

Characterization and applications of a newly synthesized inorganic cation exchanger cerium(IV) antimonomolybdate

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ABSTRACT

A novel inorganic cation exchanger cerium(IV) antimonomolybdate was synthesized and characterized by XRD, FT-IR, TGA, SEM, EDS and UV-Vis DRS etc. Its thermal and chemical stabilities, pH titration curve, and distribution coefficients towards different metal ions etc were studied systematically. The distribution studies revealed that the material is highly selective for Ca^{2+} , Pb^{2+} and Mn^{2+} metal ions. UV-Vis DRS studies shows that the material exhibits narrowed band gap energy. The applications of the material were explored by the quantitative separation of calcium from other metal ions, studying its catalytic activity towards hazardous organic dyes and antimicrobial activity of the material towards *E - coli* and *staphylococcus aureus*. The results ensure that the material face promising applications in various fields by combining its ion exchange properties, catalytic activity and antimicrobial activity.

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KEYWORDS

Inorganic cation exchanger;
pH titration curve;
Distribution coefficients;
Catalytic activity; Antimicrobial activity etc.

INTRODUCTION

The synthesis of novel inorganic cation exchange materials having the potential of removal and recovery of heavy metal ions from waste water has become one of the attractive areas of inorganic and material chemistry these days. Among these exchangers, insoluble double salts of tetravalent metals are preferred due to their excellent chemical resistivity and thermal stability^[1-5]. In recent time, a large number of cerium (IV) based ion exchangers have been prepared and their applications in various fields have been studied by many researchers. Cerium contain-

ing compounds are broadly used as efficient oxidation systems due to their special properties such as redox, oxygen release and storage abilities^[6, 7]. Cerium based ion exchangers are reported having enhanced applications like decolourisation of water by adsorption or degradation of organic dyes^[8, 9].

The present paper focuses on the physiochemical and spectroscopic characterization, ion exchange properties and applications of the synthesized material, cerium (IV) antimonomolybdate. The competence of the material has been explored by the quantitative binary separation of Ca^{2+} from Bi^{3+} , Co^{2+} , Mg^{2+} , Hg^{2+} and Cd^{2+} metal ions. The catalytic ability

of the material was studied by the degradation of methylene blue dye in aqueous solution in presence of CeSbMo. In addition to this, antimicrobial activity of the material towards *E – Coli* and *staphylococcus aureus* also extend the applications of the novel material in different fields.

EXPERIMENTAL

Materials

Ammonium ceric(IV) nitrate (E.Merck), sodium molybdate (E.Merck) and potassium antimonate(Loba Chemie, India) were used for the synthesis of the exchanger. Methylene blue dye solutions were prepared by dissolving the dye in deionised water. All other reagents and chemicals used were of analytical grade.

Instrumentation

ELICO LI613 pH meter was used for pH measurements and an electric thermostat oven was used for heating the sample at various temperatures. UV-Visible spectrophotometer model JASCO V660 was used for spectrophotometric measurements. FTIR spectrometer model Thermo Nicolet Avtar370 for IR studies, X-ray diffractometer BrukerAXS 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 of the exchanger

Different samples were prepared by adding 0.05M Ammonium ceric(IV) nitrate solution to a mixture of 0.05M sodium molybdate solution and

0.05M potassium pyroantimonate solution, in different volume ratios with intermittent shaking of the mixture and keeping the pH at 1.0 as given in TABLE 1. It was then filtered, washed with deionized water and dried. The exchanger was then converted in to the H⁺ form by treating with 1M nitric acid 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 obtain particles of 60-100 mesh.

Ion exchange capacity

The IEC of the material was determined by the column process; 1.0 g of the exchanger (H⁺ form) was packed in a glass column of 1.1cm diameter. The H⁺ ions were eluted by adding 100ml of 1M sodium chloride solution. The effluent was collected and titrated against standard sodium hydroxide solution. The exchange capacity in meq/g was calculated using the formula:

$$IEC = \frac{av}{w}$$

Where 'a' is the molarity, 'v' is the volume of alkali used during titration and 'w' is the weight of the exchanger taken.

pH titration

Topp and Pepper method^[10] was used for pH titration using NaOH/NaCl, KOH/KCl systems. 0.5g of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. After equilibrium the pH of each solution was measured and plotted against milli equivalents of OH⁻ ions.

