+ form

Zirconium oxychloride was prepared o.1M in Hydrochloric acid 0.1N which contained 12ml of HF per liter of the solution. This was added continuously to a well stirred solution of boric acid (0.1M) and orthophosphoric acid(0.1M) at 60^0C. The volumes of the solutions used were in the ratio 2:1:1. The gelatinous white precipitates were obtained which were stirred at 60^0C for half an hour, formed precipitates were allowed to cool and the mother liquid was removed by decantation. Excess of the chloride ions present in the precipitates were removed by washing the gelatinous material with distilled water a number of times and checking the presence of chloride ions using $AgNO_3$ solution. The gelatinous material was then filtered using Buckner funnel and dried in the oven at 40^0C until it broke up into lumps. Finally the lumps were washed with distilled water to get the crystals of ZrPB[63].

3.2(b) Zirconium Phosphoborate washed with 0.1N HCL , H^+ form

The crystals formed by the above process were immersed in the solution of HCl 0.1N for overnight period and washed again with distilled water to remove excess of the acid to get the ZrPb in H^+ form . The removal of excess acid was checked with the help of pH strip.

3.3 Synthesis of Zirconium phosphoborate by Using spray drier

The sol gel obtained by the method described above was allowed to settle properly and washed many times with to make it chlorine free and excess water removed using suction pump. The semi- solid gel like material obtained was converted into slurry of three different concentrations by adding different volumes of distilled water to a measured quantity of material. The three different slurries were passed through the spray drier (Labultima,India) at a inlet temperature of 140^0C and a output temperature of 50^0C. Finally very fine powdered material was collected at the output.

3.4 Preparation of composite ion exchanger granules

Many methods and different solvent systems were used to convert the powdered ion exchanger into granules. These procedures are described below:

3.4(a) Using Nylon-66 as binder

In this method a number of mixing ratios of ZrPB : Nylonn-66 were tried to get the good mechanical strength and exchange properties. From a number of combinations of binder:exchanger ratios tried, the two ratios tried 3:7 and 1:7 were found to give the most accurate results. Any other ratio used gave either too sticky material or resulted in thin sheet in which the exchanger was deposited on the polymer rather than granules. A 30% solution (w/v) of Nylon-66 was prepared is m-cresol at room temperature. The inorganic ion exchanger was mixed with nylon-cresol solution with constant stirring of using magnetic stirrer 140^0C for about half an hour. Evaporated m-cresol in a fuming hood using oil bath and vacuum pump which resulted in granular ion exchanger. The granular material was analyzed by SEM,XRD analysis and ion exchange properties.

3.4(b) Using EPDM (Ethylene Propylene Diene monomer) as binder

EPDM 0.3gm was dissolved in toluene using condenser at a 120^0C. To this 2.1gm of ZrPB was added with stirring on a magnetic stirrer at 90^0C. The blend was stirred for half an hour at same temperature . Toluene was evaporated from the blend using vacuum pump in a fuming hood. The material formed was analyzed for pH titrations and ion exchange properties.

3.5 Ion exchange capacity

Ion exchange capacity of the different samples of zirconium phosphoborate was determined by column operation. The exchanger (0.5 g) in the H+ form was put in a glass column with glass wool support. Eluted 50 mL of each electrolyte solution through the column at the rate of 5-8 drops per minute. The librated protons in each different solutions were titrated against standard sodium hydroxide solution. The ion exchange capacity was determined with respect to some monovalent and divalent cation.

3.6 pH Titration

pH titrations were performed with potassium hydroxide (0.1 N) and sodium hydroxide (0.1 N) by the added salt method. 0.2 g of the exchanger was kept in contact with varying volumes of the base and the salt solutions for 24 hours. The pH of the solutions was noted by using pH meter.

3.7 XRD studies

X-ray powder diffractometry was carried out using X-ray diffractometer with CuKα radiation beam (λ= 1.54060). Fine powdered sample of the ion exchanger was packed into a flat aluminum sample holder. X-ray source was a rotating anode operating at 45 kV and 40 mA with a copper target. Data were collected between 0° and 90°.

3.8 SEM Studies

The ground ion exchanger was stocked over a holder. Then, it was gold-sputtered before examination. The samples were scanned to identify the structure and estimate the particle diameter at different magnifications.

