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UV-Visible Diffuse Reflectance spectroscopic studies on Mn and Cu ion exchange of newly synthesized cerium zirconium antimonate and its application in dye degradation

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Abstract

A novel inorganic cation exchanger cerium zirconium antimonate (CZSb) was synthesized by co precipitation method. Zirconium substitution of cerium in the solid solution has proved to be beneficial in increasing the oxygen storage capability. Chemical composition of the compound was determined from EDS and structural studies were carried out using TGA, XRD and FTIR. UV-VIS Diffuse Reflectance spectroscopic studies were conducted to obtain information on surface coordination and different oxidation states of metal ions and to study their properties. The material synthesized showed very good cation exchange properties and the distribution studies showed that the selectivity towards various metal ions was in the order $Pb^{2+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Cd^{2+} > Y^{3+} > Ni^{2+} > Hg^{2+} > Zn^{2+} > Th^{3+} > Mg^{2+}$*. Its selectivity for lead helps the removal of it from other cations.* Cu^{2+} *ion exchange changes the color of the material from yellow to green and* Mn^{2+} *ion,s which get oxidized in the matrix of the material changes the color to dark brown /black. Thus the material can be used as an environment friendly solid indicator for the detection of trace amounts of* Mn^{2+} *ions in solution. The electron exchange property of cerium ions enable it to be used widely in various catalytic and functional systems. UV-Vis DR Spectroscopy was used for characterizing the synthesized material and its Mn and Cu ion exchanged forms. The decrease in rate of catalytic degradation of methyl orange dye with its Mn exchanged form is correlated with its UV VIS DR spectra.*

Keywords: Cerium zirconium antimonate, ion exchanger, distribution, UV- Vis DR spectroscopy, dye degradation.

Introduction

Synthetic inorganic ion exchangers have the advantage of high chemical, thermal and radiation stability[1,2,3]. New mixed materials of tetravalent metallic acid (TMA) salts with cation substitution are of interest since they show improved ion exchange properties and selectivity for particular metal ions in comparison to their single salt counter parts. Here cation substitution alters the properties, composition and dimensions of the structure[4]. Zirconium based ion exchangers have received attention because of their excellent ion exchange behavior, stability and some important chemical applications in the field of ion exchange, ion exchange membrane and solid–state electrochemistry[5]. The unique capability of cerium ions to change in between Ce^{3+} and Ce^{4+} ionic state in oxidized/ reduced conditions enable it to be used widely in various catalytic and functional systems. Examples include histochemistry[6] three-way catalytic converters[7] electrolytes in solid oxide fuel cells,[8,9]. Gas sensors[10], oxygen storage materials[11] and water decom position catalysts[12].

Ion exchangers are now extensively used in heterogeneous catalysis. During the catalytic reaction, especially when catalytic degradation of dyes present in effluents of various industries is carried out, a knowledge of the interaction of certain ions with the cations in the exchanger is very essential since the catalytic reactions are usually carried out in aqueous medium which may contain various cations. This work was carried out to study the interactions of Mn and Cu ions with the exchanger synthesized and how it affects the catalytic activity. UV-Vis Diffuse Reflectance Spectoscopy(DRS) is a more convenient technique to characterise nanomaterials than UV-Vis absorption spectroscopy, since it takes advantage of the enhanced scattering phenomenon in powder materials. Moreover the effects of light scattering in the absorption spectra of powder samples dispersed in liquid media can be avoided using DRS[13].

Material and Methods

Apparatus and instruments: A glass column was used for column operations. ELICO LI613 pH meter was used for pH measurements and an electric thermostat oven was used for heating the samples at various temperatures. UV-Visible Spectrophotometer model JASCO V660 with diffuse reflectance accessory (integrated sphere) was used for spectrophotometric measurements. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 for IR studies, X-ray

Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies, Perkin Elmer Diamond TG/DTA Analysis System for thermal analysis and an electric shaking machine for shaking were also used. Chemical composition was determined using EDS.

Synthesis and Characterization: Zirconium oxy chloride (Loba Chemie, India), Ceric ammonium nitrate (E.Merck) and potassium pyroantimonate(E.Merck) were used for the synthesis of the material. All other reagents and chemicals used were of analytical grade. Zirconium oxy chloride solution (1M), ceric ammonium nitrate solution(1M) and potassium pyroantimonate solution(1M)s were prepared. potassium pyroantimonate solution was added to mixtures of zirconium oxy chloride solution and ceric ammonium nitrate solution with constant stirring in different volume ratios, the final volume being 750ml. The resulting gel was kept for 24 hrs at room temperature maintaining the pH at 1, adjusted with 1M NaOH/IM HNO_3. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H^+ form by treating with 1M nitric acid for 24 hours with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60-100 mesh.

