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Metal ion sequestration and catalytic application of antimony tin tungstate

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Abstract

Antimony tin tungstate was synthesized by a simple ecofriendly method followed by conversion into the H^+ form. The material was found to be highly thermally stable. Chemical composition was determined by EDS method and structural characterizations were done by SEM, TEM, Thermo gravimetric analysis, X-ray diffraction analysis and Fourier Transform Infrared Spectroscopic analysis. UV-Visible 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. The ion exchanger showed very high selectivity towards the heavy metals, Pb^{2+}, Th^{4+}, Cd^{2+}, Hg^{2+} etc. which are very significant in environmental chemistry. So it can be utilized for applications involving separation and removal of these metal ions. The presence of protons in structural hydroxyl groups in the material indicates good potential for application in solid acid catalysis. Catalytic application was explored by studying the inversion of sucrose.

Keywords: *Ion exchanger, antimony tin tngstate, distribution coefficient, selectivity, inversion of sucrose.*

1. Introduction

Trivalent and tetravalent metal acid salts (TMA) have emerged as promising materials due to their high stability and applications in ion exchange, catalysis and solid state proton conduction. Recently, ion exchangers have been used extensively for metal ion recovery, regeneration of decontaminants and removal of formulation chemicals from the coolant. [1]. Even though a lot of work has been reported on the synthesis of inorganic ion exchangers, the development of new inorganic ion exchangers with specific properties and their applications in various fields is still gaining importance.

The selectivity of an ion exchange material depends considerably on the specific interaction of the counter ions with the exchanger. This interaction varies with the chemical composition of the exchanger which can be altered with greater ease in inorganic materials than in the organic ones. The synthesis of the new inorganic ion exchangers is therefore of outstanding analytical interest.

New materials with cation substitution are of interest due to their improved ion exchange properties and selectivity for particular metal ions compared to the single components. Metal ion substitution changes the properties, composition and structure. It was reported that cesium selectivity of antimony silicate could be improved by doping with Ti^{4+}, Nb^{5+}, Mo^{6+} or W^{6+} in different mole ratios and that cesium selectivity in acid increased in Sb-Si-W system [2]. Tin and antimony based materials have received attention because of their excellent ion exchange behaviour, stability and chemical applications in the field of ion exchange membrane and solid- state electrochemistry. Cations in a mixed metal salt may co-operatively catalyse different steps of a chemical process.

Many inorganic and organic reactions can be catalysed by ion exchangers. This can be explained in terms of the catalytic activity of the counter ions and is analogous to homogeneous catalysis by dissolved electrolytes. The catalytic activity of ion exchangers is thus directly related to the ion exchange properties. Reactions of liquids and solutes include esterification, ester hydrolysis, sucrose inversion, dehydration of alcohols and aldol, acyloin and Knoevenagel condensations etc. Thus a sucrose solution can be hydrolyzed into glucose and fructose by passing them through a cationic resin in hydrogen form. The aim of the present study is to synthesize, characterise and explore the catalytic efficiency of antimony tin tungstate.

Dhanitha et al [3] have investigated the applicability of a bimetallic inorganic cation exchanger zirconium tin molybdate (ZrSnMo) in environmental remediation. Binary separation of metal ions from synthetic mixtures was carried out using this ion exchanger.

2. Experimental details

2.1 Materials and Methods

Antimony trichloride, stannic chloride and sodium tungstate obtained from Loba-Chemie (India) were used for the synthesis of the exchanger. Other reagents and chemicals used were of analytical grade. Double distilled water was used throughout the work. Sucrose and Benedict's quantitative reagent was used for catalytic activity studies.

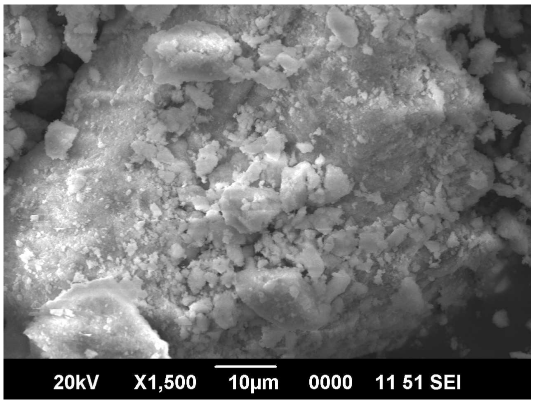
Antimony tin tungstate (SbSnW) was synthesised by adding a solution of sodium tungstate to a mixture of antimony trichloride and stannic chloride solutions (0.1M each) with constant stirring, in different volume and mole ratios. The resulting gel was kept for 24h at room temperature maintaining the pH at 0.5. It was then filtered, washed with deionised water and dried. The exchanger was then converted into H^+ form by immersing it in 1.0 M nitric acid for 24 h with occasional shaking and intermittent changing of acid. It was then washed with deionised water to remove excess of acid, dried and sieved to obtain particles of 60-100 mesh.

