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Synthesis, Characterization and Environmental Applications of a New Bio-Composite Gelatin-Zr(IV) Phosphate

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Abstract Gelatin-Zr(IV) phosphate composite (GT/ZPC) was synthesized by sol–gel method. Different techniques viz. Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray powdered diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used for the characterisation of GT/ZPC composite ion exchanger. The ion exchange capacity (IEC) of GT/ZPC was observed to be better (1.04 meq g^{-1}) than its inorganic counterpart (0.64 meq g^{-1}). The pH studies revealed the monofunctional nature of GT/ZPC with one inflection point. The distribution studies showed that the GT/ZPC was highly selective for Cd^{2+} as compare to other metal ions. The environmental applicability of ion exchanger has been analysed for binary separations of metal ions using column method. Cd^{2+} was effectively removed from synthetic mixture of metal ions (Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+}).

Keywords Gelatin · Zr(IV) phosphate · Ion exchanger · Heavy metals · Composite · Separation

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Introduction

Rapid industrialization extensively increased the release of different pollutants from numerous industries such as paint, paper, textile etc. A large number of pollutants such as phenols, pesticides, dyes and heavy metals are continuously polluting the aquatic system [1–10]. Among all of these pollutants, heavy metals are considered to be the most common constituent present in polluted water. If the level of heavy metal ions exceeded a certain limit, it causes serious health hazard to living being [11–14]. The hazardous metals include cadmium, copper, lead, aluminium, chromium, thorium, cobalt and zinc etc. causing several diseases in the living beings [15]. Therefore, these metals must be eliminated before discharged into aquatic system. A number of methodologies such as ion exchange process, adsorption, photocatalysis, membrane filtration and chemical precipitation have been exploited for the remediation of contaminants from the surroundings [15–20]. The ion exchange technique is most promising for waste water treatment due to cheap, easily operated and handled, highly efficient and sludge-free in nature.

In recent years, the synthetic inorganic ion exchangers have been extensively used for the treatment of pollutants due to their unique properties. The salts of polyacids with multivalent metals have gained increased importance due to their ease of synthesis and subsequent utilization in column separation [21–27]. The ion exchangers which are zirconium based have gained more consideration due to their outstanding ion exchange properties and analytical applications as in ion exchange membranes, solid state electrochemistry and phase transitions etc. Zirconium phosphate has a layered structure which enables exchange between protons and outer ions. It has advanced properties such as

Table 1 Conditions for the synthesis of various samples of GT/ZPC ion exchanger

S. No.	Mixing volume ratio (v/v)			Temperature (°C)	Appearance of sample	Na$^+$ IEC (meq g^{-1})	Yield (g)
	A (mol L^{-1})	B (mol L^{-1})	C (%)				
S-1	0.1	0.1	–	50	White	0.64	1.02
S-2	0.1	0.1	0.5	50	Light yellow	1.04	1.30
S-3	0.1	0.1	1	50	Light yellow	0.42	1.38
S-4	0.1	0.1	2	50	Yellow	0.2	1.43
S-5	0.1	0.1	3	50	Yellow	0.3	1.55
S-6	0.1	0.1	4	50	Yellow	0.4	1.57
S-7	0.1	0.1	5	50	Yellow	0.1	1.64
S-8	0.1	0.1	6	50	Yellow	0.3	1.66
S-9	0.1	0.1	8	50	Yellow	0.2	1.68
S-10	0.1	0.1	10	50	Yellow	0.4	1.68

A: zirconium oxychloride octahydrate; B: orthophosphoric acid; C: gelatin

Table 2 IEC of zirconium based ion exchangers

Sr. No.	Nanocomposite ion exchangers	IEC (meq g^{-1})
1	Pectin @ zirconium(IV) silicophosphate	1.01 [73]
2	Pectin zirconium(IV) selenotungstophosphate	1.27 [84]
3	Polyaniline zirconium(IV) selenotungstophosphate	1.20 [77]
4	Lactic acid–Zr(IV) phosphate	1.00 [78]
5	Polyaniline-Zr(IV) selenoiodate	1.36 [79]
6	polyaniline-Zr(IV) selenomolybdate	1.44 [79]
7	PANI-ZrPB nanocomposite	0.67 [80]
8	Gelatin-Zr(IV) phosphate	1.04 [Present study]

Table 3 Effect of temperature on the IEC of GT/ZPC

| Heating temperature (°C)	Appearance (color)	% weight loss (g)	Na$^+$ IEC (meq/g)
50	Yellow	–	1.04
100	Yellow	0.96	1.02
200	White	0.92	0.73
300	White	0.77	0.64
400	White	0.72	0.58
500	Black	0.64	0.50
600	Black	0.64	0.28

high thermal and chemical stability, solid state ion conductivity, resistance to ionizing radiation etc. [28–33].

