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Synthesis and characterization of a novel hybrid material as amphoteric ion exchanger for simultaneous removal of cations and anions

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HIGHLIGHTS

- A novel hybrid exchanger ZrD (zirconium diethylene triamine) is synthesized for the first time.
- Characterization and structure elucidation reveals that ZrD exhibits amphoteric character.
- Amphoteric behaviour of ZrD is established by simultaneous removal of cations and anions.
- Cations are exchanged in ZrD through chelation with nitrogen as coordinating sites.
- ZrD can be regenerated and reused with not much decline in performance.

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ABSTRACT

A new hybrid chelating ion exchanger zirconium diethylene triamine (ZrD) has been synthesized by a simple sol–gel route using inexpensive and easily available chemicals. ZrD has been characterized for elemental analysis (ICP-AES, CHN analysis), TGA, FTIR, X-ray diffraction, SEM and EDX. Physical and ion exchange characteristics as well as chemical stability of the material in various media have been studied. Structural determination reveals that ZrD exhibits amphoteric character. Anion exchange capacity (AEC) for Cl^-, Br^-, $Cr_2O_7^{2-}$, F^- and AsO_4^{3-} has been determined. Cations are exchanged through chelation where coordinating sites are offered by nitrogen atoms present in the amine groups of ZrD. Distribution coefficient K_d for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Hg^{2+}, Cd^{2+}, Pb^{2+} (heavy metal ions) has been evaluated by batch equilibration techniques in aqueous and various electrolyte media/concentrations. Based on α the separation factor, a few binary separations have been performed on a chromatographic column packed with ZrD. The amphoteric behaviour of ZrD has been demonstrated by simultaneous exchange of Cu^{2+} and Cl^- in $CuCl_2$. A study on the regeneration and reuse of ZrD indicates that it is effective upto four cycles without much decline in performance.

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1. Introduction

Ion-exchange chromatography is a well-known and widely used technique for the separation and preconcentration of inorganic ions. However, the innumerable separation procedures published so far are almost exclusively based on the use of monofunctional ion exchangers, mostly strongly basic anion exchangers with quaternary ammonium groups and strongly acidic cation exchangers with sulphonic acid groups [1]. Amphoteric ion exchangers in contrast to conventional monofunctional exchangers contain anionic and cationic exchange sites, and under appropriate conditions, can exchange simultaneously anions and cations from external solutions [2]. Although it was surmised long ago [3], that simultaneous presence of anion and cation exchange groups may offer new interesting separation possibilities, very few attempts to exploit these possibilities in practice can be found in literature [2,3]. Some of these amphoteric ion exchangers are chelating resins with functional groups able to form complexes with several cations and are used for the preconcentration of trace elements [3–6], the sorptive effect of ions being based on the distribution of soluble ions between an aqueous solution and a reactive

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polymer/resin/material containing a selective ligand [2,7–9]. However, the most important influence on sorption is the internal structure of the exchangers and coordinating ability of ligand end groups, which coordinate or chelate metal ions [10–13]. Resins with nitrogen atom containing ligands have been extensively reported [13].

Very early reports reveal that amphoteric exchanger thorium triethanolamine was prepared by incorporation of triethanolamine group into the matrix of thorium oxide, where in nitrogen atom present in the amine group offers chelating sites for metal ions. Zirconium-bis(triethylamine) exhibiting amphoteric character that exchanges anions and adsorbs cations through chelation action has also been reported [14,15].

In the present endeavour, a new and novel hybrid chelating ion exchanger, zirconium diethylene triamine (ZrD), has been synthesized by a simple sol–gel route using inexpensive and easily available chemicals. ZrD has been characterized by instrumental methods of analysis, physical and ion exchange characteristics as well as chemical stability of the material in various acids, bases and organic solvent media have also been studied. Anion exchange capacity (AEC) for Cl^-, Br^-, $Cr_2O_7^{2-}$, F^- and AsO_4^{3-} has been determined distribution coefficient K_d for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Hg^{2+}, Cd^{2+}, Pb^{2+} (heavy metal ions) has been evaluated by batch equilibration techniques in aqueous and various electrolyte media/concentrations. Based on α, the separation factor a few binary separations have been performed on a chromatographic column packed with ZrD. The amphoteric behaviour of ZrD has been demonstrated using $CuCl_2$ and $HgCl_2$ and amount of cation and anion simultaneously exchanged determined. The practical applicability of ZrD as an amphoteric exchanger has been further highlighted by performing a case study including regeneration and reuse of ZrD.

2. Experimental

2.1. Materials and methods

Zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$) and diethylene triamine (DETA) ($C_4H_{13}N_3$: molecular weight = 103.17 and density = 0.955 g/mL) was procured from Loba Chemicals. All other chemicals and reagents used were of analytical grade. Double-distilled water was used for all the studies.

