

## Utility of Cerium(IV)Phosphomolybdate as a cation exchanger and dye adsorbent

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**Abstract**—Cerium(IV)Phosphomolybdate, a mixed material of the class of tetravalent metal acid salt was prepared and characterized by elemental analysis(ICP-AES), FTIR, TGA/DTA and XRD in addition to chemical resistivity and ion exchange properties. The protons of the hydroxyl groups were found to be the active sites. Sodium exchange capacity was found to be high comparable to organic resins. The effect of heat on ion exchange capacity was also studied for the exchanger. The sorption behaviour of cationic dyes like methyl orange and methylene blue towards the material has been studied.

**Key words:** cation exchanger, dye adsorption, ion exchange capacity, tetravalent metal acid salt

### I. INTRODUCTION

Ion exchange materials have found extensive application in analytical and industrial chemistry in view of their elegant characteristics such as insoluble matrix, stoichiometric exchange, good selectivity, specificity and application to column operations. They play a vital role in the treatment of environmental pollutants. Amongst the important inorganic ion exchangers, tetravalent metal acid (tma) salts are promising materials as they possess robust properties, good ion exchange characteristics, thermal stability and chemical resistivity. Thus the area of study of tma salts is evergreen, with newer materials being continuously investigated[1]. The interest in using inorganic ion exchangers with rare earths is due to the ability of these ions to increase the acid sites in the structure of the material and hence improve adsorption[2]. Among tma salts mixed materials containing a cation and two different anions show improved ion exchange properties and selectivity for particular metal ions compared to their single salt counter parts[3]. It was therefore thought of interest to study the ion exchange properties of a mixed material namely Cerium(IV)Phosphomolybdate (CePMo), a tma salt containing two anions and a cation. Nowadays, the preservation of water resources to prevent their pollution by toxic elements is one of the most important challenges. Dyes employed in several industrial fields such as textiles, paper and cosmetics, when discharged into water bodies cause serious problems because of their persistence and non-biodegradable characteristics[4]. Consequently, there is considerable need to treat these effluents prior to their discharge. Adsorption processes are usually used due to their economic, ecological and technological advantages. In the present study we report the utility of CePMo as a sorbent for dyes like methyl orange (MO) and methylene blue (MB).

### II. EXPERIMENTAL

Synthesis of CePMo : Equimolar solutions of ceric sulphate, ammonium hepta molybdate and disodium hydrogen phosphate were mixed in the volume ratio 1:1:2 with slow and continuous stirring at a pH~ 2. The gel thus obtained was kept overnight, filtered, washed with conductivity water till free of sulphate and chloride ions and dried at 400C. The dried material was brought to desired particle size (30-60 mesh) by grinding and sieving and finally converted to acid form by immersing in 1M HCl, the acid being replaced intermittently. It was then washed with conductivity water till free of adhering acid and chloride ions. The material thus obtained was dried at 400C and used for all studies.

Chemical stability : 500 mg of the exchanger was kept separately in 50ml of different solvents, viz, demineralised water(DMW), solutions of metal chlorides, different concentrations of HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, acetic acid, NaOH, KOH organic solvents like acetone and ethanol at room temperature for 24 hours. The change in colour and weight were noted.

Ion exchange capacity (iec) : The iec of the material was determined by column method[5]. The effect of heating on iec was studied by heating the exchanger at various temperature in the range of 100 - 600C for 2 h in a muffle furnace and then determining the iec as usual.

Adsorption of dyes : Aqueous solution of MO and MB( 20 ml, 3x10<sup>-5</sup> M ) were equilibrated separately with 500mg of CePMo for 24 h. The sample solutions were then filtered and centrifuged to remove the adsorbent prior to analysis. Absorbances were recorded before and after equilibration with a UV-Visible Perkin Elmer Spectrophotometer at the absorption maxima of the two dyes(MO(463nm) and MB(665nm)).

Instrumentation : X-Ray diffractograms were taken from Bruker D8 Advance diffractometer using Cu K $\alpha$  radiation. Thermogram was recorded with Perkin- Elmer Diamond Thermo Gravimetric Analyzer. Infrared spectrum were recorded with a Perkin Elmer Fourier Transform Spectrometer. Elemental analysis of the compound was carried out with Thermo Electron IRIS Interpid II XSP Duo, ICP-AES Spectrometer.