The inorganic ion exchangers enhance the thermal stability, ion-exchange behaviour and also increased the electrical conductivity while the organic ion exchangers provide the mechanical and chemical stability. But these materials have some disadvantages which restrict their applicability. The synthetic inorganic ion exchange materials are expensive, non-reproducible, and unable to handle huge volume of waste discharges while organic ion exchanger materials possess low thermal and chemical stability [34, 35]. By the blending of organic units in inorganic matrix, numerous inorganic–organic composite

ion exchanger materials have been established recently. These materials provide better chemical, thermal, mechanical stabilities and possessing good selectivity for heavy metals which are very difficult to remove due to their non-degradable nature.

The growing interest in composite ion exchangers is due to their multifunctionality, selectivity and specificity in different fields [36–41]. Due to unique chemical, mechanical, electrochemical and magnetic properties composite ion exchangers have been received huge attention [42–48]. They have been used as ion selective electrode, adsorbent, catalyst, antimicrobial activity, chromatography and environmental science. At nano level, composite materials have many properties superior to the bulk materials due to their specificity, selectivity and widespread applicability [49–66].

Recently, bio-based composites have been synthesized because off their renewable nature. The biopolymers such as gelatin, alginates, cellulose, proteins, lignin, starch, pectin and chitin have been utilized for the preparation of various composites. Gelatin is an amphoteric polyelectrolyte which is a denatured derivative of collagen [67]. It was broadly used in pharmaceutical, nutrients and photographic areas [68]. However, their deprived mechanical properties restrict their applications as structural biomaterial.
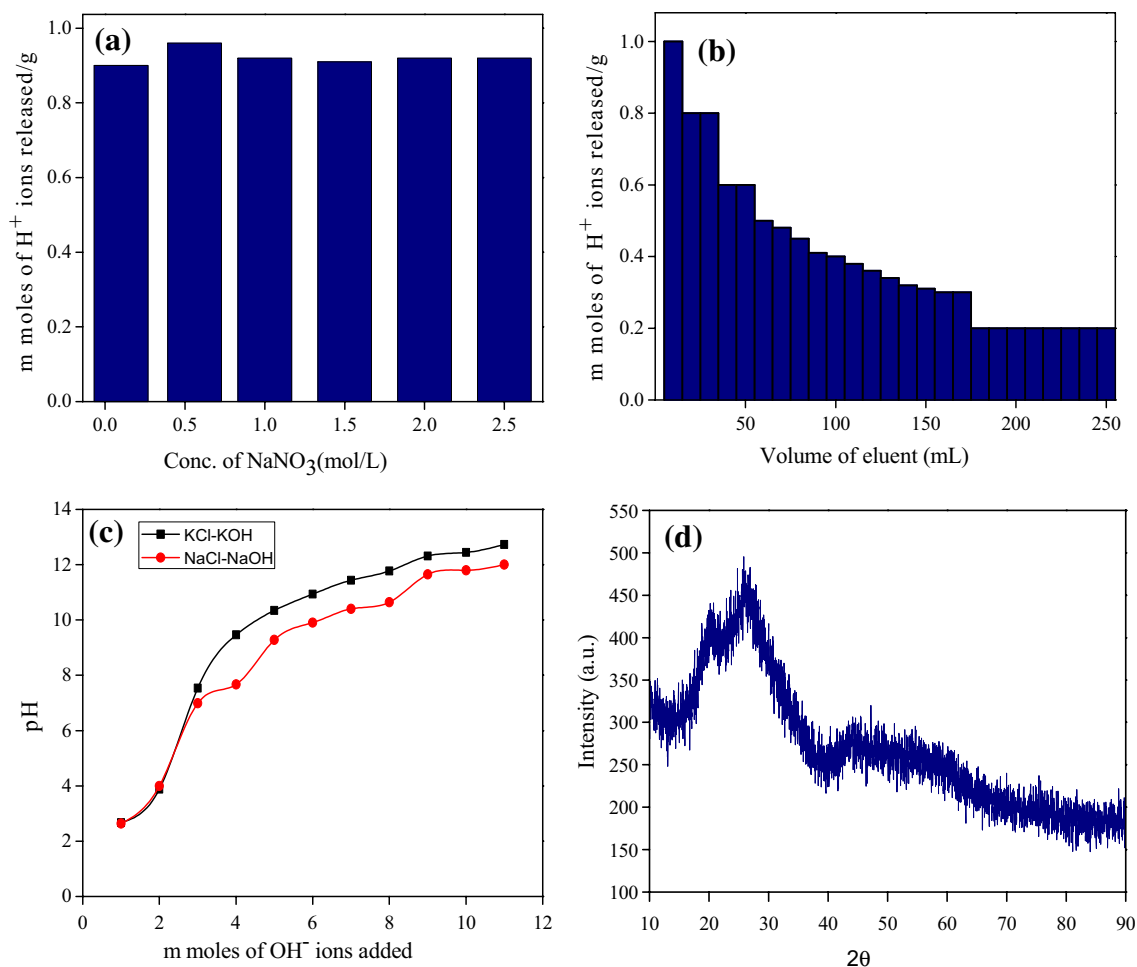
Fig. 1 **a** Effect of eluent concentration on ion exchange capacity of GT/ZPC, **b** elution behavior of GT/ZPC, **c** pH-titration *curves* of GT/ZPC, **d** XRD spectra of GT/ZPC

Consequently, many attempts have been made to improve their mechanical properties [69, 70].

