International Journal of Advanced Technology in Engineering and Science www.ijates.com
Volume No.02, Issue No. 12, December 2014 ISSN (online): 2348 – 7550

STUDY OF EFFECT OF TEMPERATURE ON THE PROPERTIES AND STRUCTURE OF ZIRCONIUM PHOSPHOBORATE ION-EXCHANGER

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ABSTRACT

The chemically and thermally most stable sample of zirconium phosphoborate is prepared by adding a 0.1 mol L^{-1} aqueous solution of zirconium oxychloride to a continuously stirred mixture of 0.1 mol L^{-1} aqueous solution of boric acid and 0.1 mol L^{-1} aqueous solution of phosphoric acid. Its ion exchange capacity for Na^+ and K^+ was found to be 0.29 and 0.58 meqg$^-$1 respectively for dry exchanger. The material has been characterized on the basis of chemical composition, SEM, EDS and XRD analysis. It has been observed that the ion exchange capacity and crystallinity of the ion exchanger decreases with increase in temperature.

Keywords: Ion Exchanger, Ion Exchange Capacity, Thermal Stability, Zirconium Phosphoborate

I. INTRODUCTION

Inorganic ion exchangers have been synthesized under different conditions of synthesis and characterized for nearly four decades now, since the classical work of Amplet[1]. Different types of inorganic ion exchangers and their applications in various fields are documented by Clearfield[2]. Inorganic ion exchangers besides other advantages are important in being more stable at high temperature and radiation fields[3-5].These possess sharp selectivity for metal ions and are stable to chemical degradation as compared to their organic analogs. Ion exchangers have played a prominent role in water processing and in chemical industry. Meeting the stringent coolant purity requirements of nuclear industry is solely attributable to ion exchangers. In the last decade, ion exchangers have been used extensively in the chemical decontamination process for metal ion recovery, regeneration of decontaminants and removal of formulation chemicals from coolant[6]. Therefore, there is continuing need to find new inorganic ion exchangers, which are capable of removing toxic substances from aqueous effluents[7], as they have good stability towards temperature, ionizing radiation and oxidizing solutions.

Synthetic inorganic ion exchangers based on tetravalent metals have been objects of considerable study in recent years because of their selectivity and intercalation properties[8-14]. Zirconium based ion exchangers have received attention because of their excellent ion exchange behaviour and some important chemical applications in the field of ion exchange, ion exchange membranes, and solid state electrochemistry. Heteropoly acid salts based on tin(IV), titanium (IV), zirconium(IV), and thorium(IV) have been reported in literature as ion exchange materials. These metals have better properties than simple salts of metals. The selectivity may be enhanced by varying the composition of the materials. Many scientists have introduced organic-inorganic hybrid ion exchangers consisting of inorganic ion exchangers and organic binding matrices[15-19]. This inorganic ion exchange refers to a composite group of inorganic exchangers, which are modified by some bonding polymeric materials for preparation of large size particles with granular strength[20]. Inorganic ion exchange materials may be encapsulated through immobilization with porous polymeric materials such as alginate, agar agar, polyacrylamide, cellulose acetate and polyvinyl alcohol[21-22]. Literature reports support the decrease in ion exchange capacity and crystalline nature with the increase in temperature[23-24]. ZrPB exchanger also exhibits decreased ion exchange capacity with the increase of temperature.

II. EXPERIMENTAL

2.1 Reagents and Chemicals

Zirconium oxychloride, boric acid and phosphoric acid required for the preparation of zirconium (IV) phosphoborate (ZrPB) [25] were procured from s.d. fine Chemicals Ltd., India. Hydrofluoric acid was procured from Ranbaxy, India. Samarium chloride and other rare earth chlorides were purchased from Indian Rare Earth Chemicals Ltd., India. All the chemicals used were of analytical grade. Double distilled water was used throughout the experiments.

2.2 Instrumentation

A temperature controlled electric oven was used for drying the ion exchanger samples. X-ray diffractometer (PANIlytical's X' Pert Pro) for X-ray diffraction, scanning electron microscope (JEOL JSM 6510LV, Japan) and Muffle furnace (Carbolite, Aston Lane, England) for heating were used.