Chapter-4

RESULTS AND DISCUSSION

4.1 Synthesis of zirconium phosphoborate

Five samples of the material were prepared as reported earlier. The material was dried in oven at 40^0C and the dried material broke down into small granules when hydrated with distilled water accomplished by a cracking sound there by indicating restructuring of the exchanger matrix in the hydrated form. The material was characterized as ion exchanger from its characteristics of possessing ion exchange capacity and controlled release of exchangeable proton in the presence of successively increasing sodium ion concentration, as measured by potentiometric titrations. Further, the potentiometric titration curves indicated monofunctional behavior of the exchangable ionic sites in the matrix. Potentiometric titrations were carried out over the two sample materials ZrPB(H^+) and ZrPB(DW).

4.2 Effect of equilibration of ion exchanger ZrPB with HCl

Half of the lot of the exchanger material prepared was equilibrated with 0.1N HCl for 24 hours. The excess of the acid was washed and the exchanger was made free of chloride ions, dried at 40^0C and stored in a closed container. The other half of the material was not given the treatment with HCl. Both of these lots were treated for ion exchange capacity using Na^+ as eluent. In contrast to the expected results both materials were found to posses the same ion exchange capacity (0.26 meq/g). The results indicate that there was no effect of the equilibration on the material with HCl, which might may be due to the reason that the material was already in the H^+ form and not in sodium or any other salt of the reagent used during synthesis, That is, H_3BO_3 and H_3PO_4 were used as reagents and not salts like Na_2HPO_4 or $NaBO_2.2H_2O$.

4.3 Granulation of the ion exchange material

In order to use the exchanger material efficiently during column operations the exchanger was converted to granules by using following three methods :

- Using Nylon-66 as binder
- Using EPDM (ethylene propylene diene monomer) as binder
- Using spray drier

The ion exchange materials prepared by above methods were tested for any change in property due to presence of the binder. Morphological studies carried out on the granular materials indicate uniform distribution of the binder in both the ratio of ZrPB : Nylon-66 as 7:3 and 7:1 (Figure 10 and 11, SEM images of material). However, the XRD patterns indicate that the tendency for crystallization is more in sample containing Nylon-66 in the ratio 7:3 than 7:1. No change in the ion exchange capacity or the material was observed, however the proton release seems to be more defined in granular materials that is ZrPB-3, ZrPB-4 (Figure 2) and also in ZrPB-5 (Figure 3) as compared to the non-granular material (Figure 1). Hence, granulation of the material improved the ion exchange characteristics of the exchanger.

Wet slurry of the gel prepared by mixing the reagent was dried to convert the material into granules but the dried material obtained was in very fine powdered form which could not be used in the column in operations. However, there is a possibility that by using concurrent nozzle, the slurry may be converted in to granules of appropriate size.

4.4 Scanning electron microscopy of ZrPB samples

SEM images of different lots of granular and non-granular materials were recorded to study the morphology of polymer mixed granular ion exchanger as compared to non-granular material. SEM images clearly indicate the mixing of the binder in a homogeneous way (Figure 10 and 11). Even the greater amount of the Nylon-66 in the sample ZrPB-3 can be seen in comparison to that of ZrPB-4, where, no binder can be seen in the images of the samples ZrPB-1 and ZrPB-2 (Figure 8 and 9).

CHAPTER-5

CONCLUSIONS

1. Equilibration with 0.1M HCl does not increase the exchange capacity of the material prepared without equilibration.

2. The method of preparation of ion exchange is reproducible as observed from the consistent ion exchange capacity for 5 different lots.

3. Granulation with Nylon-66 as a binder is better with ratio 7:1 than 7:3.

4. The process of granulation improves the ion exchange characteristics like shape of potentiometric titration curve and degree of crystallization.

Table 1: Ion exchange capacity of zirconium phosphoborate(ZrPB) samples

Sample No.	**Preparation Method**	**Metal Salt (1M)**	**Ion exchange capacity (meq/g)**
ZrPB-1	SG (DW)	$NaNO_3$	0.26
ZrPB-2	SG (H^+)	$NaNO_3$	0.25
ZrPB-3	SG_7N_3 (H^+)	$NaNO_3$	0.25
ZrPB-4	SG_7N_1 (DW)	$NaNO_3$	0.25
ZrPB-5	SG_7E_3 (H^+)	$NaNO_3$	0.26

Table 2: pH titrations of zirconium phosphoborate (ZrPB)

Beaker No.	**Volume used**		**pH of the solution**
	NaOH (0.1N) (mL)	**NaCl (0.1N) (mL)**	
B-1	0.0	20.0	2.40
B-2	2.0	18.0	5.40
B-3	4.0	16.0	7.31
B-4	6.0	14.0	8.63
B-5	8.0	12.0	10.04
B-6	10.0	10.0	11.13
B-7	12.0	8.0	11.41
B-8	14.0	6.0	11.67
B-9	16.0	4.0	11.75
B-10	18.0	2.0	11.91
B-11	20.0	0.0	11.94