Chemical stability

The chemical stability of the exchanger was as-

TABLE 1 : Conditions of synthesis and properties of different samples of CeSbMo

Sample	Molar conc.(M)			Volume mixing ratio	pH	Appearance	IEC(meq/g)
	Ce ⁴⁺	Sb(OH) ₆ ⁻	MoO ₄ ²⁻				
CeSbMo1	0.05	0.05	0.05	1:1:1	1	Orange glassy solids	0.92
CeSbMo2	0.05	0.05	0.05	1:2:1	1	Orange glassy solids	1.70
CeSbMo3	0.05	0.05	0.05	1:1:2	1	Orange glassy solids	0.94
CeSbMo4	0.05	0.05	0.05	1:3:1	1	yellow glassy solids	1.41
CeSbMo5	0.05	0.05	0.05	1:3:2	1	Orange glassy solids	0.78
CeSbMo6	0.05	0.05	0.05	1:2:3	1	Orange glassy solids	0.89

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sessed in mineral acid like HCl, HNO₃, and H₂SO₄, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this 500mg of the exchanger was kept separately in 50ml of different solvents at room temperature for 24 hours. The change in colour and weight were noted.

Effect of temperature

The effect of temperature on ion exchange capacity was studied by heating several 1g sample of the exchanger at different temperatures for three hours in an air oven and Na⁺ ion exchange capacity in meq g⁻¹ was determined by the column method after cooling them to room temperature.

Distribution studies (K_d)

Distribution studies were carried out for various metal ions in demineralised water by batch process. In this process 100mg of the dry exchanger in H⁺ form were equilibrated with 20ml of different metal ion solutions and kept for 24 hours at room temperature. The determination before and after equilibrium were carried out volumetrically using EDTA as the titrant. The K_d values obtained in TABLE 4, were obtained by 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 and 'W' is the weight of the exchanger.

Binary separations

Binary metal ions were separated quantitatively on the column of ion exchange material. This was studied by knowing the effect of electrolyte concentration on distribution coefficients and it was considered by equilibrating known amount of exchanger with metal ion solution in electrolytes of varying concentrations (0.1M, 0.01M, 0.001M NH₄NO₃ and HNO₃).

The column (30cmx 0.69cm internal diameter) on which the separations were to be carried out was filled uniformly with the exchanger (5g). First of all distilled water was added to pack the granules so that no air bubbles get stuck. Then the mixture of the

metal ion solutions of concentration about 0.005M (10 ml) was slowly added. The process was repeated for maximum sorption. The exchanged metal ions were eluted using suitable eluent. The rate of flow in all separations was 0.2 ml per minute. The concentration of metal ion in the solution was determined by collecting known volume of effluent at regular intervals.

Degradation studies

The degradation of methylene blue (MB) was studied in the presence of CeSbMo cation exchanger. 30ppm solution of MB dye was prepared in deionised water and was diluted as and when required. The catalytic degradation was observed upon addition of 0.30 g of each material to the dye solution at room temperature. To determine the percentage of dye degradation, the samples were collected at regular intervals and centrifuged to remove the fine particles. The sample absorbance at λ_{max} = 663 nm was measured using UV-Vis DRS. Degradation efficiency was determined using Beers law by knowing absorbance of initial dye solutions (A₀) and after a specific time (A_t).

$$\text{Degradation} = [1 - (C/C_0)] = [1 - (A/A_0)]$$

Antimicrobial studies

The antimicrobial effect of CeSbMo was determined for two bacterial strains such as *E - coli* and *Staphylococcus aureus* by Agar- well diffusion method. For this Muller Hinton Agar Medium, Nutrient broth and Gentamycin were prepared as mentioned below.

