Alcohol Sensing Bimetallic Tin Vanadium Metal Oxide and Their Removal Efficacy of Lead and Cadmium Metal Ions from Aqueous Solution Through Ion Exchange Method

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***Abstract* - Bimetallic tin vanadium metal oxide was synthesized by simple sol-gel method and characterized by different instrumental techniques. The material has an ion exchange capacity of 1.01 meqg-1 and carried out different metal ions distribution study. The material has high removing ability towards lead and cadmium metal ions from aqueous solutions. Synthetic binary separation of lead and cadmium ions was carried out. The material has sensing ability to detect 300ppm level phenol from aqueous solution and can be regenerated the material.**

***Index Terms* - Meatl oxide, sol-gel method, sensor**

I.INTRODUCTION

In the past decades, nanomaterials research has been attained a great attention in every field of science. Transitional metal oxide is promising materials because of its their plentiful raw materials, environmental friendliness, easy approachability, etc. [1]. In addition, they play a central part in the electrodes of electrochemical supercapacitors [2]. First of all, the co-existence of two different cations in a single crystal structure could produce more electrons than single metal oxides, which leads to the improvement in the electrical conductivity [3].

Wastewater from semiconductor manufacturing and other photo-electric industries contains organic compound. Isopropyl alcohol (IPA), acetone, propylene glycol monomethyl ether acetate, ethyl lactate, phenol, benzene, toluene, and xylene are the common organic reagents present at high concentrations in wastewater and most of them are volatile in nature [4]. These organic compounds pose direct or indirect harm to the liver, kidney, central nervous system, and skin, and some of them have already been verified as carcinogens, teratogenic agents, and gene mutagen for humans [5]. There should some good techniques for detecting or sensing and removing these pollutants from the environment. Most ethanol sensors today rely upon the use of metal oxides and powders that catalyze the oxidation of ethanol and use electrochemical, electrical conductivity, or transduction by field-effect transistors. The detection of different alcohols in aqueous solution was carried out by different method. In our laboratory methods were formulated to detect alcoholic OH group from alcohol containing aqueous solution using bimetallic metal oxide.

II. MATERIALS AND METHODS

Reagents and apparatus: A glass column were used for column operations. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies, TG Perkin Elmer Diamond TG/DTA Analysis System for thermogravimetric/ derivative Thermogravimetric analysis were used.

Synthesis of bimetallic tin vanadium oxides (SVO): Stannic chloride solution (0.1 M) was added into the sodium vanadate (0.05 M) solution with constant stirring so that final volume was 500 mL and pH was adjusted with 1.0 M NaOH/1.0 M HNO_3 and kept for 24 hrs. The orange colour gel obtained was then filtered, washed with deionized water and dried. The material was then converted into the H^+ form by treating with 1.0 M HNO_3 for 24 hrs with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove the excess acid, dried and sieved to required mesh size.

Determination of ion exchange capacity*:* For determining the ion-exchange capacity, one gram of the material was taken into a glass column (0.5 cm, internal diameter) plugged with glass wool at the bottom. The length of bed was approximately 1.5 cm. 100 ml 1 M NaCl solution was used to elute H^+ from the exchanger. The flow rate was maintained at 1.0 ml min^{-1}. The H^+ ions content of the effluent was then determined by titrating against a standard solution of sodium hydroxide (0.05 M).

Distribution coefficient (K_d): Distribution studies were carried out for various metal ions in demineralized water by batch process. In this method, 0.1 g of the material (60-100 mesh) was equilibrated with 20 ml of the metal ion solutions for 24 hrs at room temperature. Distribution coefficient is defined as the ratio of the concentration of the metal ion in the material and in the solution. The metal ion concentrations before and after sorption were determined spectrophotometrically /complexometric titration against standard EDTA solution. In the complexometric method, the K_d values were calculated using the formula,

$$K_d = \frac{(I - F)}{F} \times \frac{V}{W}$$

Where, I is the initial volume of EDTA used, F is the final volume of EDTA used, V is the volume of the metal ion solution (ml) and W is the weight of the exchanger [6].