Table 3: pH titrations of (ZrPB+Nylon-66)

Beaker No.	Volume used		pH of the solution
	NaOH (0.1N) mL	NaCl (0.1N) mL	
B-1	0.0	20.0	2.83
B-2	2.0	18.0	9.63
B-3	4.0	16.0	11.36
B-4	6.0	14.0	11.72
B-5	8.0	12.0	12.06
B-6	10.0	10.0	12.07
B-7	12.0	8.0	12.17
B-8	14 .0	6.0	12.27
B-9	16.0	4.0	12.28
B-10	18.0	2.0	12.35
B-11	20.0	0.0	12.44

Table 4: pH titration of (ZrPB+EPDM)

Beaker No.	Volume used		pH of the solution
	NaOH (0.1N) mL	NaCl (0.1N) mL	
B-1	0.0	20.0	3.90
B-2	2.0	18.0	11.62
B-3	4.0	16.0	11.92
B-4	6.0	14.0	12.22
B-5	8.0	12.0	12.30
B-6	10.0	10.0	12.45
B-7	12.0	8.0	12.50
B-8	14.0	6.0	12.55
B-9	16.0	4.0	12.62
B-10	18.0	2.0	12.66
B-11	20.0	0.0	12.68

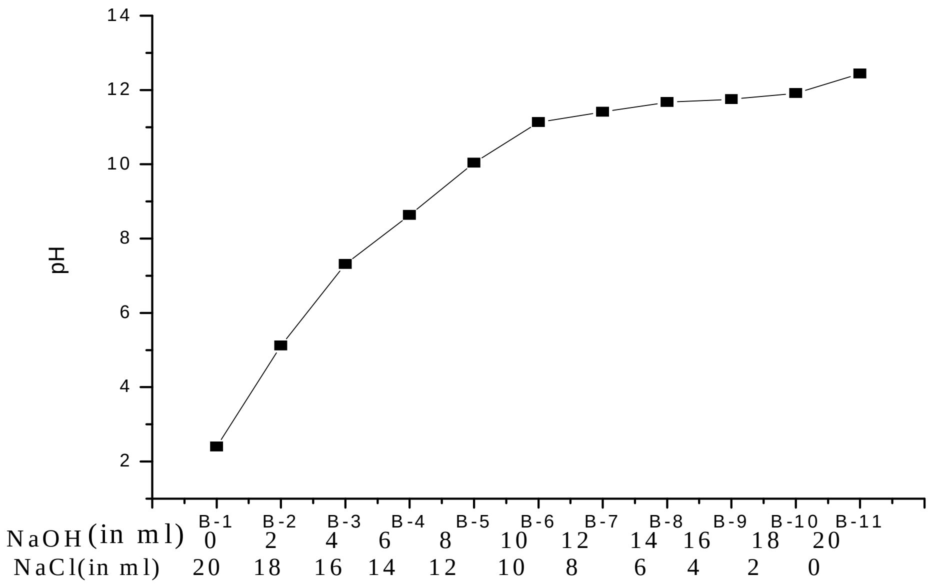


Figure 1: pH titration curve for ZrPB(H^+)