Muller hinton agar medium (1 L)

The medium was prepared by dissolving 33.9 g of the commercially available Muller Hinton Agar Medium (HiMedia) in 1000ml of distilled water. The dissolved medium was autoclaved at 15 lbs pressure at 121°C for 15 minutes. The autoclaved medium was mixed well and poured onto 100mm petriplates (25-30ml/plate) while still molten.

Nutrient broth (1L)

One litre of nutrient broth was prepared by dissolving 13 g of commercially available nutrient medium (HiMedia) in 1000ml distilled water and boiled

to dissolve the medium completely. The medium was dispensed as desired and sterilized by autoclaving at 15 lbs pressure (121°C) for 15 minutes.

Gentamycin

(standard antibacterial agent, concentration: 20mg / ml)

Petriplates containing 20ml Muller Hinton medium were seeded with 24hr culture of bacterial strains such as E coli and Staphylococcus aureus, Wells of approximately 10mm was bored using a well cutter and 25 μ l, 50 μ l and 100 μ l of sample was added to the well from a stock concentration of 0.1g/1ml. The plates were then incubated at 37°C for 24 hours. The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the well^[11]. Gentamycin was used as a positive control.

RESULTS AND DISCUSSIONS

Synthesis and characterization of exchanger

Different samples of exchanger were prepared by mixing various volume ratios of reagents. The exchanger, CeSbMo2 obtained as orange transparent solid having maximum ion exchange capacity 1.70 meq/g was selected for detailed study TABLE. 1. The exchanger could be regenerated thrice without any appreciable loss in ion exchange capacity.

Chemical composition from EDS Figure 1 revealed the cerium: antimony: molybdenum ratio of 1:1.5:1. It was found to be stable in water, acetic

acid, 1M HNO₃, 1M HCl and 1M H₂SO₄, 0.1M KOH and 0.1M NaOH.

Thermal analysis Figure 2 shows a sharp weight loss about 21% in the temperature range 50 – 180°C, attributed to the loss of moisture and hydrated water. A gradual weight loss observed up to 480°C is attributed to condensation of structural hydroxyl groups. Above this temperature lack of sudden change in weight indicates the stability of the compound. The total weight change up to 600°C is 28%.

FTIR spectra of CeSbMo Figure 3 shows a broad band in the region ~3425cm⁻¹ which is attributed to symmetric and asymmetric -OH stretching and a weak band in the region ~2360 cm⁻¹ is due to deformation vibration of the coordinated water molecule. A band at ~1625 cm⁻¹ is attributed to H-O-H bending and band in the region ~1383 cm⁻¹ is attributed to the presence of structural hydroxyl protons in CeSbMo. Bands at ~ 1041, ~ 927 and ~ 598cm⁻¹ show the presence of Ce-O, Mo-O and Sb-O bonds^[12, 13]. Based on chemical composition, TGA data and IR studies the tentative formula suggested for the material is [(CeO₂). (HSb(OH)₆)_{1.5}. (H₂MoO₄)]. 10H₂O.

XRD Figure 4 studies reveal that there was no definite angle of diffraction line to tell about the crystallinity. Hence, the spectrum indicates their amorphous nature. SEM analysis Figure 5 shows agglomeration of particles with granular nature and irregular size.

The UV-Vis DRS of CeSbMo was taken in the range of 200 – 800nm at room temperature and shown