Detection of alcoholic OH group: 0.5 g of the material was placed in beakers which contained 50 mL of 100% alcohol solutions and kept for shaking for 5 minutes. The experiment was conducted for different alcohol solutions namely methanol, ethanol, and isopropyl alcohol. The alcohol solution was decanted from this and analyzed by UV-Visible diffuse reflectance spectroscopy. The materials were dried and were taken UV-Visible diffuse reflectance spectra. UV-Visible diffuse reflectance spectrum of the material before treated with alcohol solution was also recorded. For the detailed study we selected methanol as basic alcohol and studied the effect of concentration of alcohol for the detection ability of exchanger. For this we recorded the UV-Visible diffuse reflectance spectra of SVO treated with 75%, 50% and 25% methanol solution.

Quantitative separations of some important metal ions: It was achieved on SVO columns. 1 g of the material was packed in a glass column (0.5 cm, internal diameter) with a glass wool support at the bottom. The column was washed thoroughly with demineralized water and the mixture of two metal ions (each with initial concentration of 0.1 mol L^{-1}) was loaded onto it and allowed to pass through the column at a flow rate 5–20 drops min^{-1} until the level was just above the surface of the material. The process was repeated twice or thrice in order to ensure the complete sorption of metal ions on the bead.

III. RESULTS AND DISCUSSIONS

FT-IR spectra of SVO (Figure 4.2a) shows a broad band in the region ~3429 cm-1 which is attributed to symmetric and asymmetric –OH stretching, while the band at ~1624 cm-1 is attributed to H-O-H bending. A band in the region ~1378 cm-1 is attributed to the presence of δ (MOH). This indicates the presence of structural hydroxyl protons in SVO, which is more evident from the obtained IEC values. Bands at ~942 cm^{-1}, 812 cm^{-1} and ~516 cm^{-1} may be due to the presence of Sn-O, V-O-Sn and V-O bonds.

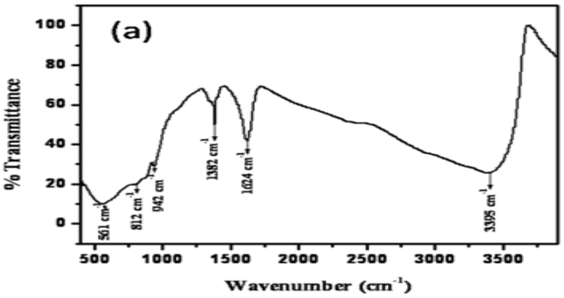

Figure 1 FT-IR spectra of SVO

XRD of SVO shows some prominent peaks together with a number of low intensity peaks which suggest semi-crystalline nature of the material.

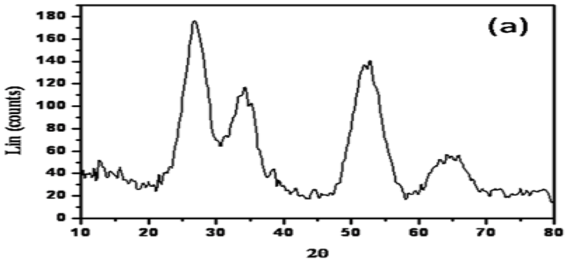

Figure 2 XRD of SVO

The thermogram of SVO (Figure 3) exhibits the weight loss of 10% up to ~ 100 °C which is due to the removal of free external water molecules. Further, a gradual mass loss (about 6%) up to 500 °C may be on account of the condensation of hydroxyl groups. Above 500 °C, the gradual loss in weight (about 1%) up to 800 °C was mainly because of the removal of structural water. There was no sudden decrease in the weight loss which indicated that there was no structural change of this material. Thus, thermogravimetric analysis clearly reveals that the sample is quite stable at high temperatures upto 600 °C and can be used in high temperature applications.

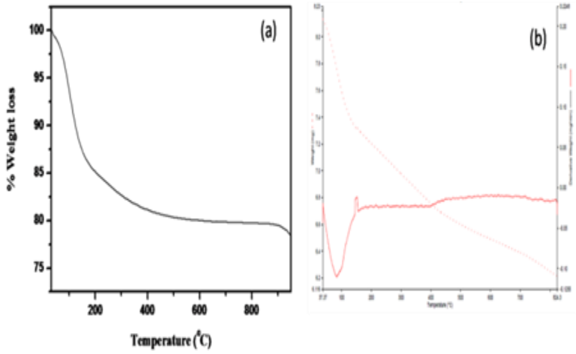

Figure 3 (a) and (b) Thermal analysis diagram of SVO

SEM analysis (Figure 4) of SVO shows that materials are in the nano meter range but there in the agglomerated form.