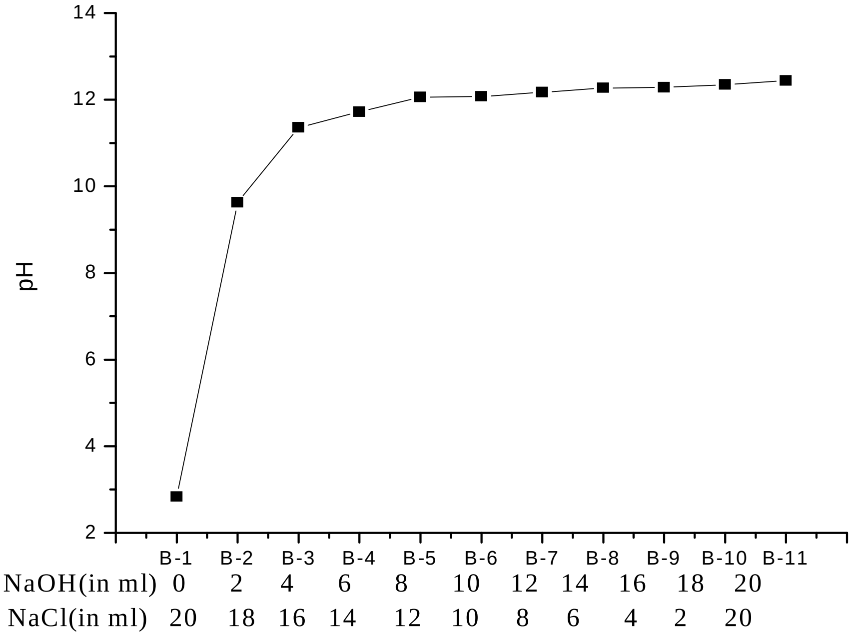


Figure 2: pH titration curve for ZrPB-3 and ZrPB-4

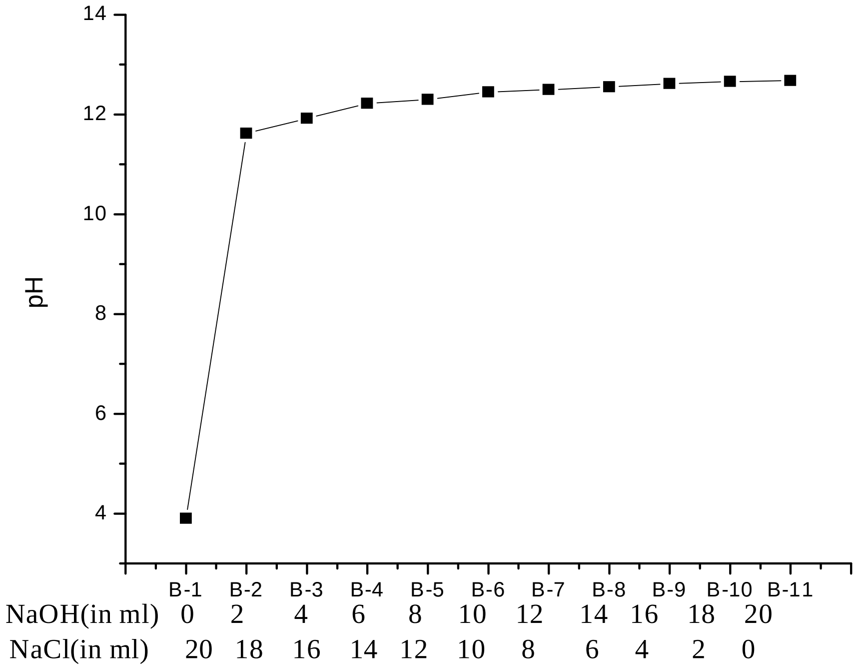


Figure 3: pH titration curve for ZrPB-5

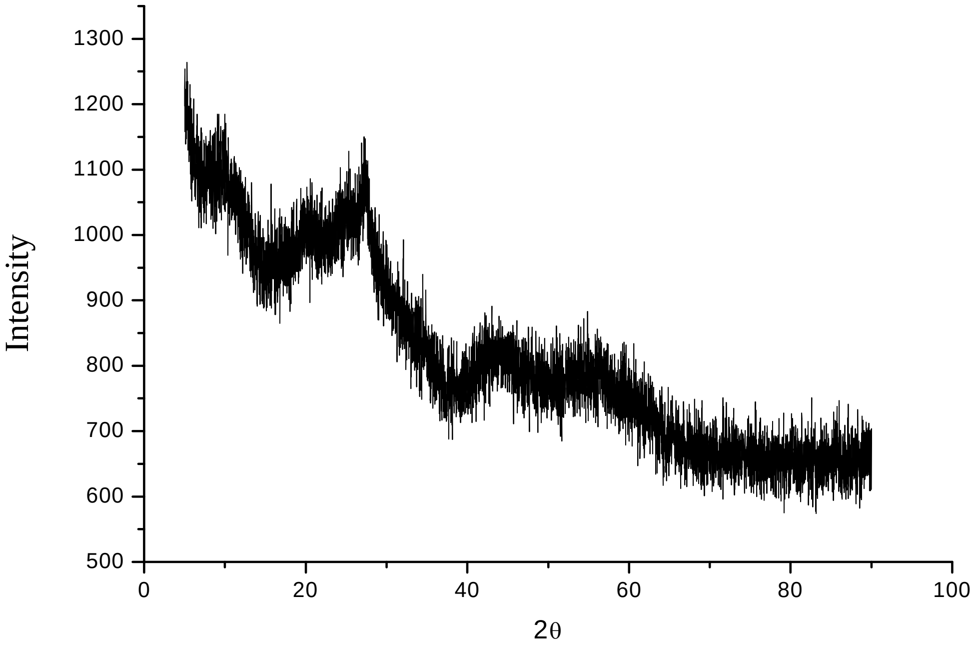


Figure 4: XRD pattern of ZrPB washed with 0.1N HCl (H^+form)

