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Ion exchange Characteristics of newly Synthesized Cerium Zirconium Phosphotungstate and its Analytical Applications

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Abstract

Growing environmental problems have necessitated the selective determination and removal of heavy metal ions, for which inorganic ion exchangers are found to be suitable. Zirconium based ion exchangers have received attention because of their excellent ion exchange behaviour. A bimetallic heteropoly acid salt,cerium zirconium phosphotungstate (CZPT) was synthesized by precipitation method. Chemical composition was determined by EDS method and structural characterizations were done by Thermo gravimetric analysis, X-ray diffraction analysis and Fourier Transform Infrared Spectroscopic analysis etc. UV-Visible diffuse reflectance spectroscopic studies were carried out for characterization as well as to study the optical properties. Ion exchange properties were studied by determining ion exchange capacity and distribution coefficients for various metal ions. pH titration studies, effect of hydrated ionic radii and temperature on ion exchange capacities and stability in various media were also studied. The distribution studies revealed that the material is a good scavenger of metal ions such as bismuth, copper, strontium, lead, thorium etc. On the basis of the selectivity pattern, the separation potential of the ion exchanger was explored by carrying out binary separations of metal ions such as Ca^{2+}, Hg^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} from Bi^{3+}on a column of the ion exchanger by using suitable eluents. The eluents were selected after studying the electrolyte effect on distribution coefficients of metal ions. Difference in selectivity towards aluminium and magnesium was used for the analysis of these ions in antacids. The material was found to absorb all the light in the UV region and this knowledge can be utilized for photo stability of pigments by introducing this. In addition to this, it shows electronic and ionic conduction also. Thus the material find promising applications in various fields by combining its ion exchange properties, catalytic activity, electron exchange properties, optical properties, electrical properties, semiconducting properties etc.

Keywords: Ion exchanger, distribution studies, UV-Vis. DRS, photostability, antacids.

Introduction

Environmental pollution by toxic metal ions is becoming a serious issue day by day. There are various methods already in this field for controlling the pollution, like chemical precipitation, ultrafiltration, reverse osmosis etc. But heavy metals removal in trace amounts is difficult by these methods. So the development of new materials and methods is required and ion exchange method has been developed for the removal of trace amounts. The inorganic ion-exchange materials of polyvalent metals are gaining importance in catalysis, kidney dialysis, ion-selective electrodes, membranes, separation of ions etc[1]. Besides other advantages, inorganic ion exchangers are stable to high temperature and radiation than organic ion exchangers.

Heteropoly acid salts of zirconium and their separation efficiencies have already been studied in detail since zirconium based materials were found to be highly stable. Also composite materials were found to possess improved ion exchange properties compared to their individual counterparts. So in this work, a novel inorganic ion exchanger, cerium zirconium phosphotungstate (CZPT) have been synthesized. Our objective is tosynthesize, characterise and to explore the separation potential of cerium zirconium phosphotungstate. Based on the studies, analysis of aluminium and magnesium in various samples of antacids is carried out and checked the results with the actual amount present in the sample which reveals the separation potential in the analysis. In addition to this, various other applications of the material are suggested.

Material and Methods

Analytical reagent grade chemicals and reagents were used for the study. Various spectroscopic and non-spectroscopic methods were used for characterization of the materials.

Synthesis of cerium zirconium phosphotungstate (CZPT): It was synthesised by first preparing 1M solutions of the reagents, sodium dihydrogen phosphate, sodium tungstate, zirconium oxychloride and ceric ammonium nitrate. A mixture of sodium dihydrogen phosphate solution and sodium tungstate solution are mixed and added with constant stirring to a mixture of zirconium oxychloride solution andceric ammonium nitrate solution at pH 1. It is kept for 24 hours for digestion. It is filtered, washed with de ionized water and dried in room temperature. Then it is keptovernight in 1M HNO_3 with occasional shaking and changing the acid for converting into the H^+ form. It is then filtered, washed with deionized water, dried and sieved to obtain particles of uniform size. Similarly various samples of the exchanger were prepared by changing the mixing volume ratios, since ion exchange capacities depend on the composition of the material. Their ion exchange capacities were determined to select the material of highest ion exchange capacity for detailed studies.

Various spectroscopic and non-spectroscopic methods used for characterization of the materials were carried out as reported earlier[2,3].