In the present investigation, an attempt has been made to explore the biopolymer based composite (GT/ZPC) ion exchanger for the separation of toxic heavy metal ions. The instrumental analysis of GT/ZPC has been attempted using various techniques such as FTIR, TGA, XRD, SEM and TEM. On the basis of K_d values, the quantitative separations of Cd^{2+} ions was attained from the synthetic mixtures of different metal ions by using GT/ZPC.
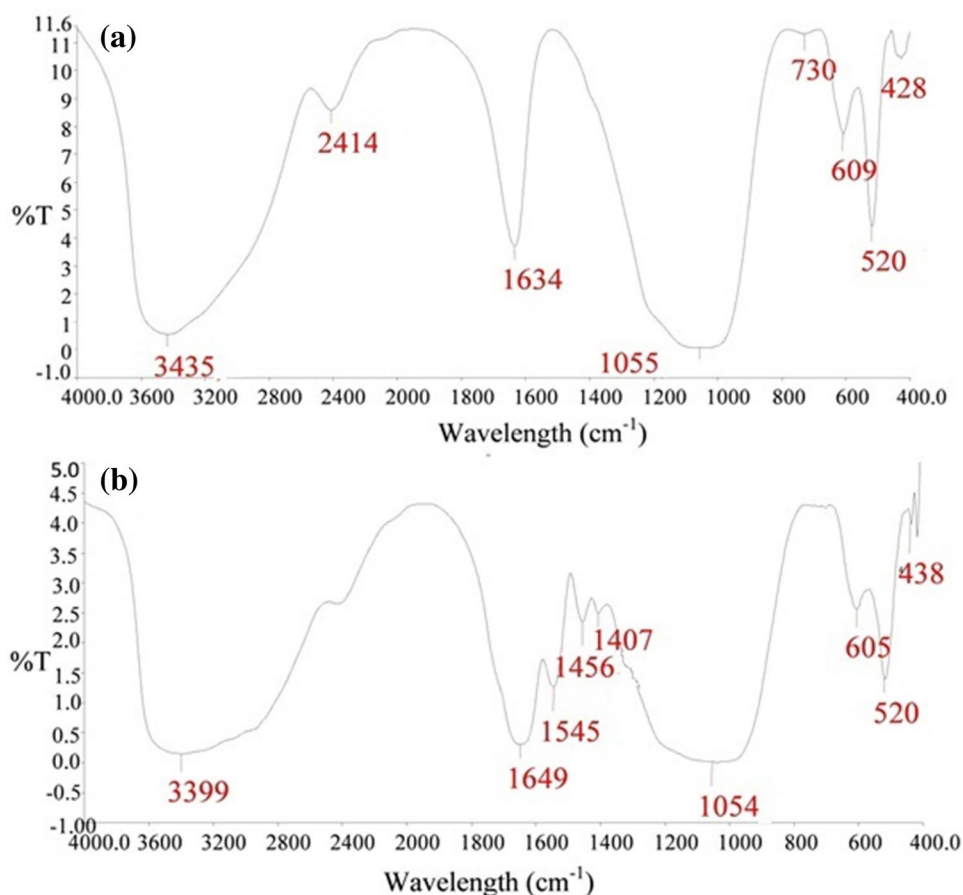
Materials and Methods

Reagents and Instruments

Zirconium oxychloride (CDH, India), orthophosphoric acid (CDH, India), gelatin (CDH, India) and nitric acid (SD Fine Pvt. Ltd., India) were used. Also, metal nitrates

such as zinc nitrate, cadmium nitrate, cuprous nitrate, aluminium nitrate, lead nitrate, nickel nitrate, cobalt nitrate and magnesium nitrate have been purchased from CDH, India. FTIR(Perkin Elmer Spectrum-BX USA), digital pH meter (Elico LI-10, India), UV–Visible spectrophotometer (Systeronics), X-ray diffractometer (Perkin Elmer Series II CHNS/O 2400), SEM (Quanta 250, FEI Make and Mode No. D9393), and TEM (FEI Tecnai F 20) were used.