Properties like ion exchange capacity(IEC), chemical resistivity and pH titration studies, distribution studies and determination of concentrations of manganese ions in $MnSO_4$ solutions were carried out as reported earlier 11.

Results and Discussion

The sodium ion exchange capacity (table-1) was found to in the order CZSb114 > CZSb113> CZSb 213 > CZSb112 > CZSb123. Increase in composition of antimonate increased the IEC values and is highest for CZSb114. A very small variation in color was found for the samples, the intensity of yellow color being highest for CZSb213 and lowest for CZSb114. Elemental composition of the samples were determined from EDS figure-1.

pH titration curve figure-2 showed mono functional nature of the exchanger. The exchange capacity obtained from the curve is in agreement with that obtained by the column method. Surface hydroxyl groups may be generated due to dissociative adsorption of water on highly polar bonds in the material. These hydroxyl groups may exhibit either Brønsted acidity or basicity. It is therefore difficult to predict quantitatively the effect of relative amounts of Ce and Zr on the acid–base properties which would depend on the preparative conditions, reducing atmosphere, exposure to water and cation site distribution in the solid solutions.

Distribution studies of metal ions figure-3 were carried out with all the samples. Sorption of ions was found to be in the order of their ion exchange capacities, CZSb114 showing the greatest distribution coefficients than other samples. The distribution studies 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 $Pb^{2+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Cd^{2+} > Y^{3+} > Ni^{2+} > Hg^{2+} > Zn^{2+} > Th^{3+} > Mg^{2+}$.

XRD analysis figure-4 showed poor cystalline nature of the exchanger and the average particle size was found to be 31 nm which is in the nano range. The particle size was calculated from the full width at half-maximum of the peak using Debye Scherrer equation,

$$D = \frac{0.9\lambda}{\beta_{2\theta} \cdot \cos\theta_{max}}$$

where D is the average crystal size in nm, λ is the characteristic wavelength of X-ray used, θ is the diffraction angle and $\beta_{2\theta}$ is the angular width in radians at an intensity equal to half of the maximum peak intensity.

Table-1
Synthesis and properties of various samples of exchanger

Synthesis and properties of various samples of exchanger				
Sample	Volume ratios of 0.1M solutions mixed	Atomic ratio of samples determined from EDS	Appearance	Ion Exchange Capacity for Na^+ (meq/g)
	Ce^{4+} : Zr^{4+} : Sb^{5-}	Ce : Zr : Sb : O		
CZSb 112	1: 1: 2	1: 4.2 : 4.4 : 100.3	Yellow glassy solid	0.90
CZSb 113	1: 1: 3	1: 4.9 : 7.0 : 23.6	Yellow glassy solid	0.93
CZSb123	1: 2: 3	1: 5.0 : 6.6 : 115.6	Yellow glassy solid	0.86
CZSb 213	2: 1: 3	1 : 1.4: 4.9: 11.2	Yellow glassy solid	0.93
CZSb 114	1: 1: 4	1: 3.3 : 8.8: 19.9	Yellow glassy solid	1.08

FTIR spectra of CZSb figure-5 showed a broad band in the region ~3365 cm^{-1} which is attributed to symmetric and asymmetric –OH stretching, while the band at ~1629 cm^{-1} is attributed to H-O-H bending. A band at ~1383 cm^{-1} is attributed to the presence of structural hydroxyl protons in CZSb and a band in the region ~1066 cm^{-1} and the band near 720cm^{-1} may be attributed to Sb-O linkage. Bands at ~608cm^{-1} and ~428cm^{-1} may be due to Zr-O and Ce-O bonds. Thermo gravimetric analysis figure- 6 indicated about 12% weight loss up to about 120^{o}C primarily due to the evaporation of water molecules. After that, gradual weight loss was observed which may be due to the condensation of fee hydroxyl groups. No abrupt change in weight indicates the stability of the compound. The total weight loss upto 800^{o}C is only 25%.