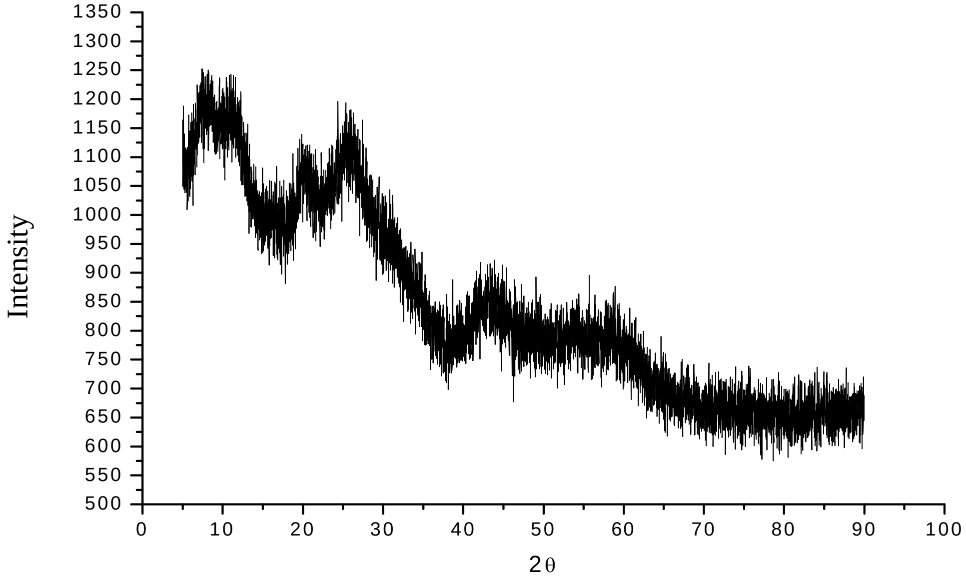


Figure 5: XRD pattern of ZrPB washed with distilled water

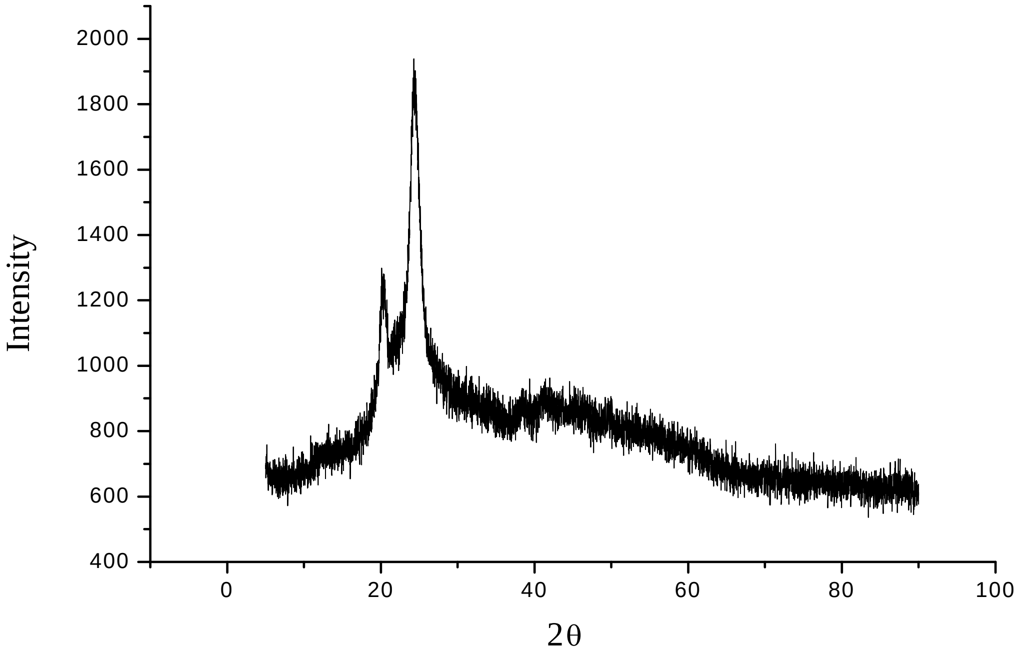


Figure 6: XRD pattern of ZrPB – Nylon66 in a ratio of 7:3