Synthesis of Zr(IV) Phosphate

Zr(IV) phosphate was synthesized by mixing of 0.1 M zirconium oxychloride and 0.1 M H_3PO_4 solutions drop wise in a fixed volume ratio (1:2) with continuous stirring at 65 °C. The pH of reaction mixture was kept between 0 and 1 with the addition of 0.1 N HNO_3. The resulting mixture was agitated for 2 h continuously on a magnetic stirrer [70]. Then the resulting precipitates were filtered, washed

Fig. 2 FTIR spectra of **a** ZP ion exchanger, **b** GT/ZPC ion exchanger

Synthesis of GT/ZPC

GT/ZPC was synthesized by sol–gel method [71–73]. At the starting, Zr(IV) phosphate was synthesized by the above method discussed in "Synthesis of GT/ZPC". Then, the gel of gelatin was prepared in hot water and added to above mixture with constant stirring. The resulting reaction mixture was kept for digestion for 24 h with infrequent shaking. The precipitates of gelatin-Zr(IV) phosphate so obtained were washed and dried at 50 °C in a hot air oven. In a similar way, different samples of GT/ZPC were synthesized by changing the percentage of gelatin and IEC of each sample was studied.

Ion Exchange Capacity (IEC)

The ion exchange capacity of gelatin-Zr(IV) phosphate composite (GT/ZPC) was determined by the well-known standard column method [72].

thoroughly with double distilled water and oven dried at 60 °C for 24 h.

Thermal Effect on IEC

The effect of temperature onto the IEC of GT/ZPC was studied in the range of 100–700 °C. 1.0 g of GT/ZPC in H⁺ form was heated in a muffle furnace at different temperature for 1 h. After cooling at room temperature, the IEC was examined by column method as explained in "Ion exchange capacity (IEC)".

pH Titration Study

The pH titration studies were performed as defined by Top and Pepper method [73]. In this method, 0.5 g of GT/ZPC in H⁺ form was placed in a number of conical flasks of 250 mL. Then, the solutions of metal chlorides and their hydroxides of same concentration was added in different volume ratio. The final volume of each flask was maintained to 50 mL. The pH of each flask was examined for every 24 h until the equilibrium was reached.

Characterization

FTIR spectrum of gelatin-Zr(IV) phosphate composite was performed by Fourier transform infrared spectrophotometer
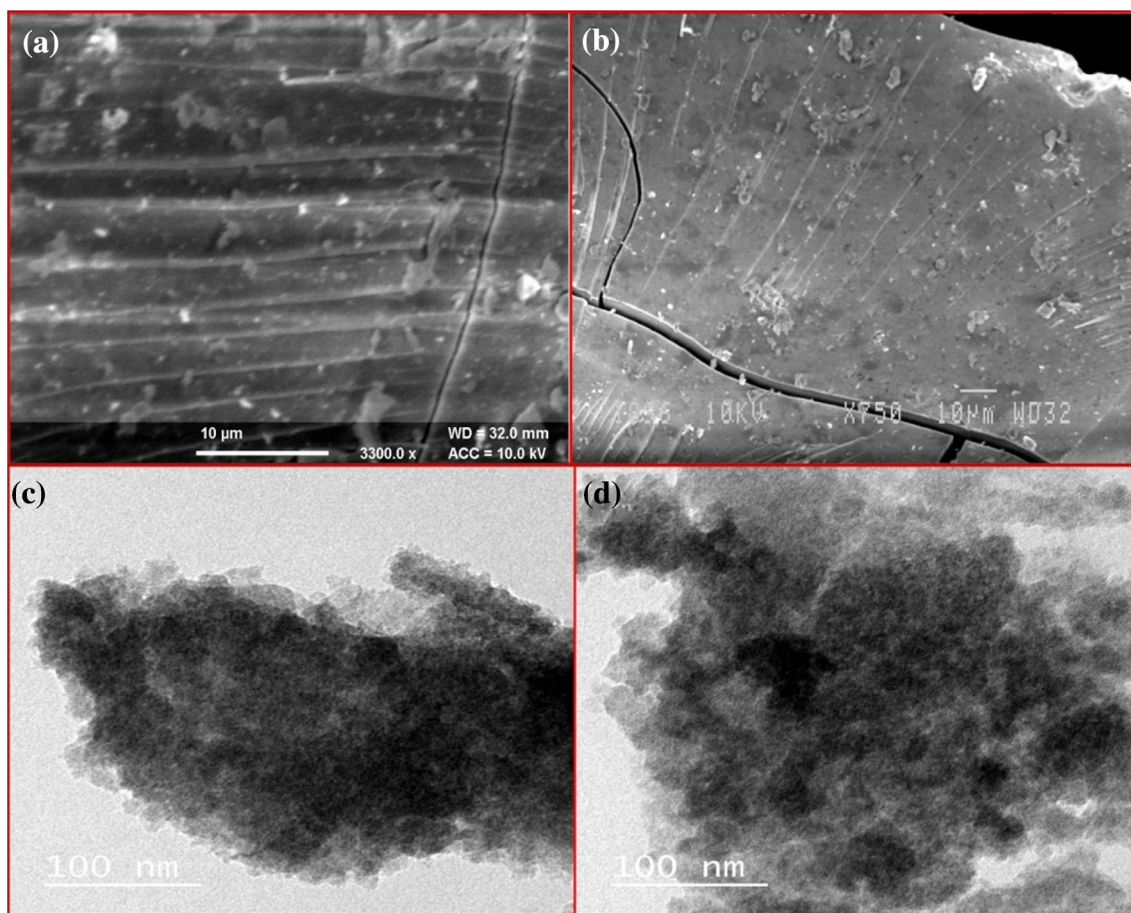
Fig. 3 Scanning electron microphotographs **a** ZP, **b** GT/ZPC ion exchanger, **c, d** transmission electron microphotographs of GT/ZPC ion exchanger