In equilibrium with manganese salt solutions, Ce^{4+} ions in the exchanger oxidizes the diffused Mn^{2+} to higher oxidation states and hence the color of the exchanger changes from yellow to intense purple/ black. It was observed that rate of change of color increased with increase of concentration and temperature. Maximum sorption of ions was found to take place at pH 2. According to the Lewis definition of acids and bases, Ce^{3+} is a base and Ce^{4+} is an acid. Therefore, a more basic solution will create more Ce^{3+}ions on the surface of the nanoparticles and a more acidic solution will create more Ce^{4+} ions on the surface which results in increase in oxidation of Mn^{2+} ions. The exchanger is kept in equilibrium with 1M $MnSO_4$ solution at pH 2 for 24 hours. Washed with double distilled water, dried at 35^{o}C. It is then shaken with 1M HNO_3 solution for 4 hours with intermittent changing of acid, washed with double distilled water and dried.

UV-Vis Diffuse Reflectance spectroscopic studies: In a diffuse reflectance spectrum (DRS), the ratio of the lights scattered from a (> 2–3 mm) thick layer of sample and an ideal non absorbing reference sample is measured as a function of the wavelength. DRS has been used extensively to study ceria-based materials and transition metal oxides to obtain information on surface coordination and different oxidation states of metal ions by measuring *d–d*, *f–d* transitions and oxygen–metal ion charge transfer bands[6].

From the UV/Vis DR spectrum of CZSb figure-7 it was found that the band gap energy lies in the visible region. Several absorption bands are observed in the UV region between 200 and 380 nm. The band around wavelength 210 nm shows inter band transition in ZrO_2 and f→d transitions of Ce^{3+}. The band at about 250nm is assigned to $Ce^{3+} \leftarrow O^{2-}$ and inter band transition in ZrO_2 and the band at about 300 nm is assigned to $Ce^{4+} \leftarrow O^{2-}$ charge transfer transitions. The presence of $Ce^{3+} \leftarrow O^{2-}$ transitions in the UV-Vis DR spectra infers the presence of oxygen vacancy defects which affect the catalytic activity of the ceria-based solid solutions[6] Presence of zirconium increased the band gap energy.

The figure figure-8 shows the UV DR spectra of Mn exchanged samples prepared by equilibrating the CZSb with 1M $MnSO_4$ solutions and picture of the sample obtained. In the spectra the intensity of absorption in the UV region was found decreased where as in the visible region it increased compared to pure CZSb.

Analysis of the Mn^{2+} ion in the equilibrated solution showed that sorption was in the order 114>113>112>213>123. The exchanged form was found to be very stable towards acids which means that the interaction between the exchange and the ion is very strong. The spectra of the Mn exchanged samples prepared from 1M $MnSO_4$ solution and that of pure MnO_2 show almost similar bands in the UV region from which we conclude that the surface is almost completely covered by manganese oxide. Amount of Mn ion in the exchanger can be controlled by decreasing the concentrations of $MnSO_4$ solutions. The DRS of Mn exchanged CZSb213 and CZSb123 show similar absorption pattern to the spectrum of MnO_2 (Mn in +4 oxidation state), the former with higher absorption intensity in the visible region than the latter which shows more amount of Mn^{4+} in it as expected from the IEC values. In Mn exchanged CZSb112 and CZSb113 absorption is less near 800nm compared to other visible regions (red color reflected more) showing that the oxidation state is in between +4 and +7.