2.2 Characterization

Ion exchange capacity of the material was determined by column method as reported earlier [4]. Effect of hydrated ionic radii of various alkali and alkaline earth metal ions on ion exchange capacity was studied by determining the ion exchange capacities(IEC) using their respective salt solutions. Effect of temperature on ion exchange capacity of the ion exchanger was studied using a muffle furnace in which a temperature up to 900^{0}C can be maintained. To find the thermal stability, different samples of same amount were heated for three hours at different temperatures. The IECs of the cooled samples were determined by the usual column method. Distribution studies were carried out for various metal ions in demineralised water by batch process as reported [4]. Catalytic activity was studied by taking hydrolysis of sucrose. 20ml sucrose solutions of various concentrations were treated with the exchanger. The amount of reducing sugars formed was determined by using Benedicts' quantitative reagent. This was repeated by varying the amount of exchanger, time and temperature.

3. Results and discussion

The ion exchange properties of various samples of antimony tin tungstate synthesized were determined and the exchanger, SbSnW obtained as white transparent solid having highest ion exchange capacity, 1.25 meq/g was selected for detailed study. The exchanger could be regenerated thrice without any appreciable loss in ion exchange capacity. The material is found to be quite stable in lower concentrations of mineral acids such as 1.0M HNO_3, 1.0M H_2SO_4 and1.0M HCl and 0.01M solutions of bases. The composition of antimony, tin, tungsten and oxygen were obtained from EDS measurements and was found in the ratio Sb: Sn: W: O as 3:2: 2: 5.



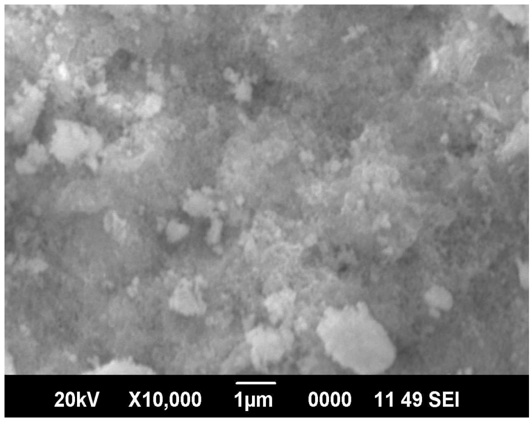


Fig. 1. *SEM image of SbSnW*

The SEM image (Fig. 1) reveals that the material consists of large agglomerates. The large particles appeared to be of small undeveloped crystallites agglomerated to each other. They are arranged in such a way that a heterogeneous surface is formed with high surface area. High surface area increases the catalytic activity. BET surface area measurement showed it to be 223 m^2/g.

The TEM image (Fig. 2) show that the particles are agglomerated and of irregular shape. The size distribution is in the narrow range of 5-15nm.