(Perkin Elmer Spectrum- BX USA) using KBr disk method. Scanning electron microphotographs of GT/ZPC were recorded at different magnifications using QUANTA250 FEI D9393 scanning electron microscope (SEM). GT/ZPC and ZP were placed on a carbon tape with silicon adhesive and mounted on an aluminum stub. The instrument was operated at 5–10 kV and 30,000 magnifications.

The TEM result of GT/ZPC ion exchanger was analyzed under transmission electron microscope FEI Tecnai F 20. The particle size and morphology was determined by preparing the suspensions of GT/ZPC in ethanol solution and placed on carbon copper grid.

X-ray diffraction of GT/ZPC ion exchanger was noted with an analytical X-ray diffractometer (XRD, Philips model X'PERT PRO) using CuKa radiation (l = 1.5418 A˚).

### Distribution Coefficient (K_d) Studies

Batch process was applied to find the K_d values of various metals onto GT/ZPC. In this method, 200 mg of GT/ZPC in H^+ ion form was taken in 20 mL solutions of diverse metal ions and preserved for 24 h with constant shaking at $25 \pm 2\,°C$ until equilibrium was attained. The concentrations of metal ions were evaluated by EDTA titration [74]. The K_d values were calculated as [74]:

$$K_d = \frac{I - F}{F} \times \frac{V}{M}\ \text{mL/g} \tag{1}$$

Binary Separations of Metal Ions

In this process, 1.0 g of GT/ZPC in H^+ form was taken in column and the mixture of two metal ions (Al^{3+}–Zn^{2+}, Mg^{2+}–Zn^{2+}, Cu^{2+}–Cd^{2+}, Pb^{2+}–Cd^{2+}, Pb^{2+}–Mg^{2+}, Al^{3+}–Cu^{2+}, Cd^{2+}–Al^{3+} and Ni^{2+}–Co^{2+}) was loaded in the column. The above mixture was permitted to pass gradually by adjusted flow rate to 2–3 drops/min. The column was rinsed with double distilled water to remove the metal ions which were not exchanged. The adsorbed metal ions get eluted on the exchanger via suitable eluting reagents [75–81]. In 10 mL divisions, the effluent was collected and titrated against EDTA solution.
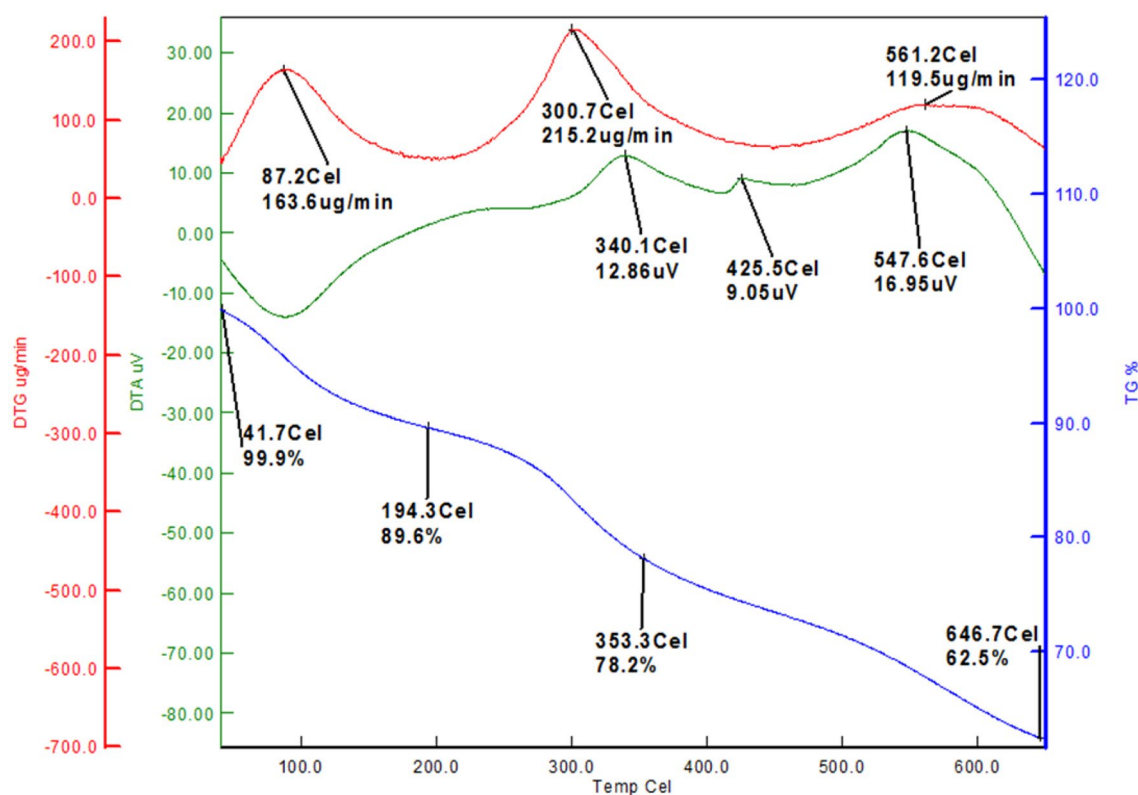
Fig. 4 Thermal analysis *curve* of GT/ZPC ion exchanger