Analysis of antacids: One tablet or 5ml of the drugs were treated with 10ml of concentrated HCl and filtered. The clear solution thus obtained was diluted to 250ml with demineralised water. 1ml of this solution was evaporated to dryness and the residue was dissolved in about 10ml of demineralised water and loaded on the column of 5g of cerium zirconium phosphotungstate. The solution was recycled thrice through the column to ensure complete sorption. Al^{3+} and Mg^{2+} were eluted using 0.1M HNO_3 and 0.2M NH_4NO_3 respectively. The concentration of ions in the eluents was determined.

Results and Discussion

Cerium zirconium phosphotungstate (CZPT) samples obtained as bright yellow glassy solids table-1 with the highest ion exchange capacity of 0.69 meq/g was selected for detailed study.

The sample, CZPT5 with highest phosphorous to tungsten ratio exhibited the highest ion exchange capacity. The composition of the sample obtained by EDS measurements figure-1 is in the ratio C:Z:P:T = 3 : 1: 4 : 1.

Thermo gravimetric analysis figure-2 shows about 17% weight loss corresponding toloss of structural hydroxyl groups[4]. The material is found stable up to 800^oC with appreciable ion exchange capacity which makes it suitable for high temperature applications.

FTIR spectrum of CZPT figure-3 shows a band in the region ~3415 cm^{-1} which is corresponding to symmetric and asymmetric –OH stretching, and the band at ~1630 cm^{-1} is due to H-O-H bending[3]. A band at ~1380 cm^{-1} shows the presence of δ (POH). This indicates the presence of structural hydroxyl protons in CZPT and a band in the region ~1080 cm^{-1} shows P=O stretching. Bands around ~730, ~605 and ~450 cm^{-1} show the presence of W-O, Zr-O and Ce-O bonds[5].

From elemental analysis by EDS, thermal analysis and FTIR a tentative formula is assigned which is $3CeO_2.ZrO_2.2P_2O_5.WO_3.13H_2O$. The number of water molecules was determined on the basis of Alberti-Torraca formula.

The SEM image figure-4 suggests that the material consists of large agglomerates with a size reaching several microns. The large particles however, appeared as though they consist of small undeveloped crystallites glued to each other. The particles are arranged so that they form a heterogeneous surface showing high surface area.

XRD analysis figure-5 shows some crystalline character with intermittent peaks of low intensity at 2θ values of 26.94^o, 32.04^o etc. The particle size calculated from Debye Scherrer equation is 33nm.

The UV/Vis DR spectrum figure-6 shows that the band gap energy is very less, showing semiconducting property[6]. The band around wavelength 210 nm shows inter band transition in ZrO_2 and f→d transitions of Ce^{3+}. The band at about 250nm is assigned to $Ce^{3+}\leftarrow O^{2-}$and inter band transition in ZrO_2 and the band at about 300 nm is assigned to $Ce^{4+}\leftarrow O^{2-}$ charge transfer transitions[3]. The presence of $Ce^{3+} \leftarrow O^{2-}$ transitions in the UV-Vis DR spectra infers the presence of oxygen vacancy defects which increases the catalytic activity of the material. Presence of zirconiumis found to increase the band gap energy.

The effect of size and charge on ion exchange capacity table-2 was studied for alkali and alkaline earth metal ions and the order was found to be $Li^+ < Na^+ < K^+$; $Mg^{2+} < Ca^{2+} < Ba^{2+}$ which confirms that ion exchange takes place with the hydrated form of the ions. The sodium ion exchange capacity decreases table-3 slightly with temperature and the sample retained prominent capacity even at 500^oC. The slight decrease in capacity is due to decrease in number of hydroxyl groups[2].

Table-1
Synthesis and properties of cerium zirconium phosphotungstate

Sample	Volume ratios C : Z : P: T				Appearance	Ion Exchange Capacity for Na^+ (meq/g)
CZPT1	2	1	1	2	Bright yellow glassy solids	0.3
CZPT2	2	1	2	2		0.65
CZPT3	2	1	2	3		0.57
CZPT4	2	1	2	4		0.59
CZPT5	2	1	4	1		0.69
CZPT6	2	1	4	2		0.57

Table-2
Effect of hydrated ionic radii and charge on IEC

Metal ion	Hydrated ionic radii[99] (A^o)	IEC meq/g
Li^+	3.40	0.60
Na^+	2.76	0.69
K^+	2.32	0.76
Mg^{2+}	7.00	0.77
Ca^{2+}	6.30	0.79
Ba^{2+}	5.90	0.82

Table-3
Effect of temperature on IEC

Temperature ^oC	Duration (hrs)	Na^+ IEC
50	3	0.67
100	3	0.61
200	3	0.48
300	3	0.39
400	3	0.29
500	3	0.21