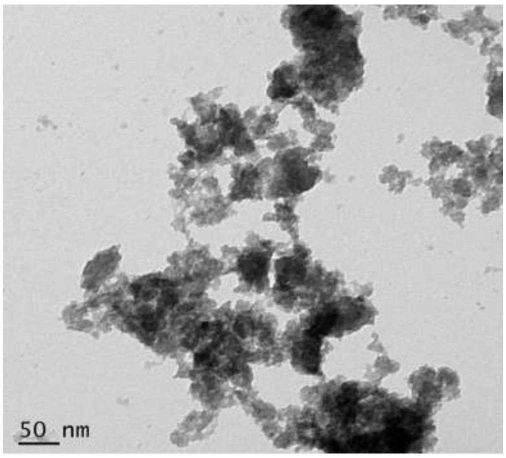
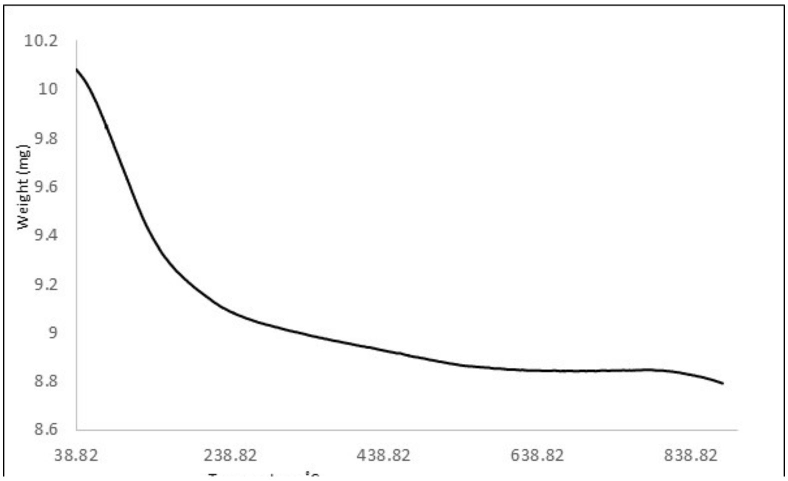


Fig. 2. *TEM image of SbSnW*

Thermal studies (Fig. 3) reveal evaporation of external water molecules causing the initial weight loss which is accompanied by an endotherm. After that only a negligible change in weight is observed, but an endotherm is seen after about 500°C which may be due to phase changes in the material. The initial weight loss of 10% upto about 200°C is due to the evaporation of external water molecules and condensation of structural hydroxyl groups. The material is found stable upto 500°C without any appreciable change in ion exchange capacity.

The effect of size and charge on ion exchange capacity was studied for alkali and alkaline earth metal ions and the order was found to be $Li^+ < Na^+ < K^+$; $Mg^{2+} < Ca^{2+} < Ba^{2+}$ confirming that ion exchange takes place with the hydrated form of the ions.