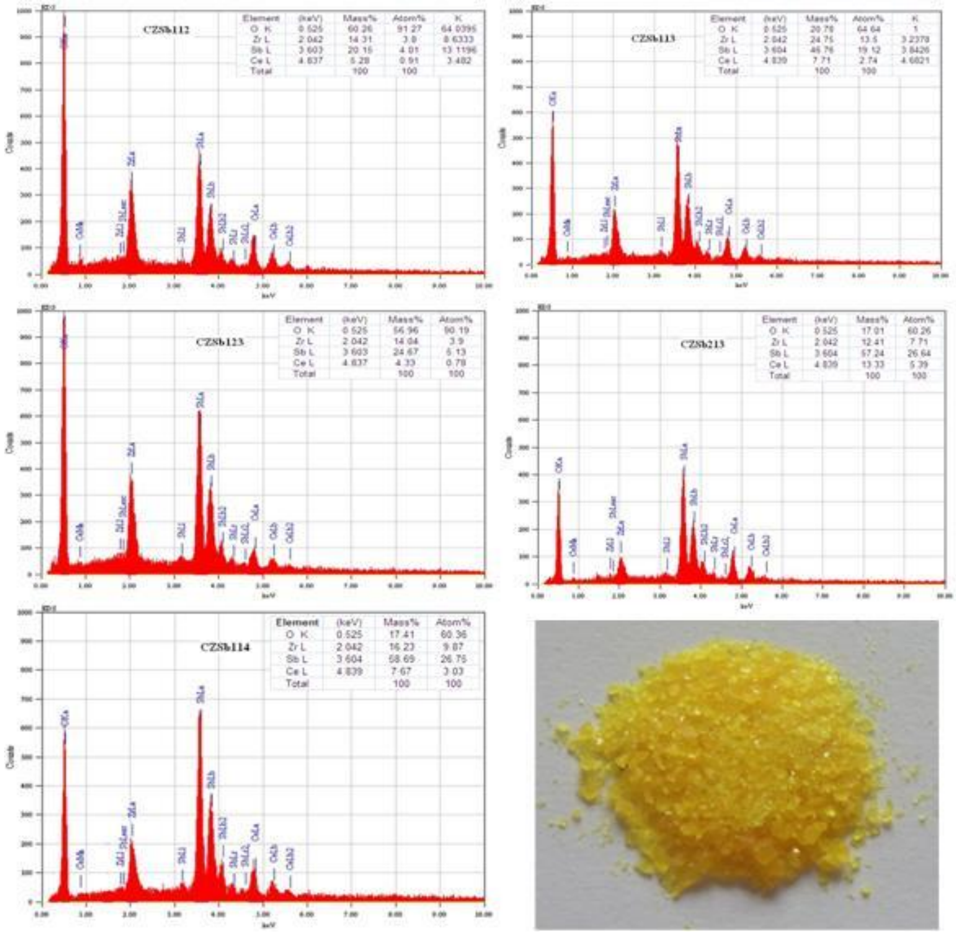
In the spectra of CZSb114 the band corresponding to the color in the region 450-550 is reflected more compared to other visible regions showing that Mn is present as Mn^{7+}also. The oxidation states of Mn in the exchangers are in the order 114>113>112>213>123 which is in the order of IEC values and decrease in band gap energies.

Application of CZSb for methyl orange degradation: The electron exchange property of Ce ions and the oxidizing character of the exchanger as a whole help dye degradation. The rate of degradation with CZSbMn figure-9 is less than that with pure CZSb. This can be explained as due to decrease in surface area of the sample due to Mn sorption as observed from Diffuse reflectance spectrum.

The diffusion of dye molecules in the pores of the exchanger may be helping the degradation even though the surface of the exchanger is almost completely covered by manganese oxide and the exchanged form was found to be very stable towards acids.

The spectra of Cu exchanged samples figure-10 and that of pure samples have similar bands in the UV region.

The spectra show different absorbing ability for visible light (reflection maximum at 550nm) which can be observed in the color of the samples (green). Desorption of Cu ions take place when the samples are treated with acids which means that the interaction with the exchanger is weak.



CZSb112

Element	(keV)	Mass%	Atom%	K
O K	0.525	60.26	91.27	64.0395
Zr L	2.042	14.31	3.8	8.6333
Sb L	3.603	20.15	4.01	13.1196
Ce L	4.837	5.28	0.91	3.482
Total		100	100	

CZSb113

Element	(keV)	Mass%	Atom%	K
O K	0.525	20.78	64.64	1
Zr L	2.042	24.75	13.5	3.2378
Sb L	3.604	46.76	19.12	3.8426
Ce L	4.839	7.71	2.74	4.6021
Total		100	100	

CZSb123

Element	(keV)	Mass%	Atom%
O K	0.525	56.96	90.19
Zr L	2.042	14.04	3.9
Sb L	3.603	24.67	5.13
Ce L	4.837	4.33	0.78
Total		100	100

CZSb213

Element	(keV)	Mass%	Atom%
O K	0.525	17.01	60.26
Zr L	2.042	12.41	7.71
Sb L	3.604	57.24	26.64
Ce L	4.839	13.33	5.39
Total		100	100

CZSb114

Element	(keV)	Mass%	Atom%
O K	0.525	17.41	60.36
Zr L	2.042	16.23	9.87
Sb L	3.604	58.69	26.75
Ce L	4.839	7.67	3.03
Total		100	100