Selective Separation of Metal Ions

Selective separation of Cd^{2+} ions from the synthetic mixture having metal ions such as Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+} was achieved on column of GT/ZPC. In this, the quantity of the Cd^{2+} ions was varied and quantity of the rest metal ions in synthetic mixture was kept constant. The determination of metal ions in the effluent was achieved by titrating against standard solution of 0.01 M EDTA.

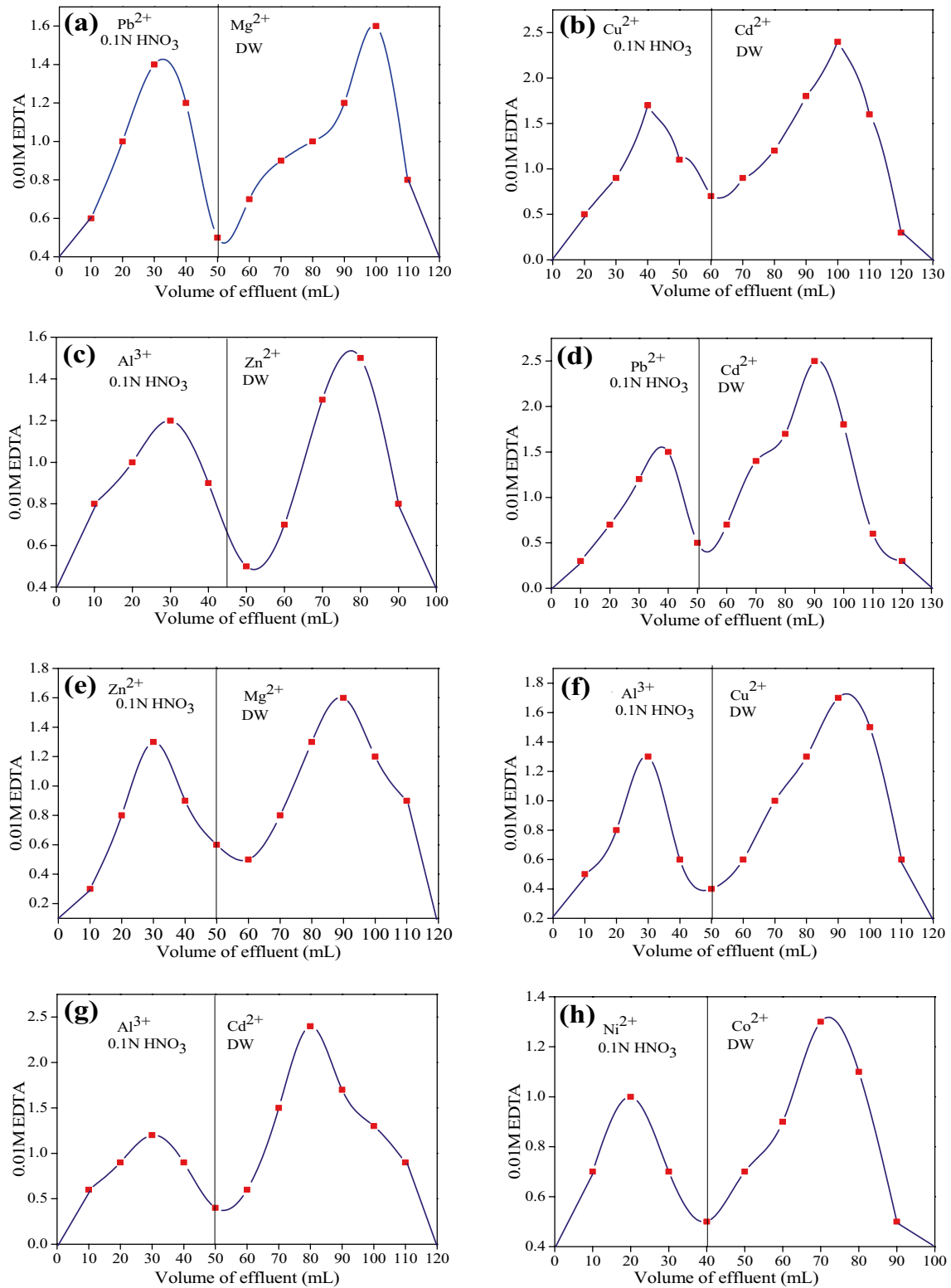**Table 4** K_d values of metal ions on GT/ZPC column in various solvent system

