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Synthesis, characterization and evaluation of nano-zirconium vanadate ion exchanger by using three different preparation techniques

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ABSTRACT

Sol–gel, homogeneous precipitation and hydrothermal synthesis are three different preparation techniques have been used as an attempt to synthesize nano-zirconium vanadate with properties suitable to be used as ion exchangers. The impact of the synthetic preparation variables such as the reactant concentrations, reaction temperature and reaction time on the ion exchange capacity of the produced ion exchanger has been considered for each preparation technique. One sample from each preparation technique having the largest ion exchange capacity has been selected to be physically and chemically characterized using various analytical techniques such as XRD, TGA, DSC, pH titration, FTIR and SEM in order to determine the properties of the ion exchanger produced from each technique. For all the studied ZrV samples it can be presumed that they have the ion exchange affinity sequences for alkali metal ions $K > Na > Li$, the order for the alkaline earth metals is $Ba > Ca > Mg$ and their affinity for radioactive metals follow $Cs > Sr$. Moreover, the prepared materials are of high thermal and radiation stabilities. Also they have high chemical stabilities toward wide concentration ranges of acid, basic as well as polar solvents. It has been deduced from the X-ray analysis that ZrV produced from the sol–gel technique has an amorphous structural. While those produced from the homogeneous precipitation and hydrothermal synthesis techniques, in the nano-scale have semi-crystalline structural. Furthermore, SEM confirms that particle size of the all studied prepared ZrV samples have nano-diameters of range 50–60 nm. Specific surface area of the three different prepared ion exchangers are found to be equal to 187, 192 and 320 m^2/g for sol–gel, homogeneous precipitation and hydrothermal, respectively. A tentative structural formula of $Zr(OH)_2(HVO_4)_2\cdot 2H_2O$ has been proposed for all studied samples on the basis of on FTIR, DSC and TGA results.

1. Introduction

Ion-exchange materials represent the essential constituents in a number of processes used to analysis, preconcentration and recovery of a number of ionic species from aqueous as well as from non-aqueous systems. These materials have also been employed in the preparation of various types of ion-exchange membrane, chemical sensors (ion-selective electrodes), etc. Ion-exchange materials have also been inducted to prepare ion-exchange fibers which will be a more suitable tool for various environmental problems [1]. Nowadays, the synthetic inorganic ion exchangers become much valuable than the organic resins because of their characteristics [2]. Since, they have excellent stabilities towards thermal and radiation doses. Moreover, they often exhibit specificity towards certain metal ions [3]. Generally, there are three different techniques used for preparation nano-inorganic materials which are sol–gel precipitation, precipitation, and hydrothermal techniques. The sol–gel technique is one of the fastest growing fields of contemporary chemistry. The attractive feature of this technology is the fact that sol–gel materials can be obtained as bulks, thin films (on various supports) and (nano) powders [4]. On the other hand, the precipitation from a homogeneous solution is a technique in which a precipitating agent is generated in the reaction solution by slow chemical reaction. Homogeneously formed precipitates are usually better suited for analysis than the solid formed by the direct addition of a precipitating reagent [5]. Finally, the hydrothermal preparation technique which is usually refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize materials that are relatively insoluble under ordinary conditions [6].

The literature survey illustrates that there are large number of the synthetic inorganic ion exchange materials that produced

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using sol–gel precipitation technique act as electron exchange material [2]. Electron exchange materials are solid oxidation and reduction agents. The advantages of electron exchangers over dissolved oxidizing and reducing agents is their insolubility in reaction medium and the ability of their are regeneration after use. Many synthetic inorganic ion exchangers have been used as electron exchangers [7].

Many studies have been done for their preparation, properties and analytical applications [8–13]. Amongst these materials, hydrous oxides, salts of heteropolyacids and insoluble ferrocyanides are worthy of mention [14]. A wide range of acidic salts of multivalent metals deserve special mention because of their unique ion exchange properties, along with several interesting applications [15,16]. They provide exchangeable hydrogen ions when immersed in aqueous solution, thus exhibiting cation exchange properties. The general formula of this type of ion exchanger is $M^{IV}(HXVO_4)_2nH_2O$ (where M = tetravalent metal such as Zr(IV), Ti(IV), Sn(IV), etc. and X may be As, P, W, Sb, V, Se, etc.) [2,14].

Acidic salts of multivalent metals, prepared in combination with anions of phosphate, tungstate, arsenate, tellurate, etc. as two component ion exchangers have been studied most intensively [17,18]. Phosphate and arsenate of zirconium [18,19] show good thermal and chemical stabilities, so the preparation and evaluation of both poorly crystalline and amorphous compounds of these materials have been extensively studied. However, little attention has been paid to zirconium vanadate until now. Zirconium vanadate with good ion exchange properties and amorphous structure has been recently prepared using sol–gel method only [14,20–22]. It is worth mentioning that poly crystalline zirconium vanadate have been initially synthesized using new preparation technique that called homogeneous precipitation technique in our previous published research [23]. These different prepared zirconium vanadate materials have been proved to be effective as ion exchange materials for removing different ions such as cesium, uranium, strontium, and cobalt and nickel [20,24].