Table-4
Distribution coefficients in water and other electrolytes

Cations	K_d						
	DMW	HNO_3			NH_4NO_3		
		0.001M	0.01M	0.1M	0.001M	0.01M	0.1M
Zn^{2+}	16.4	6.4	NS	NS	8.9	2.2	NS
Ca^{2+}	4.2	NS	NS	NS	NS	NS	NS
Hg^{2+}	7.4	NS	NS	NS	NS	NS	NS
Co^{2+}	15.8	7.4	NS	NS	8.9	NS	NS
Ni^{2+}	20.8	11.6	3.5	NS	13.6	5.8	1.2
Cu^{2+}	54.8	43.2	31.9	20.7	46.8	37.4	21.3
Mg^{2+}	28.6	19.4	9.4	NS	23.8	14.4	6.8
Pb^{2+}	42.2	29.6	18.4	7.6	32.8	27.4	15.7
Y^{3+}	4.8	NS	NS	NS	NS	NS	NS
Th^{4+}	29.4	20.4	13.7	5.4	22.5	16.4	10.2
Al^{3+}	166.6	103.7	81.7	48.4	128.6	108.3	52.7
Bi^{3+}	355.6	315.7	287.4	243.9	323.6	299.6	256,8
Sn^{2+}	30.8	24.2	17.3	7.3	26.8	20.5	14.3
Mn^{2+}	21.6	13.2	5.7	NS	17.4	11.2	4.1
Sr^{2+}	48.4	31.4	26.3	17.4	35.6	30.4	23.7

Table-5
Binary separation of metal ions on cerium zirconium phosphotungstate

Separations achieved	Eluent	Metal ion(mg)		% efficiency
		Loaded	Eluted	
Ca^{2+}	0.001M NH_4NO_3	1.91	1.81	94.8
Bi^{3+}	0.5M HNO_3+0.1M NH_4NO_3	2.62	2.54	97
Hg^{2+}	0.001M NH_4NO_3	1.71	1.68	98.2
Bi^{3+}	0.5M HNO_3+0.1M NH_4NO_3	2.62	2.55	97.3
Mg^{2+}	0.001M NH_4NO_3	1.42	1.37	96.5
Bi^{3+}	0.5M HNO_3+0.1M NH_4NO_3	2.62	2.59	98.9
Zn^{2+}	0.001M NH_4NO_3	1.53	1.48	96.7
Bi^{3+}	0.5M HNO_3+0.1M NH_4NO_3	2.62	2.57	98.1
Co^{2+}	0.001M NH_4NO_3	1.61	1.57	97.5
Bi^{3+}	0.5M HNO_3+0.1M NH_4NO_3	2.62	2.57	98.1
Ni^{2+}	0.001M NH_4NO_3	1.49	1.44	98.6
Bi^{3+}	0.5M HNO_3+0.1M NH_4NO_3	2.62	2.55	97.3

Table-6
Analysis of antacids using cerium zirconium phosphotungstate

Antacid	Manufaturer	Labelled composition		Composition found by ion exchange method		% deviation from labelled composition	
		$Al(OH)_3$	$Mg(OH)_2$	$Al(OH)_3$	$Mg(OH)_2$	$Al(OH)_3$	$Mg(OH)_2$
Diovol forte	Wallance	300	250	297.8	248.2	0.73	0.72
Tricaine MPS	RPG	300	150	296.2	148.9	1.27	0.73
Digene	Boots	300	250	298.4	249.3	0.53	0.28
GelusilMPS	ParkeDevis	250	250	249.5	249.1	0.17	0.36