Figure-1
EDS& picture of samples

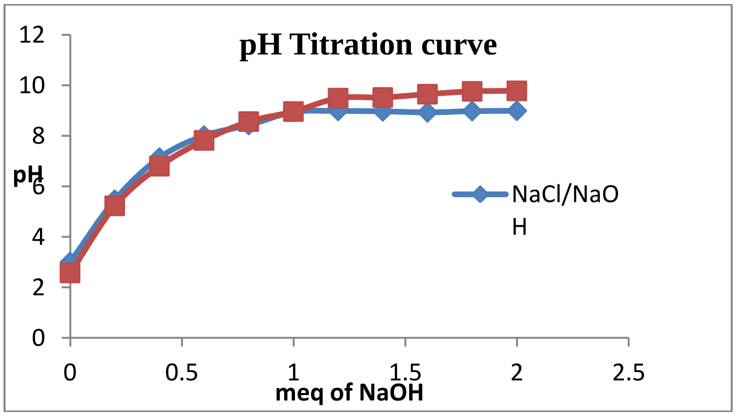


Figure-2
pH Titration Curve

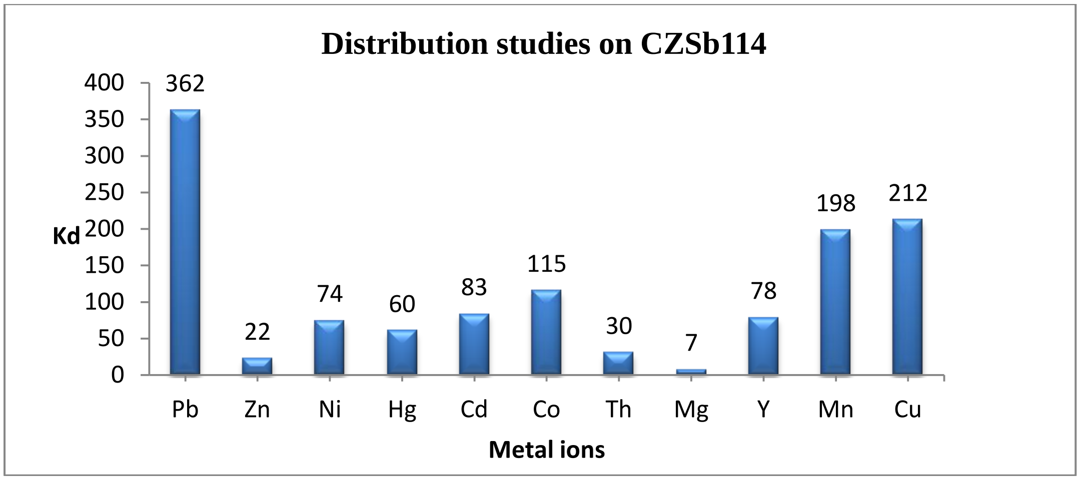


Figure-3
Distribution studies on CZSb114

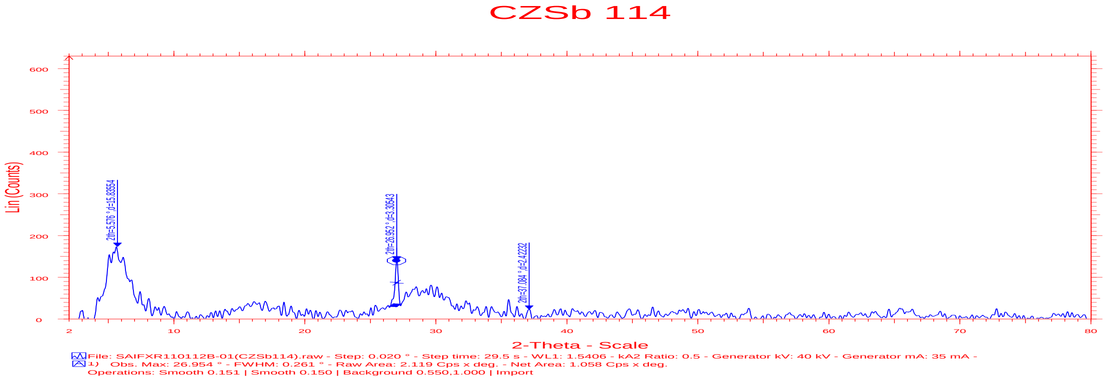


Figure-4
XRD of the sample

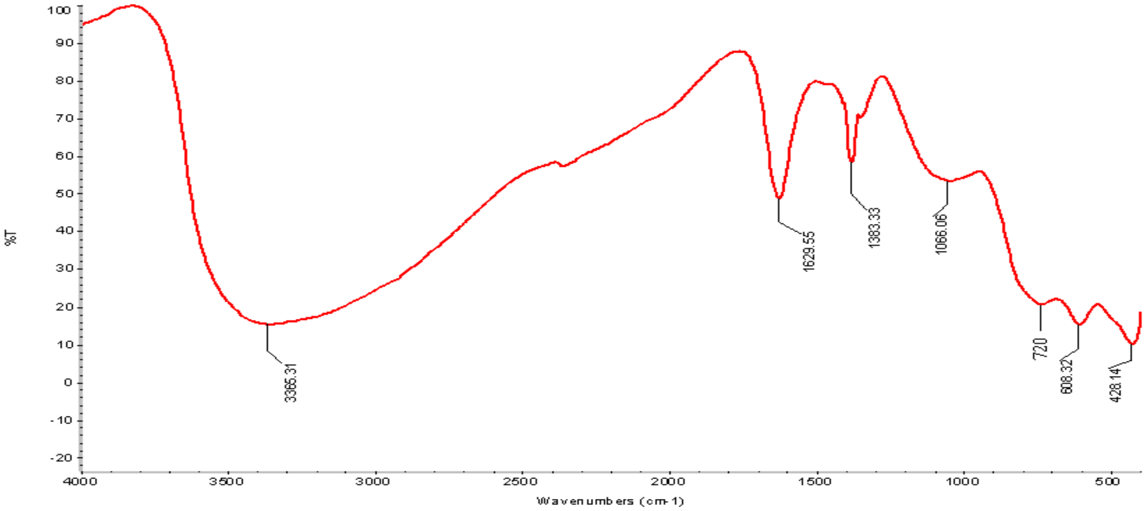


Figure-5
FTIR of CZSb

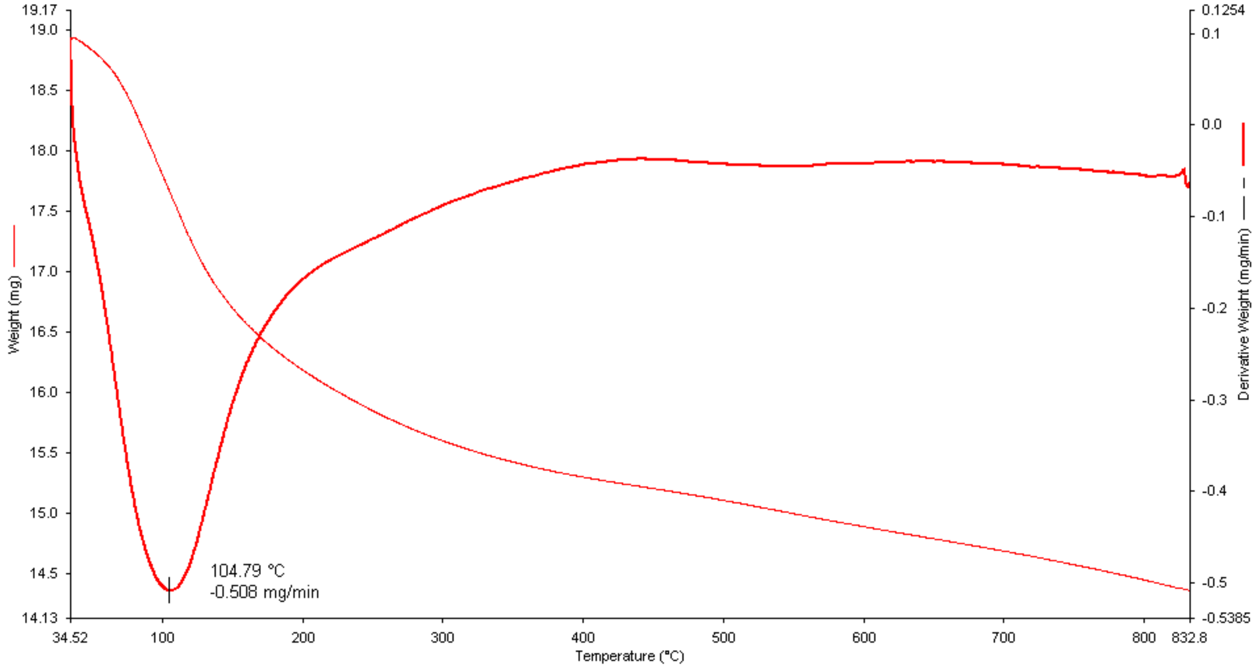


Figure-6
TG of CZSb114

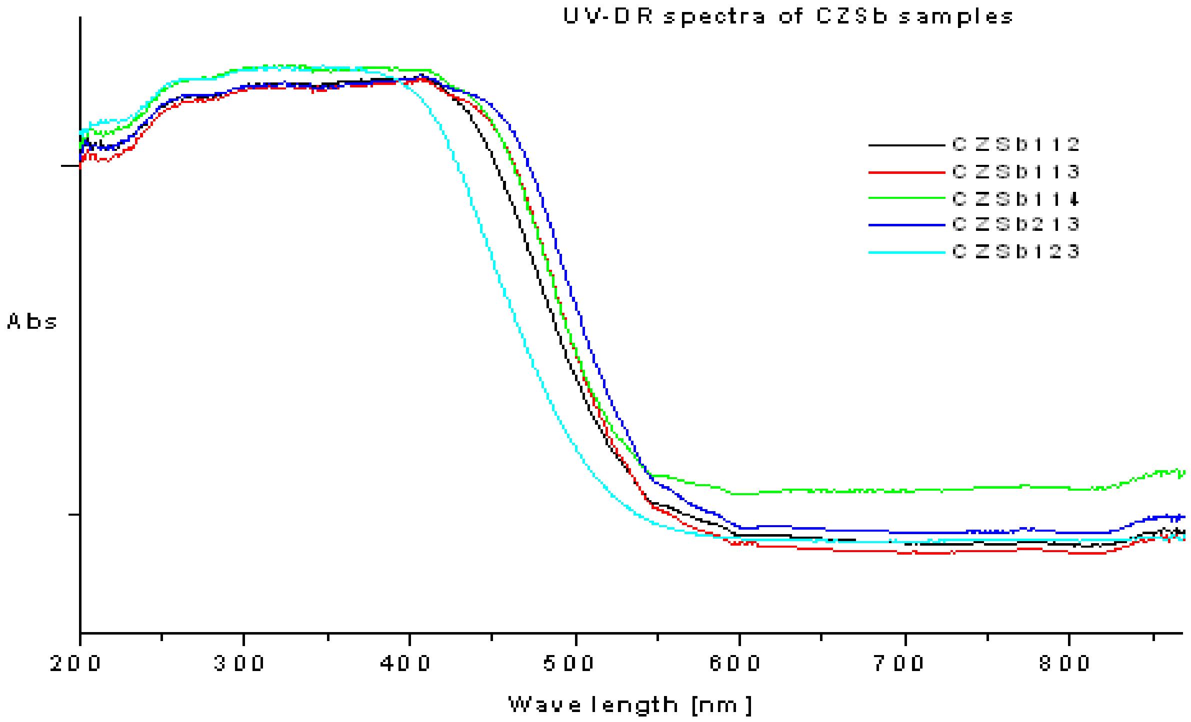


Figure-7
UV-Visible Diffuse Reflectance spectra of samples

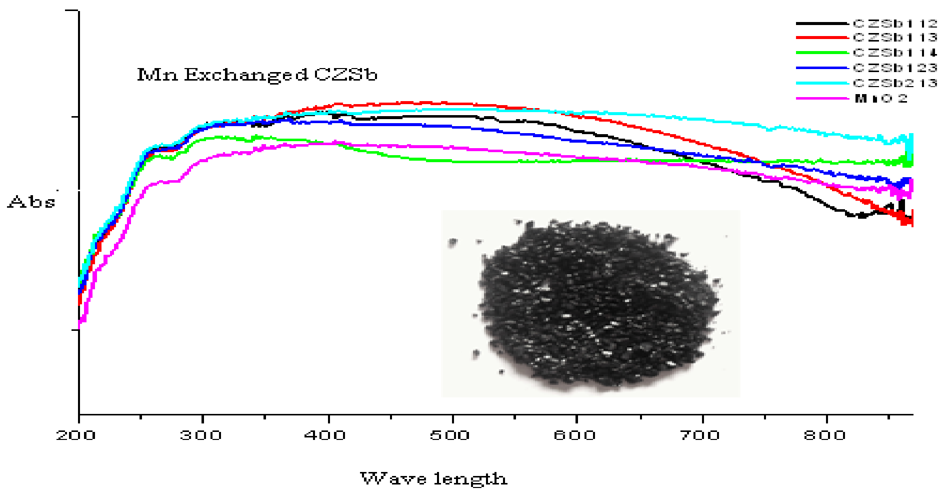