2.2. Synthesis of ZrD

The main objective was to obtain a material with maximum anion exchange capacity (AEC). Several samples of material were synthesized by sol–gel method varying several condition/parameters such as mole ratio of reactants, temperature, mode of mixing (metal salt solution to DETA solution or vice versa), pH and rate of mixing, in each case using AEC as the indicative tool. Table S1 (Supporting Information) describes optimization of parameters for synthesis of ZrD.

2.2.1. Synthesis of ZrD at optimized condition

ZrD was prepared by mixing aqueous solutions of DETA (0.1 M, 50 mL) and $ZrOCl_2$ (0.1 M, 50 mL) at room temperature, dropwise and with continuous stirring. A gelatinous precipitate was obtained, and solution along with precipitate further stirred for 1 h. The resulting gelatinous precipitate was allowed to stand for 15 h, then filtered, washed with double distilled water till removal of adhering ions, followed by drying at room temperature. The material was then broken down to the desired particle size 30–60 mesh (ASTM) by grinding and sieving. An yield of 35% was obtained. This material was used for all studies.

2.3. Characterization

Physical characteristics such as appearance, percentage moisture content, apparent density, true density, void volume fraction, concentration of fixed ionogenic groups and volume capacity were studied according to literature methods [16–18]. A study on pH titration curve, chemical stability, anion exchange capacity (AEC) and effect of calcination on AEC are described below. Further, the material has been characterized by Instrumental methods. Zr was analyzed by ICP-AES performed on Labtam, 8440 Plasma lab. While C, H, N analysis was performed on Perkin Elmer-2400. TGA was performed on a thermal analyzer Shimadzu (model TGA-50) at a heating rate of 10 °C/min. FTIR spectra was obtained using KBr pellet on a Shimadzu (model 8400S). ^1H NMR spectra was obtained using NMR spectrometer (Bruker 500 MHz) in a D_2O solvent. UV-DRS was obtained using Shimadzu (Model UV-DRS 2450). X-ray diffractogram was obtained on X-ray diffractometer (Brucker AXS D8) with Cu Kα radiation with nickel filter. SEM and EDX of the material were obtained on Jeol JSM-5610-SLV scanning electron microscope.

2.3.1. pH titration curve

The pH titration of ZrD was performed by Topp and Pepper method [16–18]. 500 mg of exchanger was treated with 50 mL 0.01 M HCl solution with intermittent shaking. The solution along with exchanger was allowed to equilibrate and pH noted when the value was constant. This was the initial reading. This solution mixture was now titrated with 0.01 M NaCl solution. After addition of every 0.5 mL of titrant, sufficient time was provided for establishment of equilibrium between the ion exchanger and the solution. A pH titration curve was obtained by plotting pH vs. volume of NaCl as depicted in Fig. 2.

2.3.2. Chemical stability

The chemical stability of ZrD in various media – acids (HCl, H_2SO_4 and HNO_3), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid) was studied by taking 0.5 g of ZrD in 50 mL of the particular medium and allowed to stand for 24 h. The change in colour, nature, weight, solubility, metal washout and particle size, etc. was observed. To confirm the solubility of exchanger in a particular medium, supernatant liquid was checked qualitatively for respective elements of exchanger. The chemical stability is expressed as maximum tolerable limits evaluated in a particular medium.

2.4. Anion exchange properties of ZrD

2.4.1. Determination of anion exchange capacity (AEC)

Two grams of the exchanger was treated with NaCl/KBr/$K_2Cr_2O_7$ (0.2 M, 20 mL) for 30 min in a conical flask with continuous shaking and material then separated from solution by decantation. This process was repeated at least five times. The material was finally washed with double distilled water for removal of any adhering ions and dried at room temperature. 0.5 g of this material [(ZrD) exchanged ($Cl^-/Br^-/Cr_2O_7^{2-}$)$_2$] was placed in a glass column [30 cm × 1 cm (internal diameter)], double distilled water was poured onto column with a flow rate adjusted to 0.5 mL min^{-1} to wash the column. A 1.0 M, 250 mL sodium nitrate solution was now passed through the column. The effluent containing (NaCl/KBr) was titrated against 0.1 M $AgNO_3$ for determination of chloride and bromide, while the effluent containing ($K_2Cr_2O_7$) was titrated against 0.1 M $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$ solution for determination of dichromate. AEC for Cl^-, Br^- and $Cr_2O_7^-$ was determined using the formula aV/W, where a is molarity, V the amount of titrant used during titration, and W is the weight of the exchanger. The AEC values for F^- and AsO_4^{3-} was

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