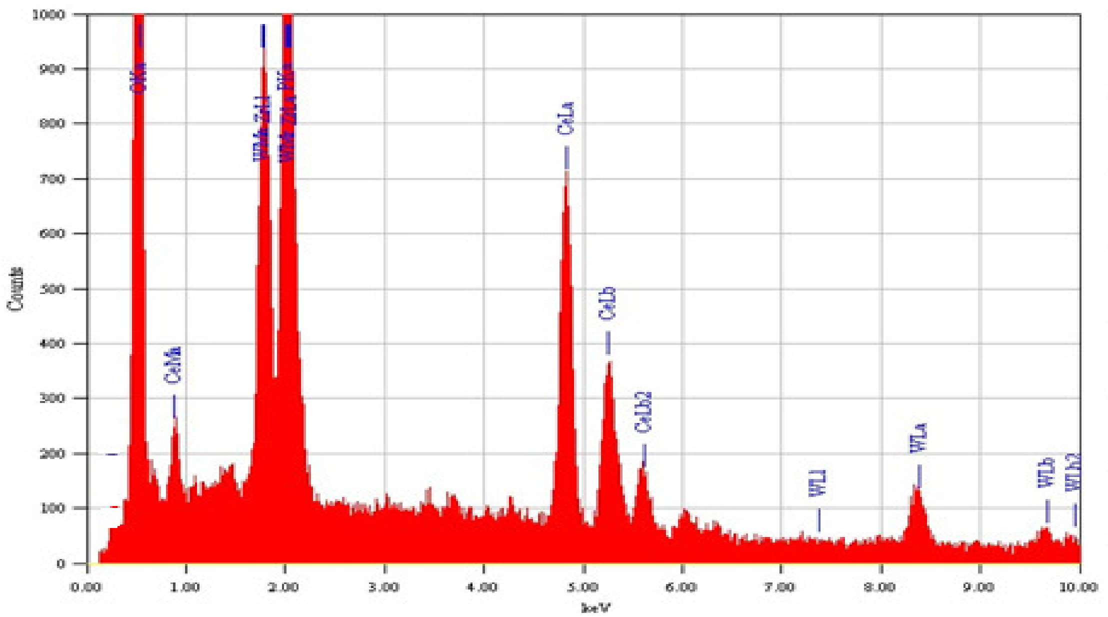

Figure-1
EDS of CZPT

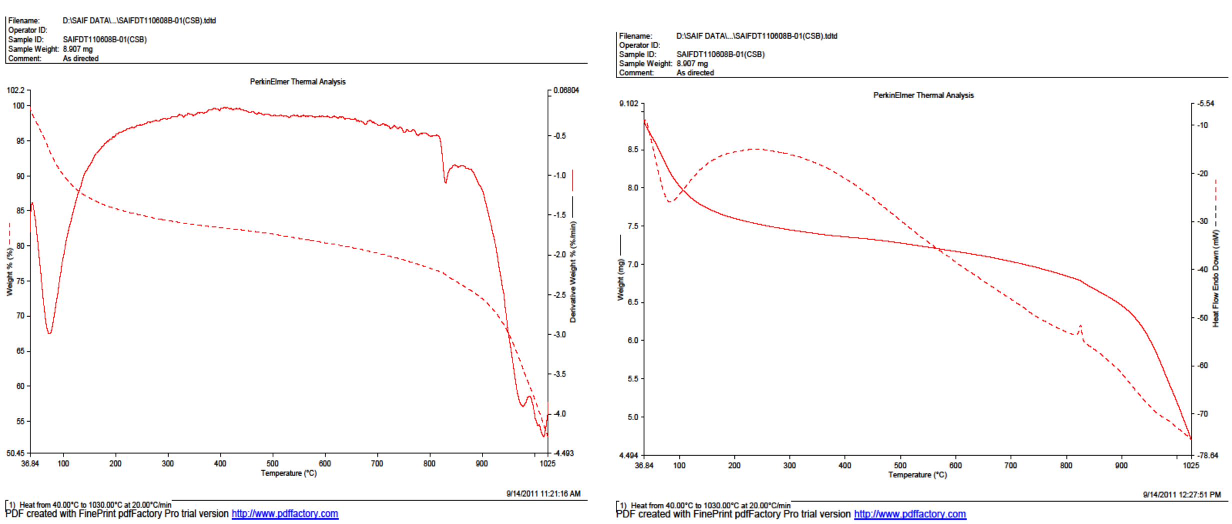

Figure-2
Thermal analysis diagrams of CZPT

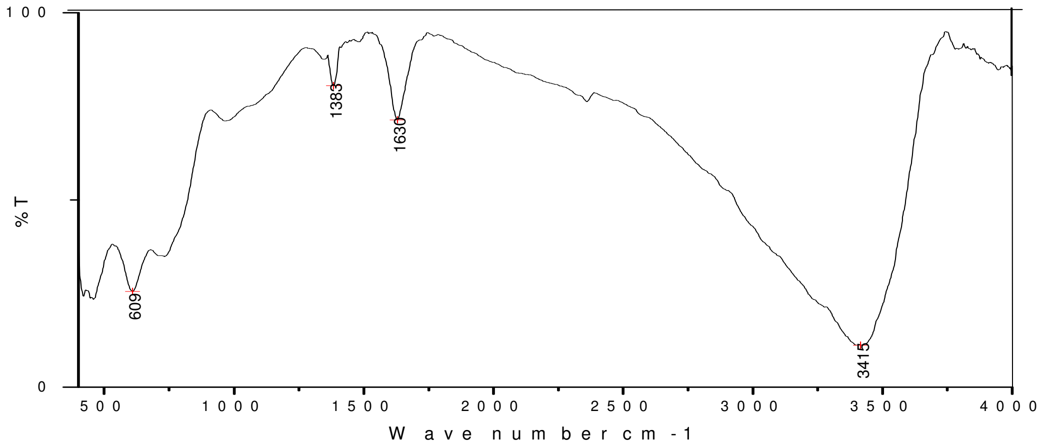

Figure-3
FTIR spectra of CZPT

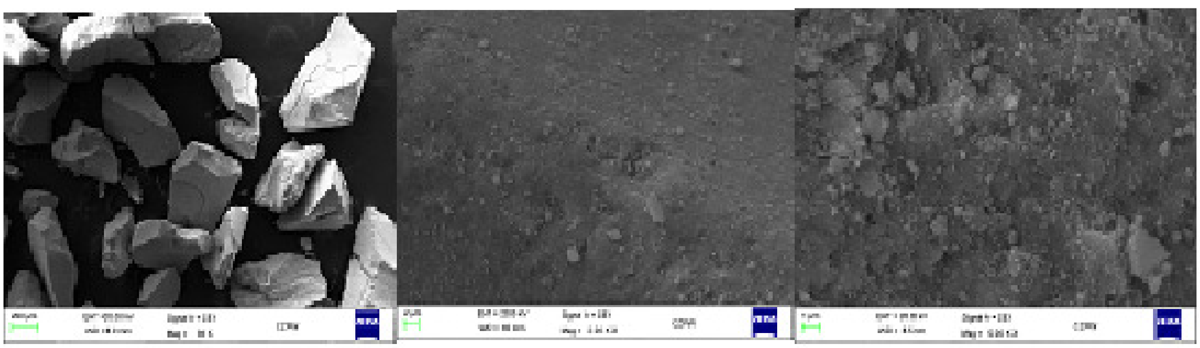

Figure-4
SEM image of CZPT

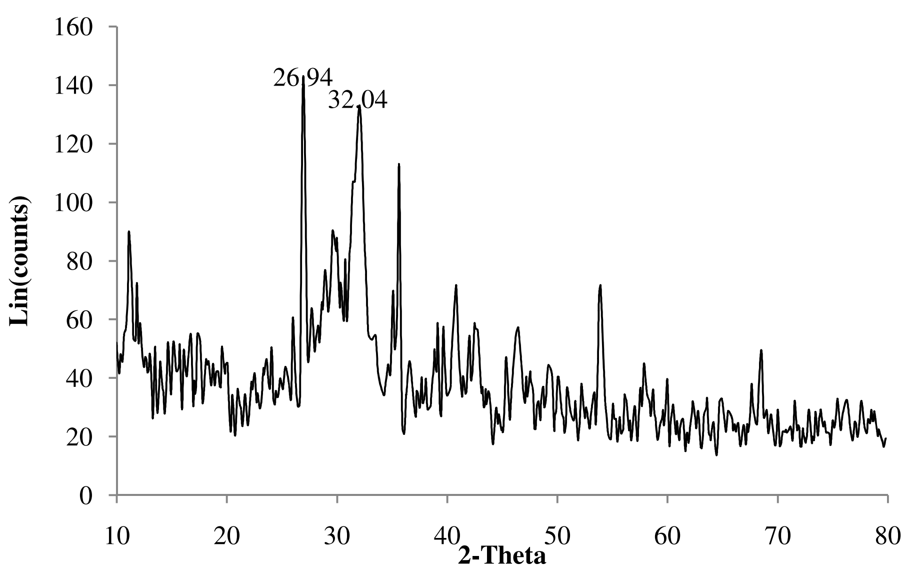

Figure-5
XRD pattern of CZPT

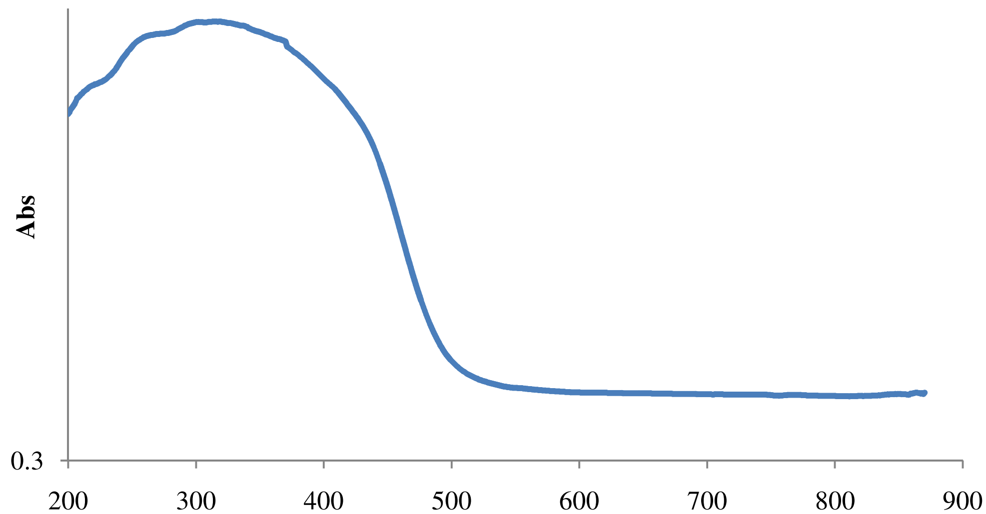

Figure-6
UV-Visible DRS of CZPT

pH titration curve shows bifunctional nature of the exchanger figure-7. The value of ion exchange capacity 0.7 meq/g as seen from the curve is almost equal to the value determined by the column method.

Disribution studies: Various factors affect the distribution coefficient of ions like charge, size, complex formation, type of bond etc..The distribution studies figure-8 conducted shows the cation affinity of the materialin the order Bi^{3+} > Al^{3+}> Cu^{2+}> Sr^{2+} >Pb^{2+} > Sn^{2+} > Th^{4+} > Mg^{2+}> Mn^{2+} > Ni^{2+}> Zn^{2+} Co^{2+} > Hg^{2+}> Y^{3+}> Ca^{2+}. The material is found to be a good scavenger of Bi^{3+}.