Sr. No.	Metal ions	Distilled water ($K_d \times 10$)	0.1 M HNO_3 ($K_d \times 10$)	0.1 M DMF ($K_d \times 10$)	0.1 M HCOOH ($K_d \times 10$)
1	Al^{3+}	13.14	10.00	14.00	12.30
2	Cu^{2+}	57.00	45.00	51.50	48.05
3	Mg^{2+}	66.66	51.21	55.00	54.51
4	Cd^{2+}	484.00	471.00	498.00	481.00
5	Co^{2+}	31.25	26.45	29.40	28. 50
6	Ni^{2+}	21.49	17.45	19.55	18.35
7	Zn^{2+}	24.25	20.00	23.54	22.30
8	Pb^{2+}	14.00	9.80	13.25	11.38

Results and Discussion

The samples of GT/ZPC were prepared by adding a fixed ratio of gelatin into the inorganic material ZP. The varying concentration of biopolymer affects the IEC. It was recorded that the addition of gelatin to Zr(IV) phosphate improved the IEC. The IEC of GT/ZPC (1.04 meq g^{-1}) was better than its inorganic counterpart (0.64 meq g^{-1}) Table 1. The better IEC of GT/ZPC was due to the bonding of gelatin with inorganic part (ZP) as gelatin provides more number of active sites to be attached of replaceable hydrogen ions [82–85]. GT/ZPC has comparative IEC in comparison to other ion exchangers as described in Table 2.

Temperature variation and mixing amount of reagents has been affected the IEC and yield percentage of GT/ZPC. Effect of heating on the ion exchange capacity was shown in Table 3. It was observed that at ambient temperature, mass, color and IEC of GT/ZPC were changed with increase in temperature. The ion exchanger has high thermal stability because it retained its IEC upto 300 °C which might due to the binding of gelatin moiety with inorganic ZP. The decrease in IEC beyond 300 °C may be due to complete degradation of gelatin from the composite.

The effect of elution behaviour and eluent concentration for the elution of H^+ ions from GT/ZPC is shown in

Fig. 5 Binary separations of metal ions on GT/ZPC columns **a** Pb^{2+}–Mg^{2+}, **b** Cu^{2+}–Cd^{2+}, **c** Al^{3+}–Zn^{2+}, **d** Pb^{2+}–Cd^{2+}, **e** Zn^{2+}–Mg^{2+}, **f** Al^{3+}–Cu^{2+}, **g** Al^{3+}–Cd^{2+}, **h** Ni^{2+}- Co^{2+}

Table 5 Binary separation of metal ions achieved on the column of GT/ZPC

Binary mixtures	Amount loaded (mg)	Amount found (mg)	% Recovery	Eluent used	Volume of eluent required for elution of metal ions (mL)
Pb^{2+}	20.72	8.72	42.23	0.1 M HNO_3	40
Mg^{2+}	2.43	1.62	67.57	0.1 M HNO_3	70
Cu^{2+}	6.35	3.17	50.03	0.1 M HNO_3	50
Cd^{2+}	11.24	9.44	84.34	0.1 M HNO_3	60
Al^{3+}	2.69	1.05	39.03	0.1 M HNO_3	40
Zn^{2+}	6.53	3.13	48.67	0.1 M HNO_3	50
Pb^{2+}	20.72	8.7	42.95	0.1 M HNO_3	50
Cd^{2+}	11.24	9.77	92	0.1 M HNO_3	70
Zn^{2+}	6.53	3.07	39.12	0.1 M HNO_3	50
Mg^{2+}	2.43	1.48	60.9	0.1 M HNO_3	60
Al^{3+}	2.69	0.99	36.11	0.1 M HNO_3	50
Cu^{2+}	6.35	4.38	69.08	0.1 M HNO_3	60
Al^{3+}	2.69	0.94	35.11	0.1 M HNO_3	50
Cd^{2+}	11.24	9.41	83.77	0.1 M HNO_3	60
Ni^{2+}	5.86	1.87	31.05	0.1 M HNO_3	40
Co^{2+}	5.89	2.65	45.47	0.1 M HNO_3	50

Fig. 1a,b which demonstrated that 250 mL of 0.5 M sodium nitrate solution was the best eluant. The pH titration curve showed one inflection point in the curve confirming the monofunctional behaviour of GT/ZPC ion exchanger (Fig. 1c). The composite material was found to be strong cation exchanger as inferred from itsintial low pH values, when no OH^- ions were added. The weak acidic groups remain undissociated at low pH and the solution was neutralized by the addition of NaOH at higher pH. Hence weak group has been dissociated and ion exchange process moves toward completion. The exchange level was noted fast for H^+–Na^+ in contrast to H^+–K^+ system as shown in Fig. 1c.