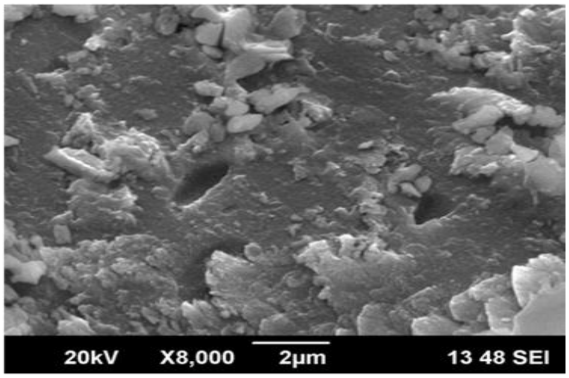

Figure 4 SEM analysis of SVO

UV-Visible spectra of alcohols which obtained after treating with SVO show that there is no change in the corresponding peak of alcohols which implies that there is no chemical change took place while treating with SVO. The UV-Visible diffuse reflectance spectra of solid samples which were put in the alcohol solutions are shown in Figure 5. The colour of SnMoV changed within 5 minutes after putting in the alcohol solutions (Figure 6) and these differences can be seen from the spectra. From the colour change of the material, we can detect the presence of alcohol in aqueous solution. The conducting nature of the material also changed. The pure SVO has 2.15eV band gap energy value whereas for the material after putting in alcohol solution, the band gap energy changed. The methanol treated SVO has the band gap energy value of 1.65eV and ethanol and isopropyl alcohol treated material has the same band gap energy values of 1.46 eV. These values were obtained using the UV-Visible diffuse reflectance spectra (Figure 7.10). The optical energy band gap was calculated using equation [7,8]:

$$E_g = \frac{hc}{\lambda} = \frac{1240}{\lambda}$$

where *Eg* is the band gap energy (eV), *h* the Planck's constant (4.135 x 10-15 eV . s), *c* the light velocity (2.997 x 108 ms-1) and λ the band gap wavelength of titanium oxides (nm). The material after use can be regenerated with 2.0 M HNO_3 to regain its colour and can be used repeatedly.

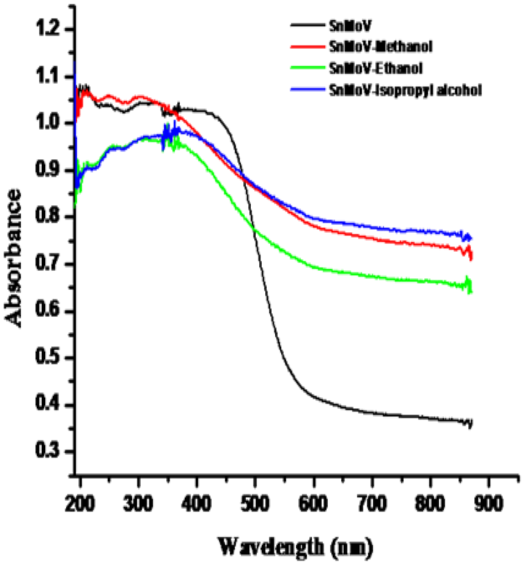

Figure 5 UV-Visible reflectance spectra of SVO and by the treatment with different alcohols

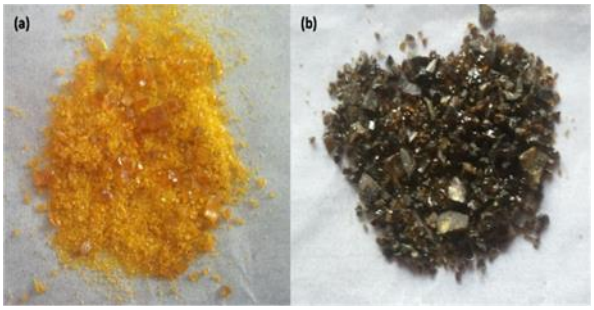

Figure 6 (a) SVO and (b) SVO-methnaol (100%)

The variation of the detecting ability of SVO in different percentage solution was analyzed using UV-Visible DRS techniques (Figure 7). The study shows that even the 25% alcohol solution was detectable using this material. The material can detect the presence of alcoholic OH group even the solution contains 300 ppm concentration of alcohol. The material is inactive in acid and changed the colour in alcoholic solution only which enables its use for the selective detection of alcoholic OH group. While putting the material in the alcoholic solution colour of the material changed but the decomposition of alcohol did not take place.