On the basis of the selectivity pattern table-4, metal ions such as Ca^{2+}, Hg^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}were separated from Bi^{3+} with high separation factors[8]. Table-5 on a column of the ion exchanger by using suitable eluents selected after studying the electrolyte effect on distribution coefficients.Elution curves for the separations were also drawn figure-9. The efficiency ranged from 94 - 99% with a variation of 2% for repetitive determinations.

Analysis of antacids: Antacids are used as medicines for the treatment of acidity in stomach. They contain mainly Al^{3+} and Mg^{2+}. Distribution studies conducted on cerium zirconium phosphotungstate have revealed that the material was very selective to Al^{3+} and showed less selectivity to Mg^{2+}. This difference in selectivity was used for the analysis of these ions in antacids. The ion exchange method for the estimation of the ions in the drugs is found to be in agreement with the labelled composition with a variation below 1% table-6.

Conductivity: Cerium based ion exchangers can show both electronic and ionic conduction. Their electrical properties depend on various factors. Ce^{3+}-Ce^{4+} charge transfers takes place in these materials[9]. As a result, electrons, holes and oxygen vacancies carry the charges. At high temperatures and low oxygen partial pressures, cerium based materials behave as n-type semiconductor and electrons liberated following reduction are the primary charge carriers. Transition from n-type to p-type conduction can be observed at lower temperatures and higher oxygen partial pressures where conductivity arises from holes due to impurities[10].

Optical properties: The UV –Visible DRS reveal that the material can prevent damages caused by UV radiation. Thus the presence of the material in glass will not transmit UV-radiation but transmit visible light only. Similarly the photo-stability of pigments[11] can be increased by adding the materialin it, resulting in light fastness and protecting clear polymers from the damages caused by sunlight. Since television glass face plates are subjected to electron bombardment, browning of the glass takes place due to the creation of colour centres. The material can be used for preventing this also.

Conclusion

The material find promising applications in various fields by combining its ion exchange properties, catalytic activity, electron exchange properties, optical properties, electrical properties, semiconducting properties etc.