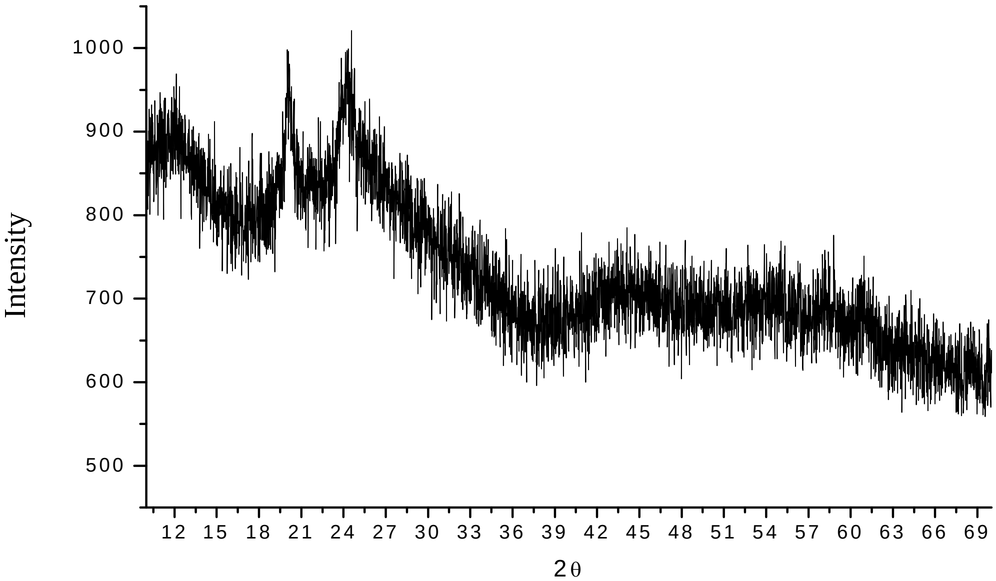


Figure 7: XRD pattern of ZrPB – Nylon66 in a ratio of 7:1

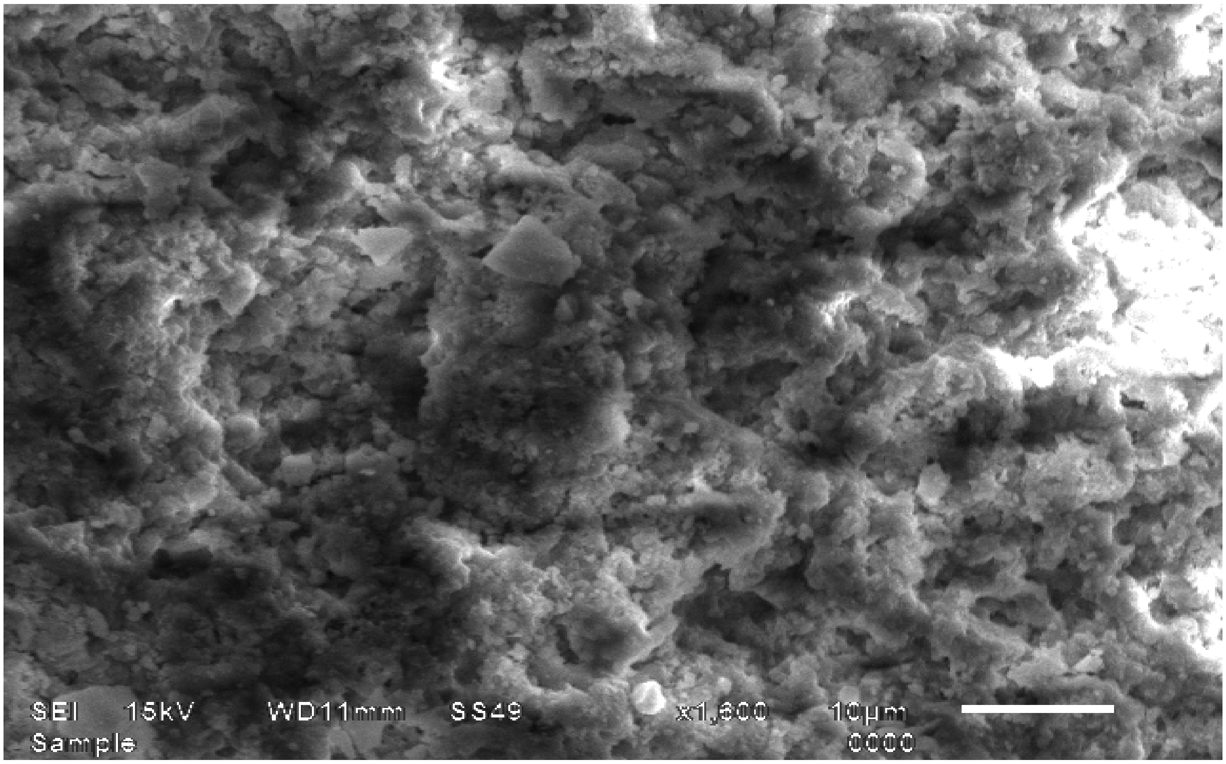


Figure 8: SEM image of zirconium phosphoborate exchanger (ZrPB-1)