### III. RESULTS AND DISCUSSIONS

CePMo was obtained as bright yellow solid. Chemical stability studies showed that the material was stable in DMW, solutions of metal chlorides, acid media(7N HCl, 7N HNO<sub>3</sub>,

5M H<sub>2</sub>SO<sub>4</sub>, glacial acetic acid) and organic solvents as evidenced by no change in colour, form or weight of the sample. It was however unstable in bases like NaOH and KOH. The material changed to colourless in alkaline media due to hydrolysis of the exchanger at higher pH values. Elemental analysis by ICP-AES showed that the material contains 5.88%Ce, 3.99% P and 41.7% Mo. The X-ray diffractogram of CePMo (Fig.1) confirmed the presence of nanocrystallites. The Debye Scherrer formula has been used to calculate the crystallite size(D)[6]. The crystallite size was found to be 33nm. The crystal structure, interlayer spacing(d-spacing) and particle size of the calcined material obtained from their respective diffractogram are summarized in Table1. The TG of CePMo (Fig.2) shows a sharp weight loss in the temperature range 50-165°C, attributed to the loss of moisture and hydrated water. A gradual weight loss observed upto 400°C, is attributed to condensation of structural hydroxyl groups and a continuous weight loss in the temperature range 500-800°C is due to decomposition of the material to the corresponding oxide. DTA also shows endothermic peaks at various temperatures corresponding to these changes. Based on the

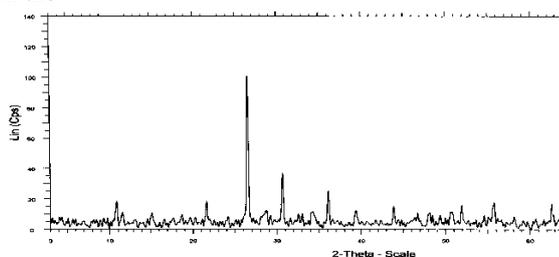


Fig.1 XRD of CePMo

elemental analysis by ICP-AES and TGA, CePMo has been formulated as CeO<sub>2</sub> . 3/2P<sub>2</sub>O<sub>5</sub> . 10MoO<sub>3</sub> . nH<sub>2</sub>O . The value of n was found to be 8.4 using Alberti and Torraca formula[7]. FTIR spectrum (Fig.3) of CePMo showed peaks in the region 3600-3200cm<sup>-1</sup> attributed to symmetric and asymmetric -OH stretches. A medium peak observed at 1620cm<sup>-1</sup> is attributed to the bending vibrations of water molecule. The peak around 1400cm<sup>-1</sup> is assigned to the deformation vibration of interstitial water. A sharp intense peak around 1064cm<sup>-1</sup> indicates the presence of phosphate anion. A sharp peak at 960cm<sup>-1</sup> is attributed to the presence of Ce-O-H group. The peak around 790cm<sup>-1</sup> is due to the presence of Mo-O-Ce linkage. A combination of peaks in the region 860-450cm<sup>-1</sup> are attributed to metal-oxygen vibrations. The Na<sup>+</sup> exchange capacity of the material was found to be 7.00 meqg<sup>-1</sup>. CePMo possesses high exchange capacity compared to their single salt counterparts, Cerium(IV)Phosphate (2.26meqg<sup>-1</sup>) and Cerium(IV)molybdate (5.08meqg<sup>-1</sup>).

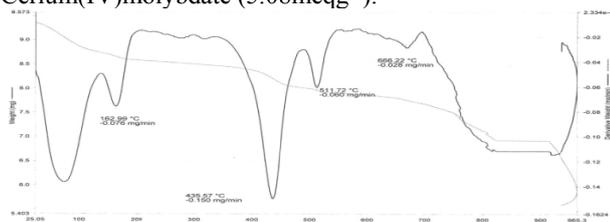


Fig.2 TGA/DTA of CePMo

The effect of calcination on iec was studied in the temperature range 100-600°C, at intervals of 100°C are also given in Table1. The analysis of the diffractograms showed that interlayer spacing remained almost the same for the material calcined at 100 and 200°C which indicated that absorbed water molecules are removed at these temperatures. An increase in iec value is observed which is attributed to the complete removal of adsorbed water thereby increasing the active exchanger content for same weight of the material taken for iec determination. The interlayer spacing showed a decrease on heating which is attributed to some structural changes that occur in the material. A drastic decrease in iec at 400°C is attributed to the condensation of structural hydroxyl groups. The formation of oxides are confirmed at higher temperatures as evidenced by the colour change to blue. Non-stoichiometric ceria samples are reported to be blue, related to Ce(IV) – Ce(III) transitions [8]. It is also evident from Table1 that, there is an increase in i.e.c for the material heated to 500°C which may be attributed to the decomposition of the material to their respective oxides. These oxides when hydrated behave as bronsted acids, thereby increasing the acid sites in the material. Therefore, the mixed material CePMo is a superior ion exchanger with high ion exchange capacity even at elevated temperatures. Such materials with high selectivity for Na<sup>+</sup> find application in electro-deionization which is a desalination method based on a combination of ion exchange resin and ion exchange membrane as reported by other authors [9].