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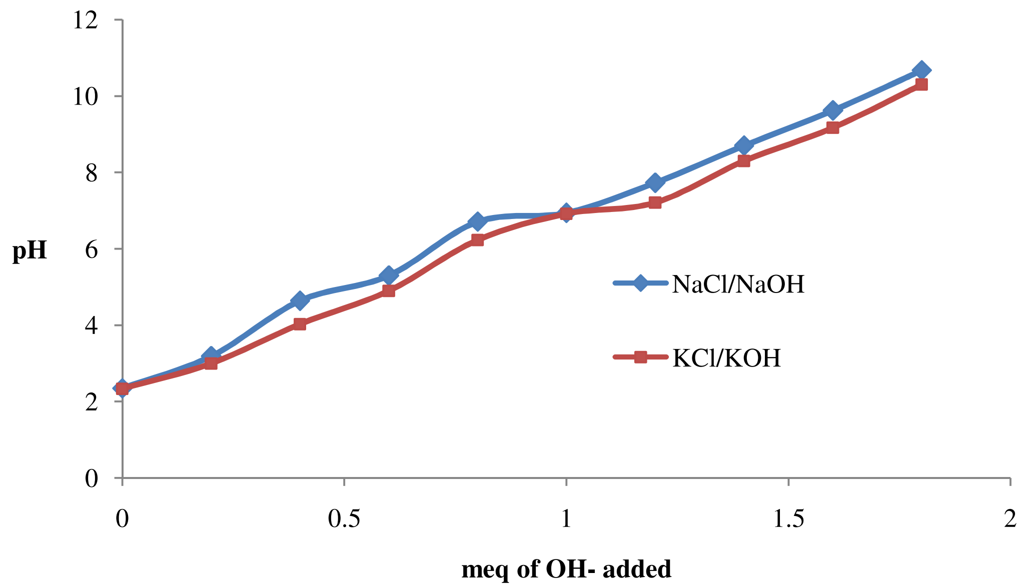