2.3 Synthesis of Ion-Exchange Material

The ion-exchanger was prepared by adding zirconyl oxychloride (0.1M) solution to a continuously stirred mixture of boric acid solution (0.1M) and phosphoric acid solution (0.1M) at 60^0 C, in the volume ratio 2:1:1. The gel produced in round bottomed flask was allowed to stand overnight. Then the gel was repeatedly washed with distilled water to remove chlorides from the mother liquor. The absence of chlorides in the mother liquor was tested with $AgNO_3$ solution. After the gel became free from chlorides, it was filtered through Whatmann No.1 filter paper using Buchner funnel and suction pump. The gel was transferred from Buchner funnel to Petri dish. The gel in the Petri dish was dried in an air oven at 40°C. When the gel dried completely, distilled water was added. Small granules of the ion-exchanger were formed with crackling sound.

2.4 Ion Exchange Capacity (IEC)

The ion exchange capacities of various samples were determined by column operation at room temperature. The exchanger in H^+ form was placed in a column containing a glass wool support. Sodium nitrate solution (1.0 M) was used as an eluent and about 400 ml of it was passed through the ion exchange column containing 1 g of ion exchanger at the rate of 5-10 drops per minute. Hydrogen ions eluted from column were determined titrimetrically against standard solution of sodium hydroxide.

2.5 Regeneration of Ion Exchanger

The exhausted exchanger was regenerated by keeping it overnight in hydrochloric acid (0.1N). It was then washed with demineralised water till neutral. The exchange capacity was determined and this process was repeated five times.

Table 1 Ion Exchange Capacity (Meq G^{-1} Dry Exchanger) Of Zirconium (IV) Phosphoborate[26]

Sr.No.	Cation	Salt used	I.E.C.(meq g^{-1})
1	Na^+	NaCl	0.29
2	K^+	KCl	0.58
3	Mg^{2+}	$MgCl_2$	0.32
4	Ca^{2+}	$CaCl_2$	0.52

2.6 Thermal Stability

The effect of heating on ion exchange material was examined. The material in H^+ form was heated at different temperatures for 2 h in muffle furnace and the ion exchange capacity for Na^+ was evaluated by column process after cooling it at room temperature. The results are summarised in Table 2.

Table 2. Ion exchange capacity of zirconium (IV) phosphoborate (ZrPB) after heating at various temperatures for 2 h

Sr. No.	Drying Temperature (°C)	Na^+ ion exchange capacity (meq/g)	Colour after Heating
1	40	0.29	White
2	100	0.46	White
3	200	0.38	White
4	300	0.34	White
5	400	0.26	White
6	500	0.23	Gray White
7	600	0.17	Gray White
8	700	0.04	Dark Gray

Table 3. Effect Of Temperature On Ion Exchange Capacity Of Various Inorganic Ion Exchangers[23]

Sr. No.	Inorganic ion exchangers	Ion exchange capacity (meq g^{-1} dry exchanger) at different temperatures							
		40° C	100° C	200° C	300° C	400° C	500° C	600° C	700° C
1	ZrWIP	2.20	1.82	1.60	1.35	1.00	0.90	0.78	--
2	SnWVP	1.83	1.80	1.50	1.25	0.97	0.85	--	---
3	ZrIP	1.75	1.60	1.40	1.00	0.92	0.82	0.66	---
4	ZrIMo	1.54	1.30	1.00	0.78	0.66	0.42	0.16	0.16

III. RESULTS AND DISCUSSION

The results of the study of effect of temperature on ion exchange capacity of various samples of zirconium (IV) phosphoborate are presented in table 1. Zirconium Phosphoborate was heated at different temperatures for 2 hours and the ion exchange capacity for Na^+ ions was determined. The ion exchange capacity data of ZRPB heated at different temperature reveals that zirconium phosphoborate retained 80% of its ion exchange capacity up to 500°C and thus can be used safely in high temperature separations. It is also observed that the ion exchange capacity of ZrPB first increases with increase in heating temperature up to 100°C and above this temperature, the ion exchange capacity goes on decreasing with rise in temperature. The analogous behaviour has been shown by stannic arsenate[27] and satanic arsenoantimonate[28]. These results can be correlated with the observation from various analytical techniques like SEM, EDS and X-ray diffraction pattern as discussed below.

3.1 Scanning Electron Micrograph

Surface study has been found to be of great use for understanding the surface features of materials. The Scanning Electron Micrographs of zirconium phosphoborate at different temperatures (RT, 100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C) are given in Fig. 1. The SEM images reveal an increase in crystal size above 300°C temperature, leading to the decrease in the ion exchange capacity of the ion exchanger on heating above 300°C. These observations are more evident from the magnification of the images (15 KV 1000X, 10000X).