We are going to prepare nano-zirconium vanadate using the innovative hydrothermal preparation technique as a new trend. In this respect, the different factors that affect in the properties of the produced zirconium vanadate will be discussed. Also, these preparation factors will be applied on the other traditional preparation techniques that previously used for zirconium vanadate preparation, to the compare the chemical and physical properties of the synthesized zirconium vanadate using the three different techniques.

2. Materials and methods

2.1. Reagents and instrumentation

The main reagents used for zirconium vanadate preparation using the three different techniques are zirconium oxy chloride (Avonchem, United Kingdom), sodium vanadate (Acros, USA), urea (Sisco Research Laboratories (Pvt. Ltd., India), and hydrochloric acid (Polskie Odczynniki Chemicze, Poland). All other chemicals and reagents used for properties identification of the prepared zirconium vanadate were of analytical reagent grade.

pH measurements were performed using A single electrode digital pH-meter (Denver Instrument Co., USA). For hydrothermal preparation technique an Autoclave (Systec 3850-EL) has been used. Magnetic stirrer model-526 (J.P. Selecta Co., Spain) was used during the preparation procedure for both sol–gel and homogenous precipitation techniques with the aid of identical magnets. An electron microscope (JEOL JSM 6360LA, Japan) has been used for studying morphological properties of the synthesized materials. IR studies were made using an FTIR (Shimadzu FTIR-8400 S, Japan). For studying the thermal properties, a thermo gravimetric analyzer TGA (Shimadzu TGA-50, Japan) and DSC (Shimadzu DSC-60A, Japan) were used. X-ray diffractometer (Schimadzu-7000, USA) was used for determining the X-ray diffraction pattern of the prepared materials. Thermal stabilities of the different prepared materials have been studied using muffle furnace (Carbolite, Aston Lane, England).

2.2. Synthesis of zirconium vanadate using sol–gel precipitation technique

A sodium vanadate solution of different molarities was added drop wise into a solution of 0.1 M zirconium oxychloride in the presence of hydrochloric acid with constant stirring. After the addition was complete a fine yellow precipitate appeared. The reaction mixture was diluted to 1 L and allowed to settle for 24 h for complete digestion [21,22]. The supernatant liquid was decanted and gels were filtered by suction and the excess acid was washed thoroughly with hot water. The washed precipitate was then dried by gentle heating at 40 °C. Then the product is grounded and immersed in 1 M nitric acid for 1 day with gentle stirring in order to transform the ion exchanger to its hydrogen form. The effect of hydrochloric acid concentration (0–2 M), gelation temperature (25–100 °C) and sodium vanadate concentration (0.1–0.8 M) were studied. Hence, a number of samples of zirconium vanadate ion exchanger were prepared using this technique, on the basis of Na^+ ion exchange capacity one sample was selected to be characterized.

2.3. Synthesis of zirconium vanadate using homogenous precipitation technique

The material was synthesized by adding a solution of sodium vanadate of different molarities to the mixture of 0.1 M of zirconium oxychloride that dissolved in an aqueous hydrochloric (0.04 mol/L) and 1.5 g of urea. The resulting solution was heated to 90 °C on an electrical plate with continuous stirring to decompose the precipitating agent, leading to the formation of zirconium vanadate. After precipitation, the material was allowed to rest at 90 °C for another hour [23]. The produced precipitate was filtered and washed repeatedly with distilled water for the removal of chloride traces, and then dried at 40 °C for 24 h. The product was then ground and transformed to its hydrogen form as mentioned before [5]. The effect of urea precipitating agent amounts (0.5–6 g), preparation temperature (50–120 °C), hydrochloric acid concentration (0–2 M) and sodium vanadate concentration (0.1–0.8 M) were studied. A large number of zirconium vanadate samples were produced; the most proper prepared sample which has the largest ion exchange capacity, IEC, will be selected in order to studying its properties.

2.4. Synthesis of zirconium vanadate using hydrothermal technique

Yellow precipitate of zirconium vanadate can be obtained when mixing a solution of 0.1 M of $ZrOCl_2 \cdot 8H_2O$, dissolved in an aqueous hydrochloric acid (0.5 mol/L), with a solution of sodium vanadate. The mixture was heated under pressure at different temperatures using Autoclave by varying the heating times. The reaction mixture was diluted to 1 L and allowed to settle for 24 h for complete digestion. The precipitate was washed thoroughly and dried by gentle heating. Then the product is grounded and transformed to its hydrogen form as mentioned previously. The effect of heating time (20 min–4.5 h), preparation temperature (60–120 °C), hydrochloric acid concentration (0–2 M), and sodium vanadate concentration (0.1–0.8 M) were studied. In order to determine the chemical and physical properties of the prepared zirconium vanadate using this technique, only one sample that has the highest IEC was selected for details characterization.