Figure-7
pH titration curve

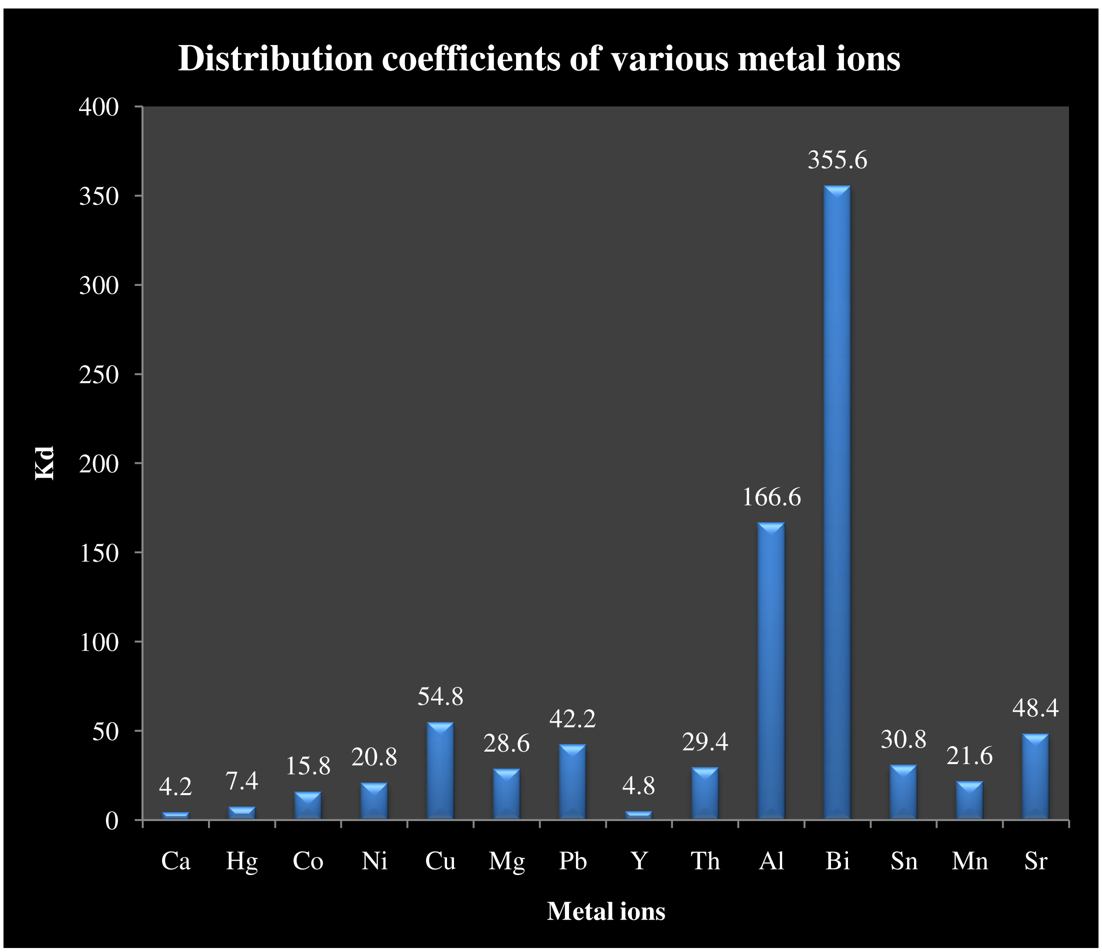

Figure-8
Distribution coefficients of various metal ions on CZPT

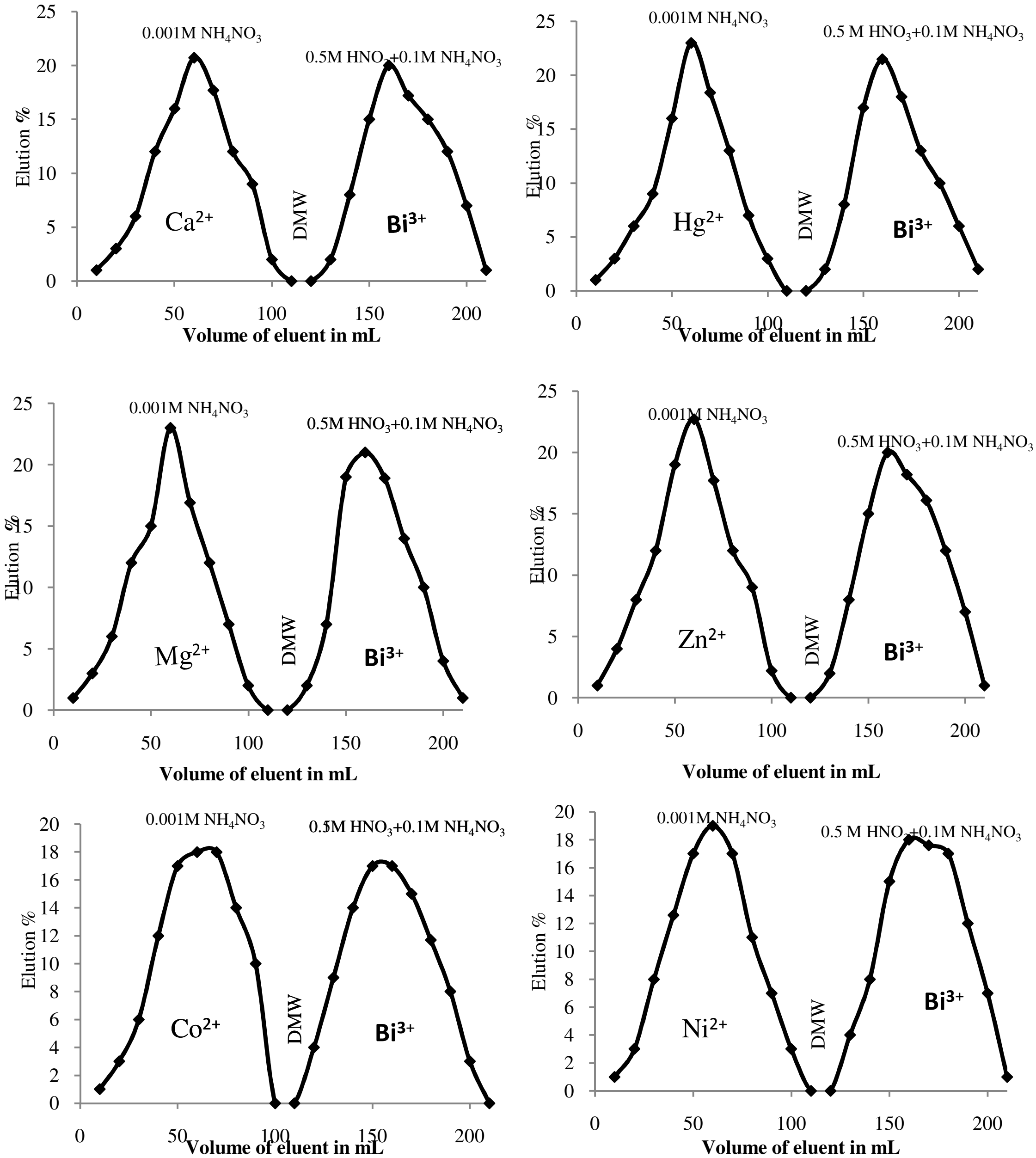

Figure-9
Elution curves for the binary separation of metal ions on CZPT

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