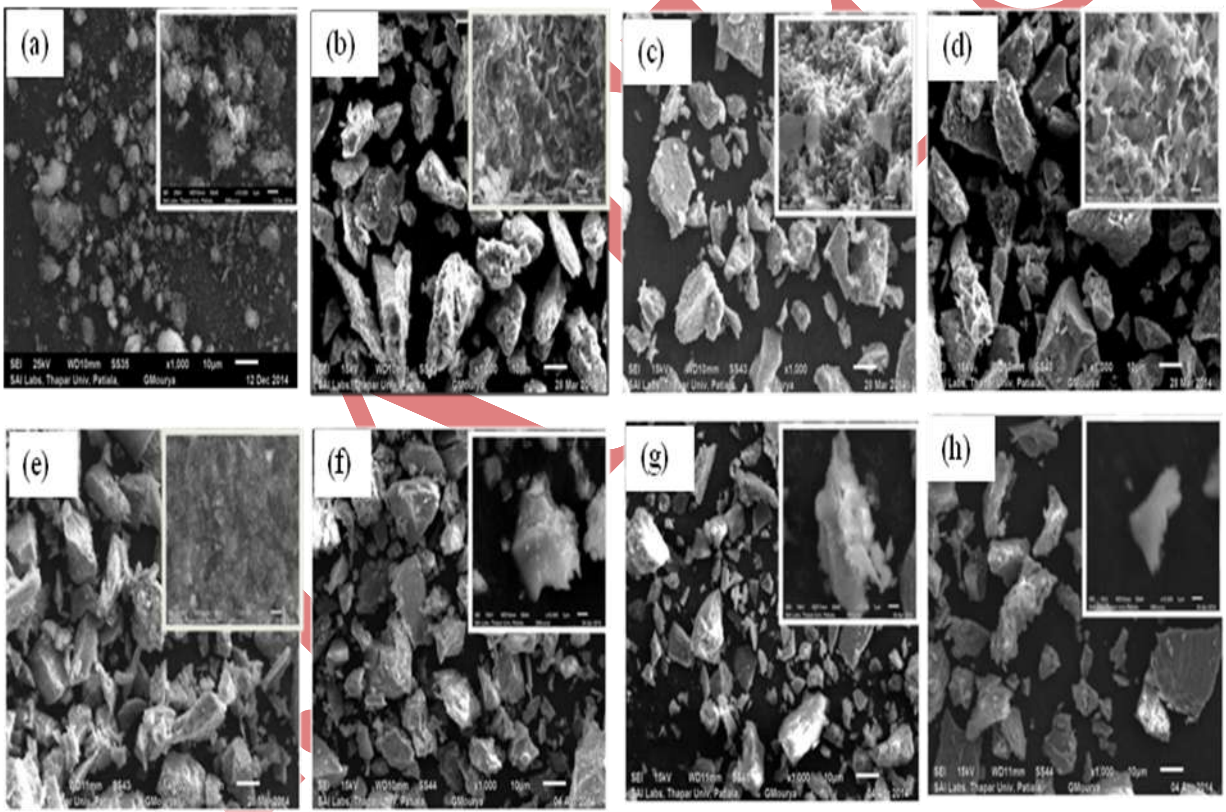

Fig.1. SEM surface images 1000X (inset 10000X) magnification for prepared ion exchanger at (a) RT (b) 100°C , (c) 200°C, (d) 300°C, (e) 400°C, (f) 500°C, (g) 600°C, (h) 700°C

Energy – Dispersive X-ray Spectroscopy

EDS Studies of zirconium Phosphoborate at different temperature are shown in Fig. 2. The EDS data reveals that Zr, P, B and O elements are present in the synthesized samples of zirconium phosphoborate.