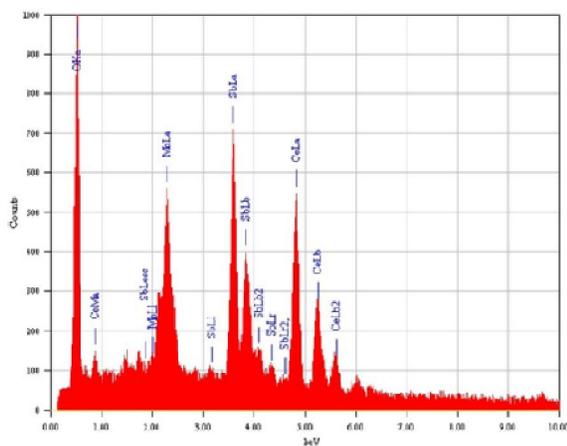


Figure 1 : EDS of CeSbMo

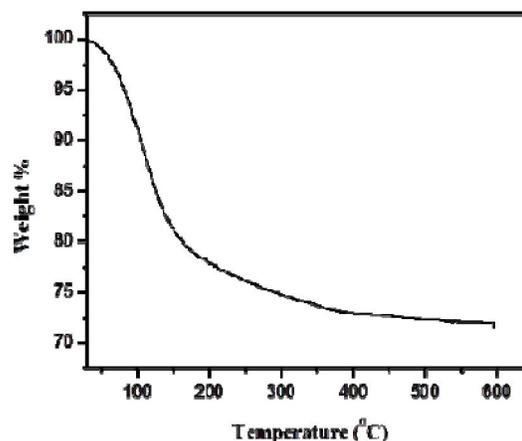


Figure 2: Thermal analysis diagrams of CeSbMo

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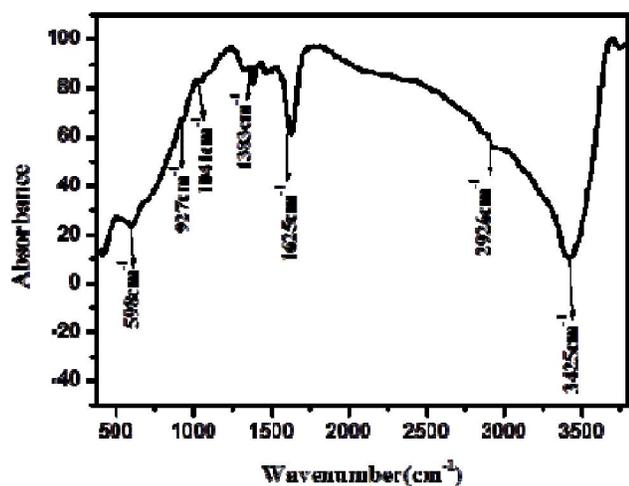