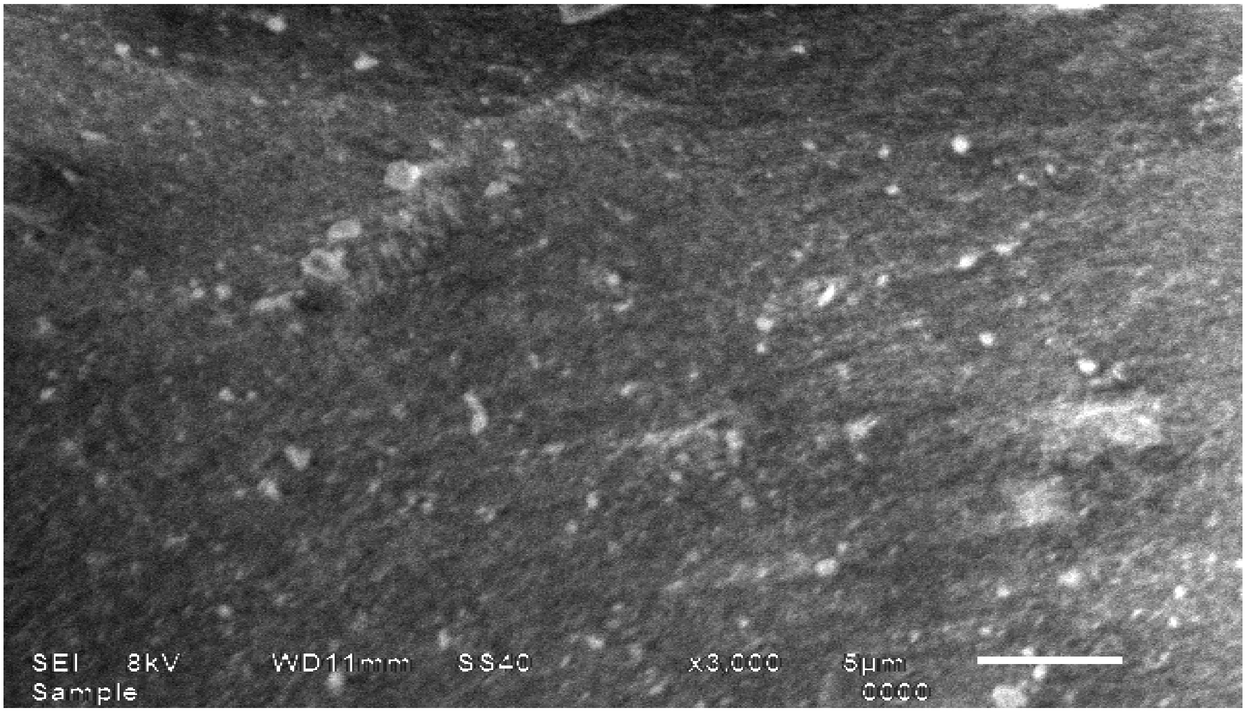


Figure 9: SEM image of zirconium phosphoborate exchanger (ZrPB-2)