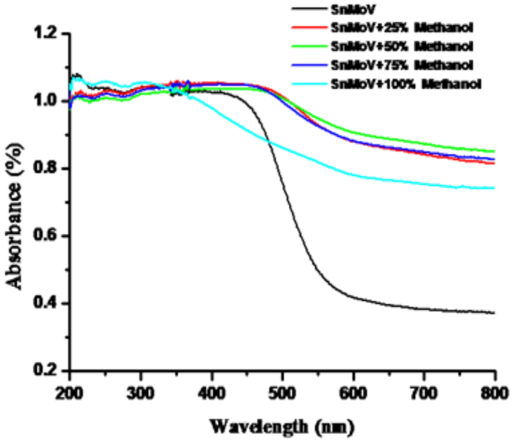

Figure 7 UV-Visible reflectance spectra of SVO by the treatment with different concentration of methanol

While making it as thin film, we can effectively use this material as sensor for alcoholic OH group by measuring the conductivity of the materials. Detection of phenolic OH group is also possible by this exchanger. The exchanger can detect the presence of phenol group even the solution contains 300 ppm concentration of phenol.

The sample SVO obtained was orange in colour having sodium ion exchange capacity of 1.01 meqg^{-1} selected for further study. The material was found stable in mineral acids such as 1.0 M HNO_3, 1.0 M H_2SO_4 and 1.0 M HCl, 0.01 M solutions of bases and organic solvents such as ethanol, acetone, carbon tetrachloride etc.

In order to explore the potentiality of the material in the separation of metal ions, distribution studies for metals ions were performed in different solvent systems (Table 1). The distribution coefficient data show that the material was found to be selective for Pb (II) and Cd (II) ions. The practical utility of the composite material was demonstrated by separating lead and cadmium from synthetic mixtures.

Table 1 Kd values of various metal ions in different electrolyte

Metal ion	DMW	0.001M HNO_3	0.01M HNO_3	0.1M HNO_3	0.001M NH_4NO_3	0.01M NH_4NO_3	0.1M NH_4NO_3
Pb(II)	960.0	955.1	832.9	600	945.60	873.2	542.1
Zn(II)	52.30	46	42.1	31	42.90	38.10	22
Mn(II)	30.50	30	12	2	29	10	2
Ni(II)	29.00	25	8	NA	23	4	NA
Hg(II)	9.10	NA	NA	NA	6.29	NA	NA
Ca(II)	26.10	24	19	9	34	25	12
Cd(II)	749.6	621	523.8	431.2	700	438.9	233.6
Co(II)	19.86	9	NA	NA	16	2	NA
Cu(II)	308	73	46	29	80	73	66
Bi(III)	NA	NA	NA	NA	NA	NA	NA
Mg(II)	20.47	18.2	10	NA	17	5.8	NA

NA: No noticeable adsorption

Table 2 Selective separation of Pb(II) from synthetic mixtures containing Pb(II), Zn(II) [2.15 mg], Mg(II) [2.97 mg], Co(II) [3.70 mg] and Ni(II) [1.93 mg]

Amount of metal ion loaded (mg)	Amount of metal ion found (mg)	Recovery (%)	Eluent used	Volume of eluent(mL)
3.10	3.05	98.39	0.5 M HNO_3	70
2.31	2.29	99.13	0.5 M HNO_3	50

Table 3 Selective separation of Cd(II) from synthetic mixtures containing Cd(II), Zn(II) [2.15 mg], Mg(II) [2.97 mg], Co(II) [3.70 mg] and Ni(II) [1.93 mg]

Amount of metal ion loaded (mg)	Amount of metal ion found (mg)	Recovery (%)	Eluent used	Volume of eluent(mL)
2.68	2.54	94.78	0.5 M HNO_3	70
2.29	2.16	94.32	0.5 M HNO_3	50

IV.CONCLUSION

The material SVO has high ion exchange capacity and can be utilized for the removal of lead and cadmium ion from industrial effluent. Bimetallic oxides usually show better sensing response than the single component if the catalytic actions of the components complement each other. SVO will be a promising material in the field sensor due to its sensing ability towards alcoholic OH group detection.

ACKNOWLEDGMENT

The authors gratefully acknowledge STIC, Cochin, Biogenix, Trivandrum for instrumental support.

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