Figure 3 : FTIR spectrum of CeSbMo

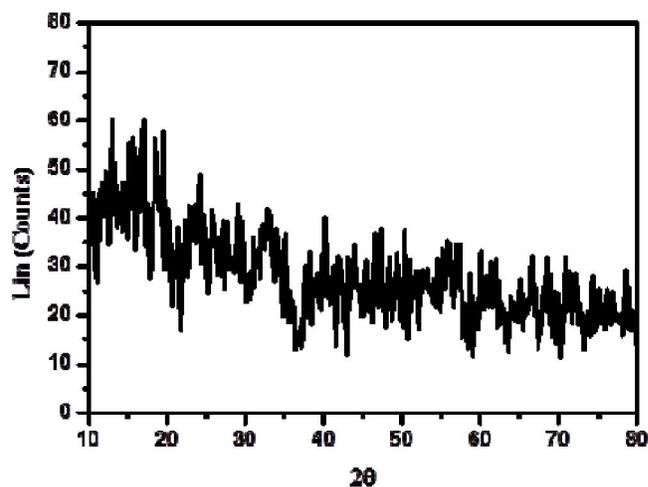


Figure 4 : XRD pattern of CeSbMo

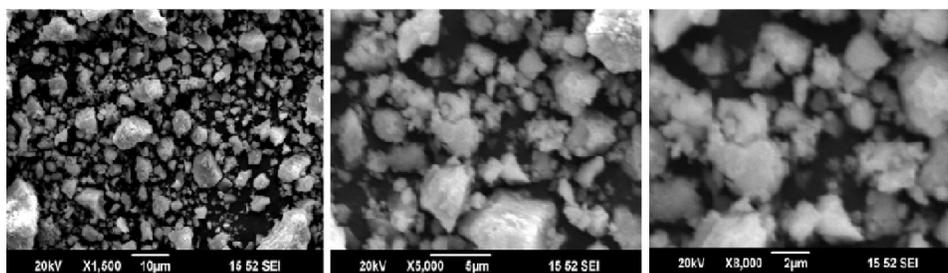


Figure 5 : SEM of CeSbMo

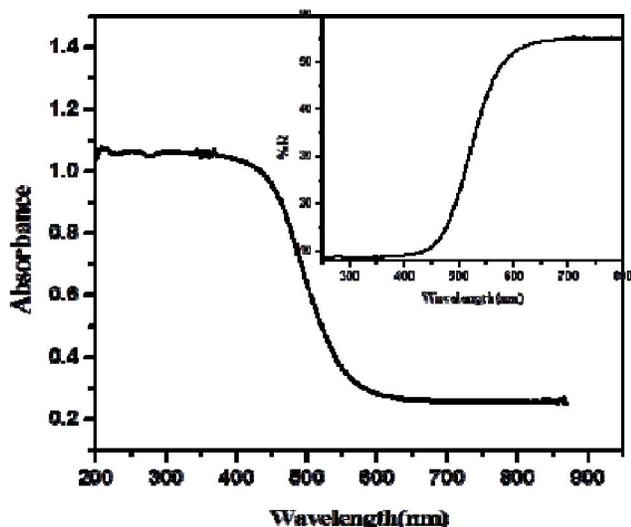


Figure 6 : UV/Vis DR spectrum of CeSbM

in Figure 6. This showed that the UV-Vis absorption edge lies in the visible range. A number of absorption bands are observed in the UV region between 200 and 380 nm. The bands around wavelength 210 nm shows $f \rightarrow d$ transitions of Ce^{3+} and the band at about 250 is assigned to $Ce^{3+} \leftarrow O^{2-}$. 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

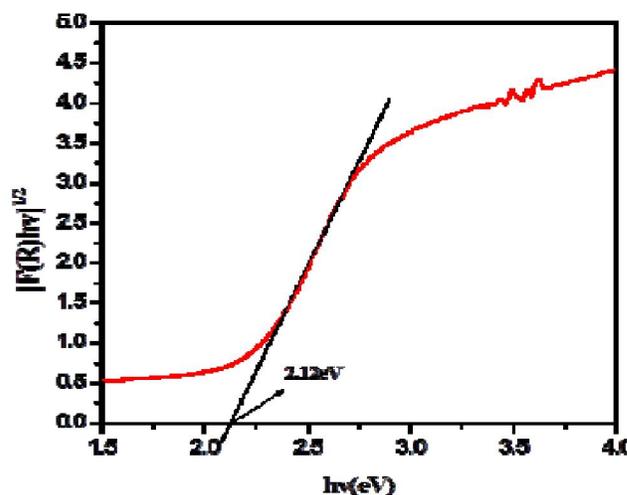


Figure 7 : K-M function Vs eV for CeSbMo

in the UV-Vis DR spectra infers the presence of oxygen vacancy defects which affect the catalytic activity of the ceria-based solid solutions. The band around 360 nm may be due to inter band transition in CeO_2 ^[14, 15].

The band gap energy, E_g of the sample was calculated by Kubelka-Munk function^[16, 17] (K-M function) $F(R)$, which is related to the diffuse reflec-