Figure-8
Mn exchanged samples

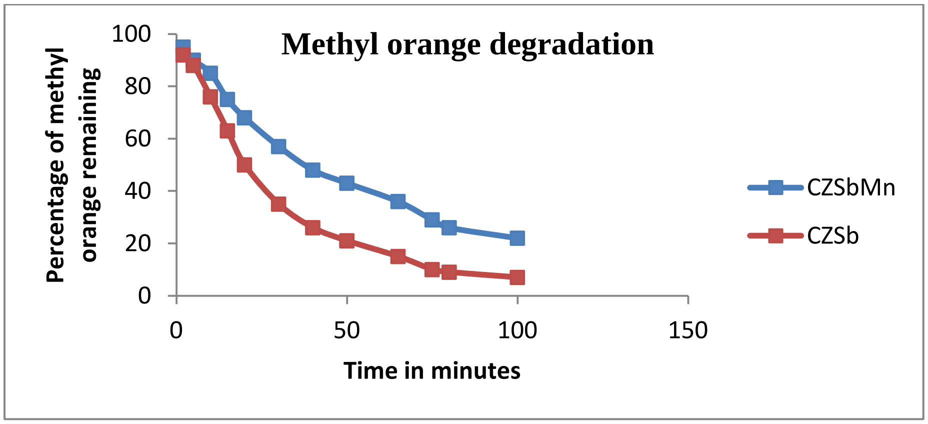


Figure-9
Methyl orange degradation

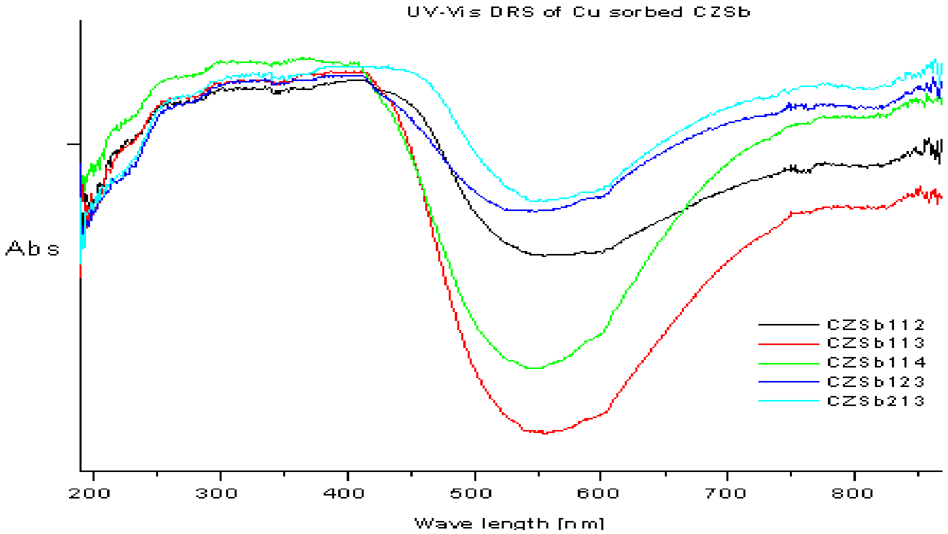


Figure-10
UV- Visible Diffuse Reflectance Spectra of Cu sorbed CZSb

Since UV DRS measurement can be a useful characteristic technique for investigating the interaction between transition metal cations under a given set of conditions and may give good informations regarding electronic states we can infer that there is no electronic interaction between the exchanged Cu ions.and the cations in the exchanger. The band energy is found decreased with increase in sorption of Cu ions. Further studies have to be carried out on this and its applications. The difference in absorbance value at 545nm (reflection maximum) and on the higher wavelength region are in the order 114>113>213>123>112 which is the intensity of the observed color of samples and also the order of distribution coefficients.

Conclusion

UV visible Diffuse Reflectance studies help us to study the interactions of various cations with the cations of the exchanger and its catalytic activity. The exchanger synthesized can be used as an environment friendly solid indicator for the detection of trace amounts of Mn^{2+} ions in solution. The exchanger can be effectively used for the degradation of methyl orange dye. The rate of degradation can be controlled using the Mn ion selectivity of the exchanger. Since the exchanger shows very high selectivity for Pb^{2+} ions, it can be separated from various cat ions.

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