XRD pattern of GT/ZPC ion exchanger was presented in Fig. 1d. The low intensity peaks supported the amorphous nature of GT/ZPC.

FTIR spectra of ZP and GT/ZPC ion exchanger are shown in Fig. 2a, b. A strong and broad peaks at 3399 cm^{-1} for –OH stretching which shows the presence of lattice water [86], 1649 cm^{-1} for N–H stretching

frequency of amide group, 1545 cm^{-1} for COO^- asymmetric stretching, 1456 cm^{-1} was due to CH_3 asymmetric bending [87, 88] and peak at 1407 cm^{-1} was due to C–H bending of methylene group of gelatin.The additional bands observed at 1054 and 605 cm^{-1} was may be due to adsorption peak of C–O and phosphate peaks [89]. The diverse variation in the intensities of bands and appearance of new bands clearly indicated the assimilation of gelatin in the inorganic moiety.

Thermal analysis of GT/ZPC is shown in Fig. 3. The initial loss of about 10% was observed up to 194 °C which was due to loss of surface water molecules of GT/ZPC composite [90]. The weight loss of 21.8, 37.5% between 353 and 647 °C might be due to the breakdown of organic part of the composite.

Figure 4a, b shows the scanning electron microscope images of ZP and GT/ZPC ion exchangers. Figure 3b confirmed the incorporation of the inorganic material with the organic polymer. It was found that after binding of organic part the morphology was completely changed.

Table 6 Selective separation of Cd^{2+} ions from a synthetic mixture of Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+} on the column of synthesized GT/ZPC ion exchanger

Metal ion	Amount loaded (mg)	Amount found (mg)	% Recovery	% Error	Volume of eluent used	Eluent used
Cd^{2+}	11.2 (a)	10.8	96.9	−3.1	50	0.1 M HNO_3
	22.4 (b)	21.9	97.76	−2.24	50	
	44.8 (c)	44	97.82	−2.18	50	

Category (a): Cd^{2+} (11.2 mg), Ni^{2+} (0.58 mg), Pb^{2+} (2.07 mg), Co^{2+} (0.58 mg), Cu^{2+} (0.63 mg) and Zn^{2+} (0.65 mg)

Category (b): Cd^{2+} (22.4 mg) and the amount of rest metals was taken same as in category (a)

Category (c): Cd^{2+} (44.8 mg) and the amount of rest metals was taken same as in category (a)

The rough surface of inorganic part was completely reformed into irregular surface with large surface area.

TEM images of GT/ZPC were shown in Fig. 3c, d. TEM images indicated homogeneous distribution of gelatin and ZP particle with two different morphologies. The darker portion in TEM images specified the wrapped gelatin in ZP particles while grey portion corresponds to gelatin. TEM results confirmed the particle size ranged from 50 to 100 nm with the average particle size 80 nm.

Distributions coefficient studies of GT/ZPC for separations of heavy metal ions were accomplished in various solvents as given in Table 4. It has been found that the K_d values depends upon the solvent nature. The highest K_d values for Cd^{2+} metal ions showed that this metal was strongly adsorbed on the GT/ZPC. The lowest K_d values for all metal ions in nitric acid was due to the presence of high concentration of H^+ ions in acidic medium which inverted the adsorption/ion exchange process [91–95]. The elution of various metal ions viz. Al^{3+}–Zn^{2+}, Mg^{2+}–Zn^{2+}, Cu^{2+}–Cd^{2+}, Pb^{2+}–Cd^{2+}, Pb^{2+}–Mg^{2+}, Al^{3+}–Cu^{2+}, Cd^{2+}–Al^{3+} and Ni^{2+}–Co^{2+} is shown in Fig. 5. The metal–ligand stability through the column plays vital role for the consecutive elution of metal ions [96, 97]. It has been observed that weakly adsorbed metal ions were eluted first and strongly eluted at last (Table 5). The Cd^{2+} metal ion was selectively separated from a synthetic mixture of metal ions containing Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+} and Cd^{2+} on the column of GT/ZPC. The amount of Cd^{2+} ion was varied and other metal ions remained constant in the synthetic mixtures. Table 6 showed the separation of Cd^{2+} was efficient and the recovery was more than 96%.

Conclusion

GT/ZPC was characterized by various techniques. The material had better IEC as compared to its inorganic counterpart (ZP). Due to the differences in K_d values of metal ions, a few binary separations have been performed on the columns of GT/ZPC. Sorption studies revealed that GT/ZPC was selective for Cd^{2+} metal ion. This material was favourably used for the separation of Cd^{2+} ions from binary and synthetic mixtures of metal ions. GT/ZPC was selectively used for the separation of Cd^{2+} ions, one of the most noxious metal ions existing in environment.

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