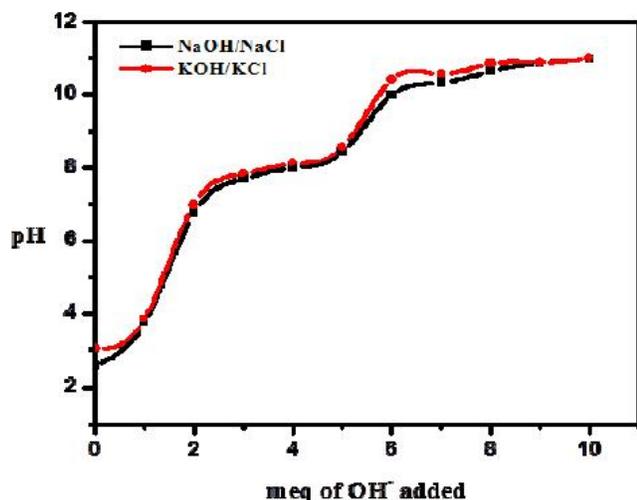


Figure 8 : pH titration curve of CeSbMo

tance of the sample according to the following equation

$$F(R) = \frac{(1-R)^2}{2R}$$

Where 'R' is the reflectance value of the sample. The band gap absorption was obtained by plotting $[F(R)hv]^{1/2}$ against photon energy hv (eV) as shown in Figure 7. The resulting plot has a distinct linear regime which denotes the onset of absorption. Thus, extrapolating this linear region to the abscissa yields the energy of the optical band gap (E_g) of the material. By this method the assignment of band gap can be made with certainty. The band gap energy of CeSbMo was found to be about 2.12 eV(585nm) which is seem to be lower than the band gap ener-

gies of some reported ceria molecules^[17,18]. The band gap narrowing may be due to the presence of more defects (Ce^{3+} and oxygen vacancy) which might be helpful in improving the defect related properties^[18]. This recognition can be applied to extend the application of this ion exchange material in various fields other than heavy metal ion separation.

The pH titration curve Figure 8 shows that the ion exchanger releases H^+ ions easily on addition of NaCl and KCl solutions to the system in neutral medium. As the volume of NaOH and KOH added to the system is increased, more OH^- ions are consumed suggesting in the increase of the rate of ion exchange in basic medium due to the removal of H^+ ions from the external solution. Titration curve shows bifunctional nature of the material. The I.E.C. calculated from the titration curve found to be 1.53 meqg^{-1} . The value is close to the value obtained by column operations.

The effect of charge and size of the exchanging ion on exchange capacity of the material was studied for alkali and alkaline earth metals (TABLE 2) and from the result it can be concluded that the affinity sequence for monovalent ions is $K^+ > Na^+ > Li^+$ and for bivalent ions is $Ba^{2+} < Ca^{2+} > Mg^{2+}$. Usually Ion-exchange capacity decreases with increase in the hydrated radii. However in the case of alkaline earth metals the order is not followed. Mg^{2+}

TABLE 2 : Effect of hydrated ionic radii and charge on IEC

Metal ion	Hydrated ionic radii (\AA°)	IEC meq/g
Li^+	3.40	1.47
Na^+	2.76	1.70
K^+	2.32	1.81
Mg^{2+}	7.00	1.74
Ca^{2+}	6.30	1.79
Ba^{2+}	5.90	1.71

TABLE 3 : Effect of temperature on IEC

Temperature $^{\circ}C$	Duration (hrs)	Na^+ IEC
50	3	1.70
100	3	1.68
200	3	1.07
300	3	0.91
400	3	0.76
500	3	0.65
600	3	0.49

TABLE 4 : Distribution coefficients in water and other electrolytes

Cations	K_d						
	DMW	HNO ₃			NH ₄ NO ₃		
		0.001M	0.01M	0.1M	0.001M	0.01M	0.1M
Al ³⁺	NS	NS	NS	NS	NS	NS	NS
Bi ³⁺	7.08	NS	NS	NS	NS	NS	NS
Ca ²⁺	517.24	234.33	99.89	21.02	248.78	106.89	38.45
Cd ²⁺	37.68	6.43	NS	NS	10.04	NS	NS
Co ²⁺	26.49	NS	NS	NS	NS	NS	NS
Cu ²⁺	86.16	38.07	11.23	NS	43.84	15.64	NS
Hg ²⁺	31.71	NS	NS	NS	NS	NS	NS
Mg ²⁺	20.58	NS	NS	NS	NS	NS	NS
Mn ²⁺	166.47	74.53	28.93	6.34	89.76	37.54	10.55
Ni ²⁺	NS	NS	NS	NS	NS	NS	NS
Pb ²⁺	304.53	201.65	99.87	28.59	210.95	104.37	35.65
Th ⁴⁺	165.43	93.42	38.65	NS	97.84	40.04	2.34
Zn ²⁺	NS	NS	NS	NS	NS	NS	NS

NS: no sorption

and Ba²⁺ ions were found to exchange very slowly on CeSbMo. This is attributed to very high heat of hydration of Mg²⁺ and large size of Ba²⁺ ions compared to Ca²⁺ ion. The rate of exchange may also depend up on both the size of the cation and its heat of hydration^[2].