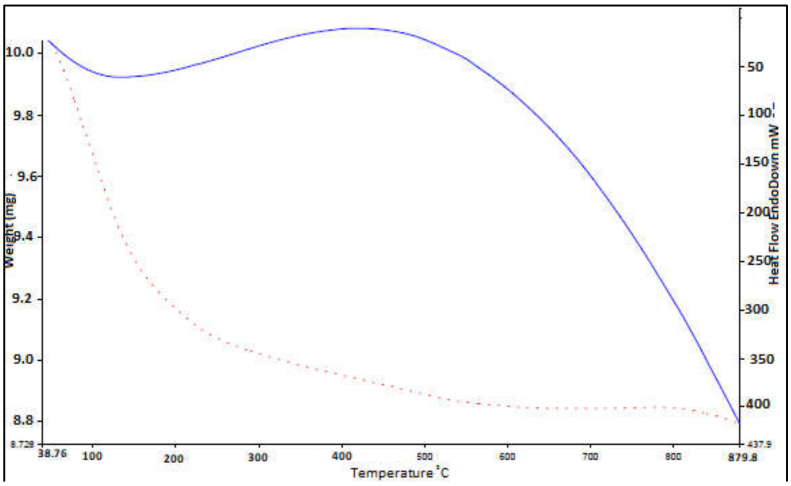


Fig. 3. *Thermal analysis diagrams of SbSnW*

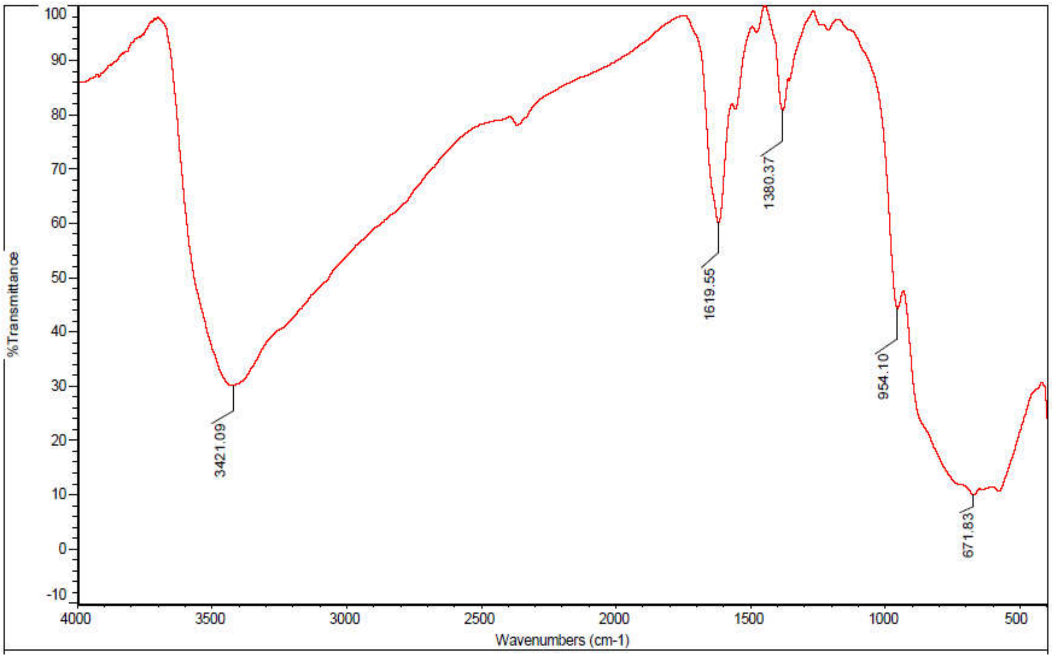


Fig. 4. *FTIR spectrum of SbSnW*

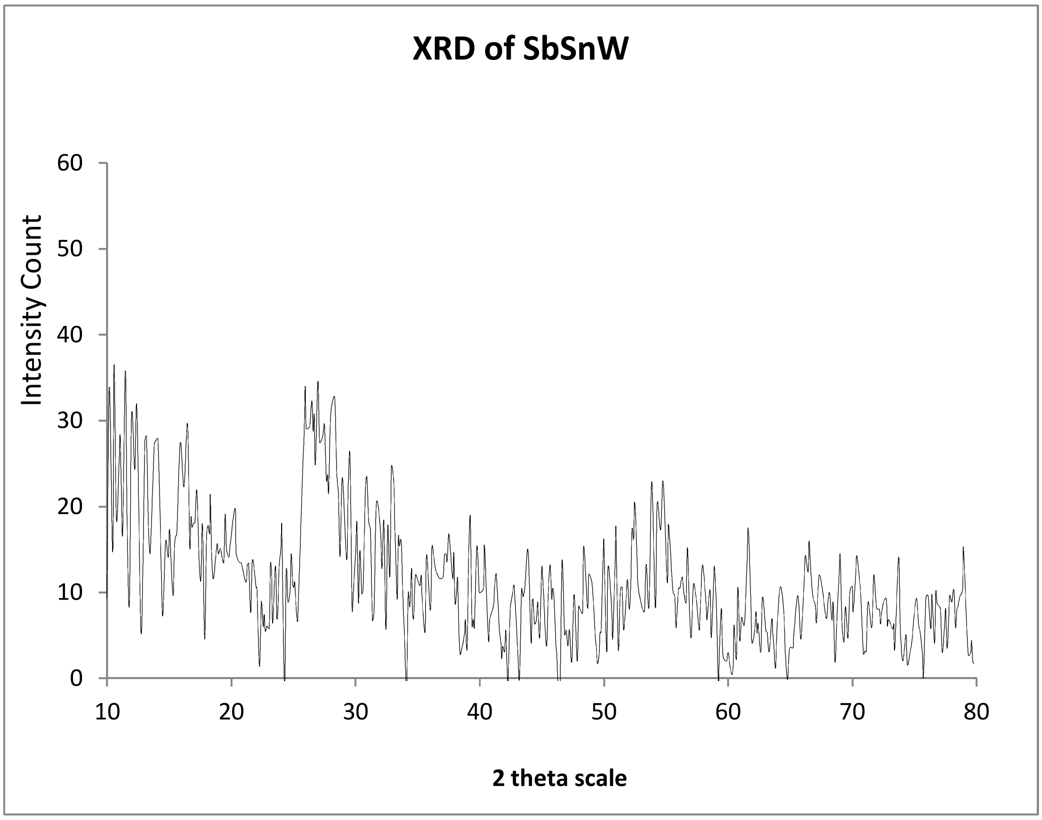


Fig. 5. *XRD Pattern of SbSnW*

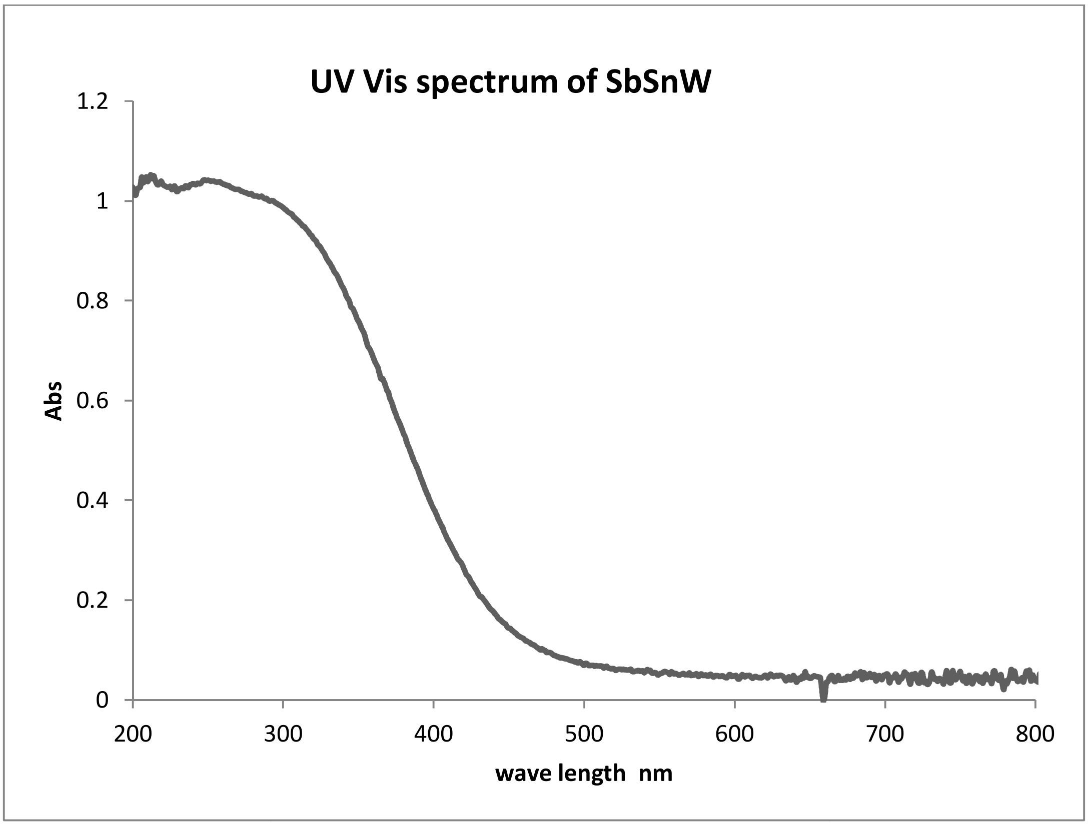


Fig. 6 *UV-Vis spectrum of SbSnW*

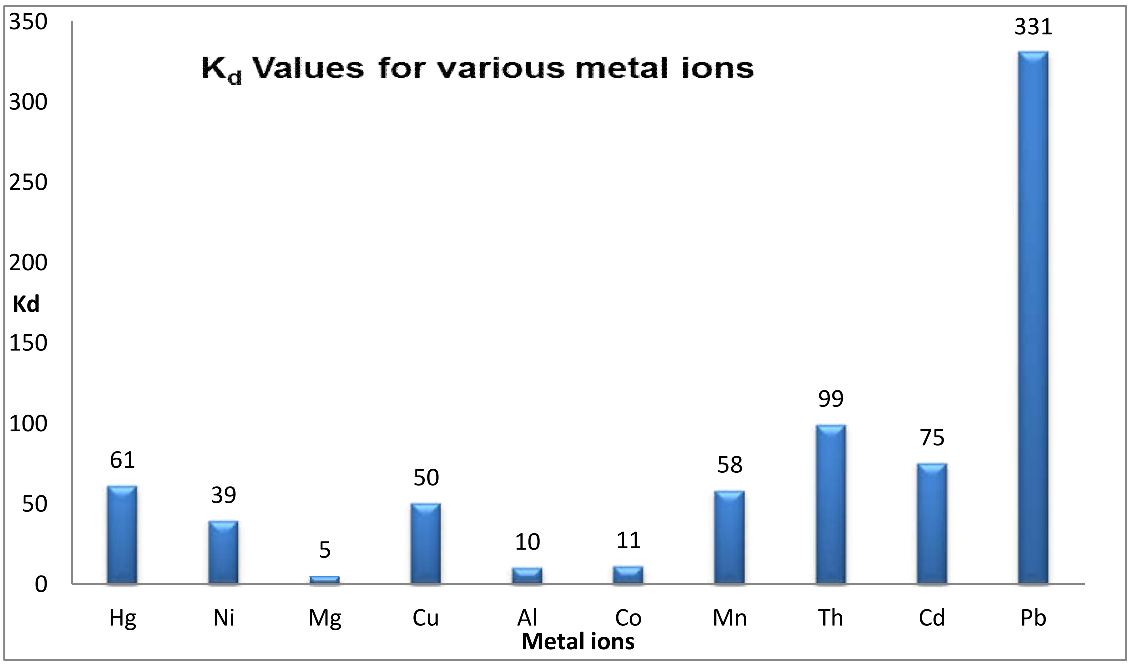


Fig. 7. *Distribution studies of metal ions*

The sodium ion exchange capacity decreases slightly with temperature and the sample retained prominent capacity up to 300°C which can be explained with the obtained thermogram also [5].

FTIR spectrum of SbSnW (Fig. 4) shows a broad band in the region ~ 3421 cm^{-1} which is attributed to symmetric and asymmetric –OH stretching, while the band at ~ 1619cm^{-1} is attributed to H-O-H bending. A band in the region ~1380 cm^{-1} is attributed to the presence of δ (WOH) indicating the presence of structural hydroxyl protons. Band around 600 cm^{-1} show the presence of various metal-oxygen bonds [6, 7].

From the UV-Visible spectrum of SbSnW (Fig. 6) it is found that the material can absorb almost all the wavelength of light in the UV region and this property can be used for various applications. A moderately intense band observed at 215 nm corresponds to the charge transfer from oxygen to metal [8].