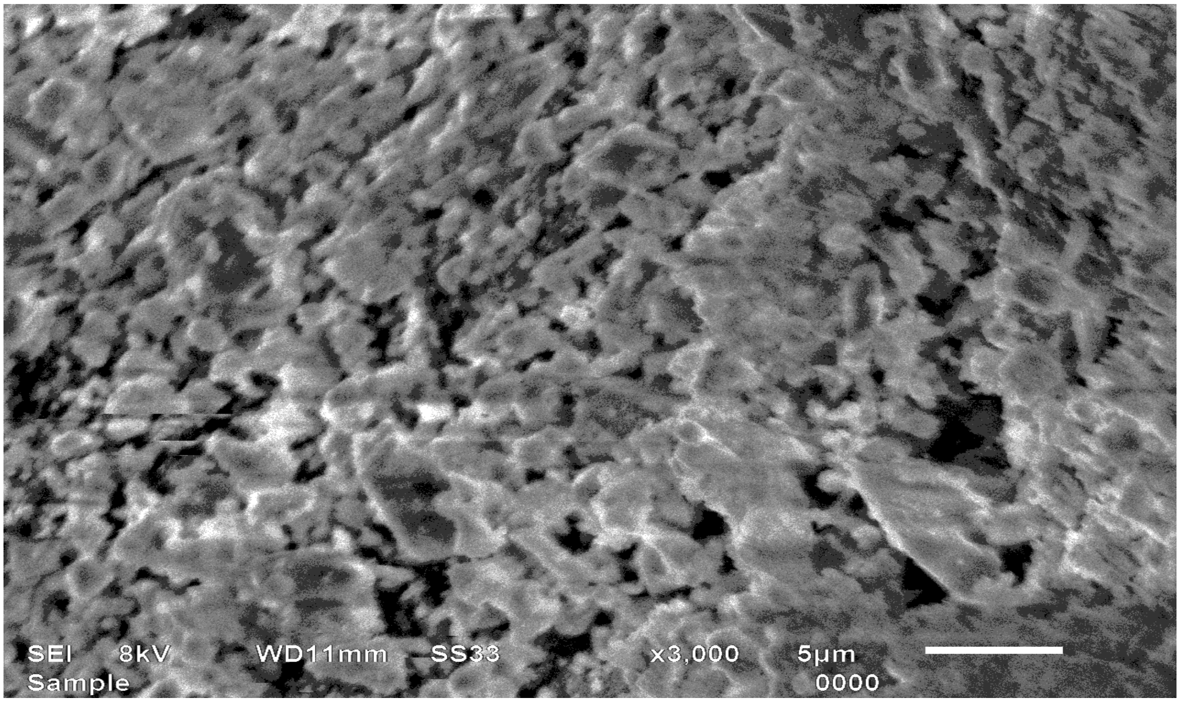


Figure 10: SEM image of zirconium phosphoborate with nylon66 as a binder in the ratio of 7:3

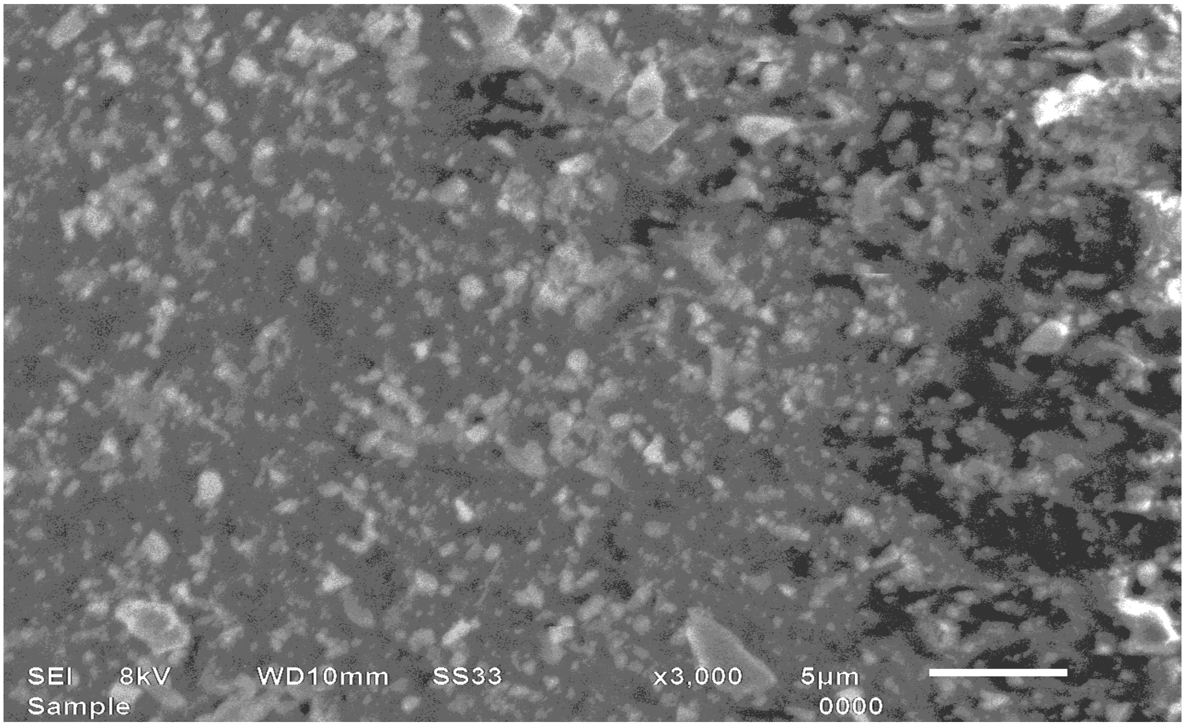


Figure 11: SEM image of zirconium phophoborate with nylon66 as a binder in the ratio of 7:1

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