TABLE1 ANALYSIS OF X-RAY DIFFRACTOGRAMS FOR CEPMO AND HEATED SAMPLES (C100 - C600)

Sample	Crystal structure	d-spacing (nm)	Crystallite size (nm)	Na <sup>+</sup> exchange capacity (meqg <sup>-1</sup> )	Colour
CePMo	Cubic	0.82	36	7.00	Yellow
C <sub>100</sub>	Cubic	0.79	28	8.20	Yellow
C <sub>200</sub>	Cubic	0.81	31	8.63	Yellow
C <sub>300</sub>	Cubic	0.65	43	7.11	Bluish yellow
C <sub>400</sub>	Cubic	0.69	36	1.47	Blue
C <sub>500</sub>	Polycrystallin	0.52	33	10.61	Bluish green
C <sub>600</sub>	Amorphous	-	-	10.86	Green

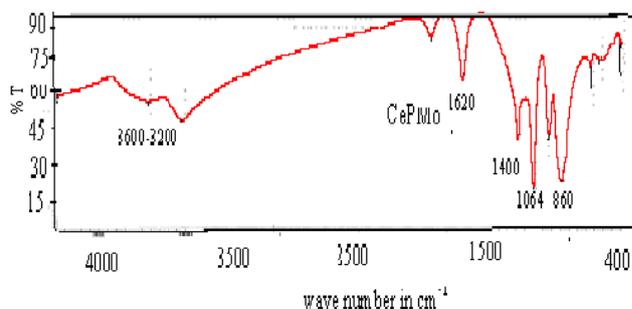


Fig. 3 FTIR spectrum of CePMo

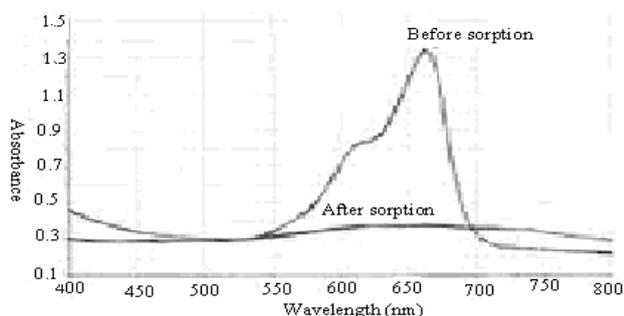


Fig. 5 UV-Visible absorption spectra for MB

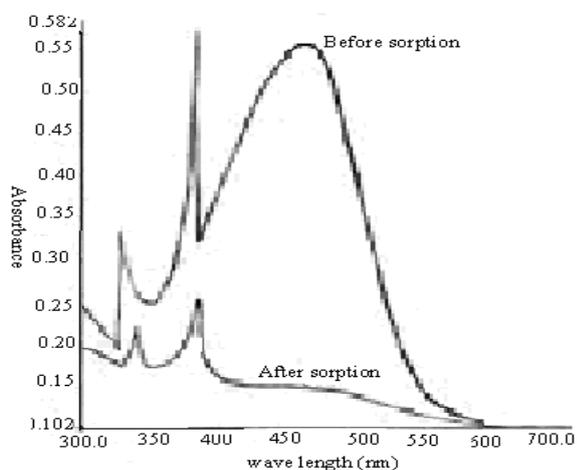


Fig. 4 UV-Visible absorption spectra for MO

UV-Visible absorption spectrum of MO and MB before and after equilibration are shown in Fig. 4 and 5 respectively. The absorption intensity of the peak at 463 nm for methyl orange showed a drastic decrease after equilibration with CePMo. A similar decrease is also observed in the absorption intensity of methylene blue at 663 nm. The decrease in intensity of absorption after equilibration, indicate that the dyes Mo and MB exhibit good sorption towards CePMo, which could be attributed to to both the cation exchange nature of the sorbent and cationic nature of the dyes. CePMo possess structural hydroxyl groups. Therefore the dyes could bond to the sorbent either by hydrogen bonds or weak van der Waals forces. The high adsorption for methylene blue could be due to the positive charge on the hetero atom [10]. Even small changes in the dye structure can significantly influence its adsorption capacity. The efficiency of CePMo towards removal of MO and MB from aqueous solution indicates its promising use in waste water containing dyes.

#### IV. CONCLUSION

Inorganic ion exchangers are usually appreciated for their chemical, thermal and radiation stability, but most of them

have low ion exchange values. Cerium(IV)Phosphomolybdate is a stable ion exchanger with very high ion exchange capacity comparable to organic resins. The material shows remarkable adsorption for cationic dyes like methylene blue and methyl orange. All these properties make it an ideal adsorbent for the treatment of industrial waste water containing dyes.

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