Studies on the effect of temperature on ion exchange capacity showed that the sample retained 29% ion exchange capacity for Na⁺ even on heating up to 600°C. The ion exchange capacity decreases with increase of temperature TABLE 3.

DISTRIBUTION STUDIES AND BINARY SEPARATIONS

The distribution studies indicate that the material is highly selective for calcium ion (TABLE 4). The decreasing order of K_d values for various metal ions in demineralised water is given as follows: Ca²⁺ > Pb²⁺ > Mn²⁺ > Th⁴⁺ > Cu²⁺ > Cd²⁺ > Hg²⁺ > Co²⁺ > Mg²⁺ > Bi³⁺ > Al³⁺ ≈ Zn²⁺ ≈ Ni²⁺.

The effect of electrolyte concentrations on distribution coefficients showed that the value decreases with increase in electrolyte concentrations TABLE 4.

On the basis of differences in K_d values, some quantitative separations of analytically important metal ions were performed on the column of CeSbMo

by using suitable eluents selected after studying the electrolyte effect on distribution coefficients of metal ions. In binary separations the ion exchange material separates calcium from bismuth, mercury, magnesium, cadmium and cobalt metal ions.

In all cases the recovery ranged from 97% to about 100% with a variation of 2% for repetitive determinations. Moreover CeSbMo removed 97.87% Mg²⁺ and 99.09% Ca²⁺ from their binary mixtures. The results promise that the ion exchanger can be effectively used for the separation of hardness causing metal ions from water.

Degradation studies on methylene blue

Earlier we reported that some cerium containing inorganic ion exchangers exhibit degradation efficiency towards various harmful organic dyes in water^[19, 20]. This material also shows similar promising application and here we considered degradation of methylene blue dye on CeSbMo catalyst. The material show very good visible result with removal of blue colouration of dye solution and gave about 99% degradation at pH 6.0 after 3 hours Figure 9a. Original peaks at 663nm for MB dye get departed and no new peaks were observed after the catalytic degradation. The UV-Vis Diffuse Reflectance spectrum of each samples of CeSbMo collected from MB dye solutions after equilibrium shows close agree-

TABLE 5 : Binary separations of metal ions on CeSbMo

Separations achieved	$\alpha = K_{d1}/K_{d2}$	Eluent	Met ion (mg)		Efficiency (%)
			Loaded	Eluted	
Bi ³⁺ - Ca ²⁺	73.06	0.01M NH ₄ NO ₃ 1M HNO ₃ +0.1M NH ₄ NO ₃	5.20	5.11	98.27
			1.10	1.08	98.18
Mg ²⁺ - Ca ²⁺	25.13	0.01M NH ₄ NO ₃ 0.5M HNO ₃ +0.1M NH ₄ NO ₃	1.41	1.38	97.87
			1.10	1.09	99.09
Co ²⁺ - Ca ²⁺	19.53	0.01M NH ₄ NO ₃ 1M HNO ₃ +0.1M NH ₄ NO ₃	1.52	1.49	98.02
			1.10	1.07	97.27
Hg ²⁺ - Ca ²⁺	16.31	0.01M NH ₄ NO ₃ 0.5M HNO ₃ +0.1M NH ₄ NO ₃	4.94	4.91	99.39
			1.10	1.08	98.18
Cd ²⁺ - Ca ²⁺	13.72	0.01M NH ₄ NO ₃ 1M HNO ₃ +0.1M NH ₄ NO ₃	2.81	2.74	97.51
			1.10	1.09	99.09