The distribution studies of metal ions (Fig. 7) showed that the exchanger has very high affinity towards Pb^{2+} ion in comparison to other metal ions studied. The selectivity was found to be in the order $Pb^{2+}>Th^{4+}>Cd^{2+}>Hg^{2+}>Mn^{2+}>Cu^{2+}>Ni^{2+}>Co^{2+}>Al^{3+}>Mg^{2+}$.

The differential selectivity of SbSnW towards metal ions with separation factor more than 5 enable it to act as an efficient material for the separation of various metal ions from each other.

The studies show the potential of the material for removal of heavy metal ions like Pb^{2+}, Th^{4+}, Cd^{2+}, Hg^{2+} etc. from polluted water. A review of heavy metal removal using inorganic ion exchangers revealed that as the pH of solution increases sorption increases.

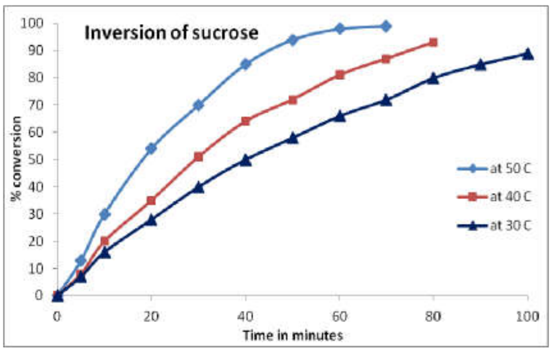


Fig. 8. *Effect of temperature on inversion of sucrose*

Hydrolysis of sucrose: For catalytic studies, hydrolysis of sucrose was carried out using the exchanger. With increase in catalyst amount and concentration of reactant the yield increases. From the graph it is found that by using 1 g of catalyst for 20 ml of 1 M sucrose solution at 50°C, 99% conversion could be achieved within 70 minutes. The catalyst was recycled and reused with negligible loss in the activity.

4. Conclusions

Antimony tin tungstate was synthesized by a simple general method. The material was characterised by using various spectroscopic and non-spectroscopic techniques and revealed very high selectivity towards Pb^{2+}, Th^{4+}, Cd^{2+}, Hg^{2+} etc. These results are very remarkable in environmental chemistry and can be utilized for applications involving separation and removal of these metal ions. The presence of protons contained in structural hydroxyl groups in the material indicated good potential for application in solid acid catalysis and is used for the inversion of sucrose. The studies on synthesized ion exchanger have shown entirely different selectivities and enhanced properties than that of their single salt counter parts and this result encourages us to pursue studies on synthesis of new materials of this class, their properties and applications. The properties can be used to extend the studies to various fields.

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