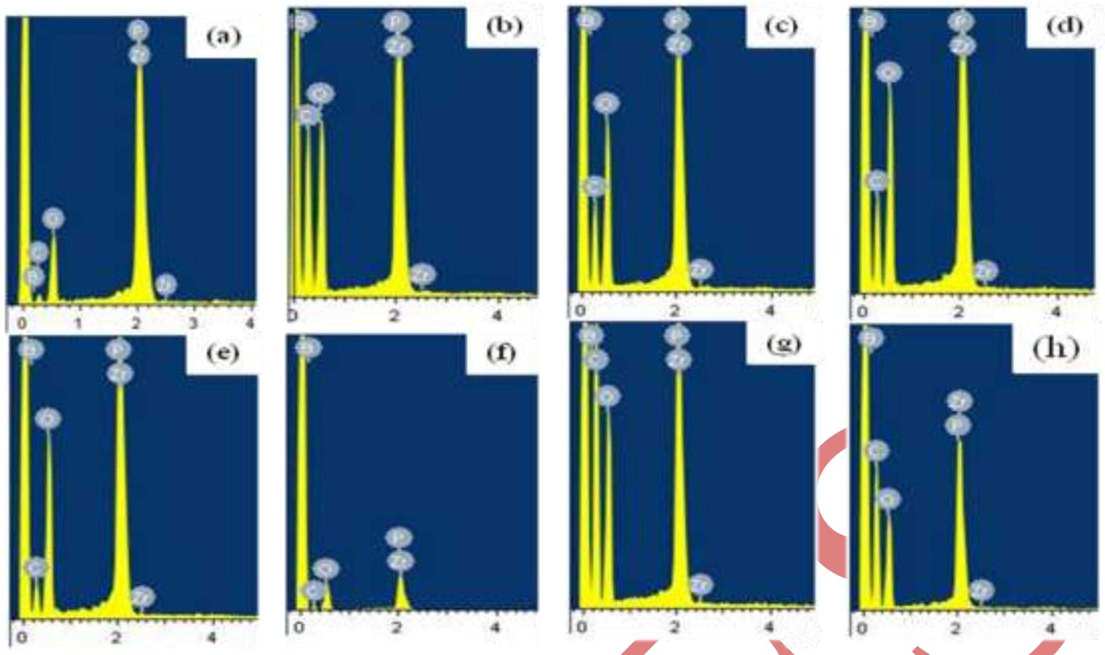

Fig.2. EDS studies for prepared ion exchanger at (a) RT (b) 100°C , (c) 200°C, (d) 300°C, (e) 400°C, (f) 500°C, (g) 600°C, (h) 700°C

3.2 X-Ray Diffraction

Crystaline nature of the ion exchanger zirconium phosphoborate is evident from the X-ray differaction spectrum (Fig. 3), that exhibits a number of peaks with different 2 theta values.

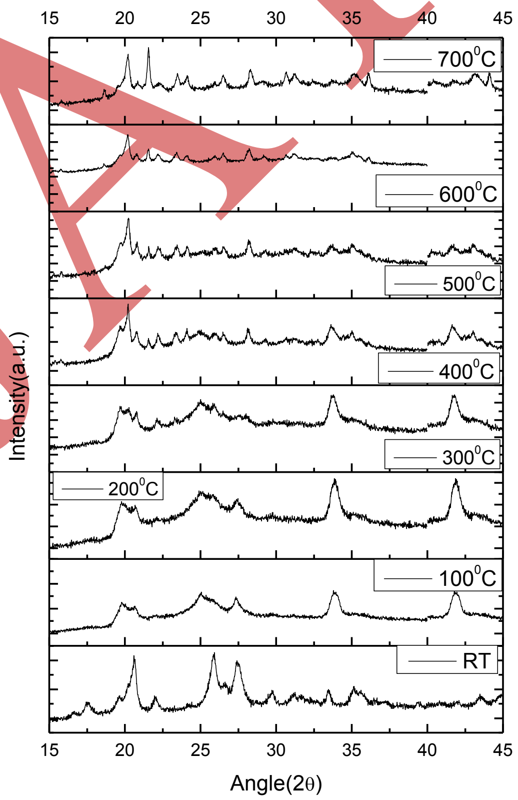

Fig.3. XRD pattern of ZrPB ion exchanger at (a) RT, (b) 100°C , (c) 200°C, (d) 300°C, (e) 400°C, (f) 500°C, (g) 600°C, (h) 700°C

XRD results show that with increase in temperature from room temperature to 300°C, there is small decrease in crystallinity with appearance of new peaks in the region of 30-45 degrees. But with further increase in temperature all major peaks disappear, indicating decrease of crystalline nature. It has also been observed that the colour of sample changes from white to grey white with increase in temperature from room temperature to 700°C. It is observed from SEM studies that there is increase in particle size of the ion exchanger with increase in temperature that leads to decrease in ion exchange capacity due to reduced crystallinity and reduced surface area.

IV. CONCLUSION

The results of this investigation show that the ion exchange capacity of zirconium (IV) phosphoborate initially increases with rise in temperature upto 100°C and after that, the ion-exchange capacity decreases as temperature inceases. Zirconium phosphoborate ion exchanger has good resistance to heat and retains considerable ion exchange capacity upto 500^0C. Thus, zirconium (IV) phosphoborate can be employed for high temperature separation of metal ions.

V. ACKNOWLEDGEMENT

SK and PPS gratefully acknowledge Punjab Technical University (PTU), Jalandhar for permission to work on the project. SKM is thankful to Director, Thapar University, Patiala for the support

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