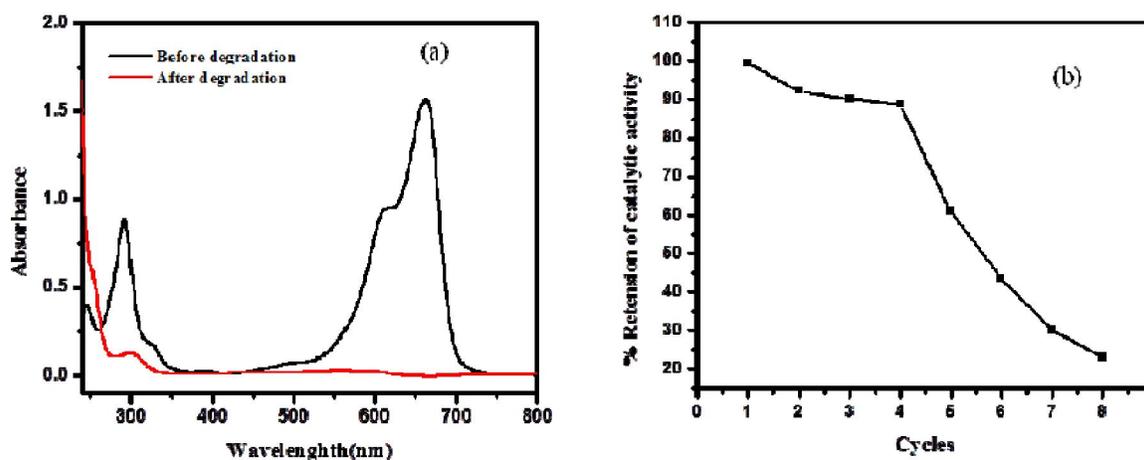


Figure 9 : (a) UV/Vis DRS spectra of MB during degradation (b) Recycling power of catalyst



Staphylococcus



E - Coli

Figure 10 : Comparison of the inhibition zone test

ment with the spectrum of each pure sample. This indicates the absence of adsorbed dye molecules on the surface of CeSbMo. These results point out the strong catalytic ability of the material come about

by the oxidizing power of heteropoly acid units (antimonomolybdate) in the material and electron exchange character of Ce metal ions.

It is easy to separate the catalyst for recycling

TABLE 6 : Zone of inhibition test results

Sample	Volume of sample(μ l)	Zone of inhibition	
		<i>Staphylococcus</i>	<i>E - coli</i>
Gentamycin		3.5	2.8
CeSbMo	25	Nil	Nil
	50	1.4	Nil
	100	1.8	1.1

uses after the reaction is completed, and significant dye conversions are achieved in the fourth runs Figure 9b suggesting that the catalytic activity of CeSbMo is stable under room temperature.

Antimicrobial activity

The material was screened for the antibacterial against two bacterial strains *E - coli* and *Staphylococcus aureus* by Agar – well diffusion method. The antimicrobials present in the plant extract are allowed to diffuse out into the medium and interact in a plate freshly seeded with the test organisms. The resulting zones of inhibition will be uniformly circular as there will be a confluent lawn of growth. The diameter of zone of inhibition can be measured in centimeters. Area of zone of inhibition is used as a criterion to ascertain the antimicrobial activity. Figure 10 illustrates, the microbial susceptibility assays for CeSbMo materials (25 μ l, 50 μ l & 100 μ l). The material shows significant antimicrobial activity towards *staphylococcus aureus* and 100 μ l of sample shows significant zone of inhibition towards *E - Coli* strains. Obtained results are summarised in TABLE 6.

CONCLUSION

CeSbMo exhibits good ion exchange properties, thermal stability and chemical resistivity. Analytical applications of the material were explored by the quantitative and efficient separation of Ca^{2+} ions from Bi^{3+} , Mg^{2+} , Hg^{2+} , Co^{2+} and Cd^{2+} ions. Moreover, CeSbMo shows catalytic activity towards degradation of hazardous organic dyes and antimicrobial activity towards *E - Coli* and *Staphylococcus aureus*. The results ensure that the material face promising applications in various fields by combining its ion exchange properties, catalytic activity and

antimicrobial activity.

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