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Efficient Degradation of Dyes in Water by a Novel Inorganic Cation Exchanger Cerium(IV) arsenomolybdate

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Abstract

An advanced inorganic cation exchange material of the class of tetravalent metal acid salt, cerium(IV) arsenomolybdate has been synthesized by co-precipitation method. The chemical composition was determined from EDS and other physio-chemical analyses carried out are TGA, FTIR and X-ray diffraction studies. Its ion exchange capacity was found to be 2.19 meqg^{-1}*.The distribution coefficient(Kd) has been determined for transition metal ions (* Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} *and* Mn^{2+} *), heavy metal ions(* Cd^{2+}, $Hg^{2+,}$ Pb^{2+} *and* $Bi^{3+)}$ *and alkaline earth metals(* Mg^{2+} *and* Ca^{2+} *) using cerium(IV) arsenomolybdate. Distribution studies showed that the selectivity of the exchanger towards various metal ions was in the order* $Pb^{2+} > Co^{2+} > Cu^{2+} > Mn^{2+} > Bi^{3+} > Cd^{2+} > Mg^{2+} > Zn^{2+} > Ni^{2+} > Ca^{2+} > Hg^{2+}$*. The analytical importance of the material has been established by studying degradation of various dyes (methylene blue, methyl orange, congo red and crystal violet) in water using UV-Visible diffuse reflectance spectrophotometer. The remarkable change in intensity of absorption of aqueous solution of these dyes, before and after the treatment with the exchanger showed clearly that these dyes are significantly degradable by cerium(IV) arsenomolybdate. The efficiency of the exchanger towards the removal of methylene blue, methyl orange, congo red and crystal violet from aqueous solution indicates its promising use in waste water treatment for the removal of these dyes.*

Keywords*: Cation exchanger; Distribution coefficient; Dye degradation; Water treatment.*

1. INTRODUCTION

Ion exchangers have played a prominent role in the water processing and in the chemical industry. Synthetic inorganic ion exchangers have the benefit of high chemical, thermal and radiation stability (Amphlett 1964; Janardanan et al. 1990 & Mu.Naushad 2009).Inorganic ion exchangers of the class of tetravalent metal acid (tma) salts have focused as promising advanced material, due to their high thermal and chemical stability, resistance towards ionizing radiations as well as its important applications as ion exchangers in separation science (Varshney 1991; Clearfield 1982& Amphlett 1961).They play a vital role in the treatment of environmental pollutants.

Residual dyestuff, although only present in small amounts are sources of aesthetic pollution and eutrophication of water bodies and thereby have to be removed from waste water before it is discharged. Dyes employed in several industrial fields such as textiles, paper and cosmetics when discharged in to water bodies cause severe problems because of their persistence and non biodegradable characteristics

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(Barhon 2009). At the moment several biological, physical and chemical processes are used to minimize dye effluents. But considering the large quantities of benzene rings, naphthalene nuclei, amino groups and azo groups, which are very common in dye structure, it is very difficult to remove them efficiently and completely. More over with the rapid development of the textile industry in recent years more and more new types of dyes have been produced and that are more resistant to photolysis, oxidation and biodegradation.

In this paper we wish to report our findings using the novel cation exchanger cerium(IV) arsenomolybdate. The prepared cation exchanger was characterized and their analytical importance were studied for the degradation of different dyes like methylene blue (MB), methyl orange (MO), crystal violet (CV) and congo red (CR) in water.

2. EXPERIMENTAL METHODS

Ammonium ceric(IV), nitrate(E.Merck), sodium molybdate(E.Merck) and sodium arsenate(Loba Chemie,India) were used for the synthesis of the exchanger. All other reagent**s** 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. FT-IR 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 0.1M Ammonium ceric(IV) nitrate solution to a mixture of 0.05M sodium arsenate solution and 0.05M sodium molybdate solution, in different volume ratios with intermittent shaking of the mixture and keeping the p^H 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 (IEC)

The ion exchange capacity of the material was determined by the column method (Samuelson 1952). 1g 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 .

Chemical stability

The chemical stability of the exchanger was assessed in mineral acid like HCl, HNO$_3$, and H$_2$SO$_4$, 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.

pH titration

Topp and Pepper method (Topp 1949) was used for p^H 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 p^H of each solution was measured and plotted against milliequivalents of OH^- ions.

Distribution studies (Kd)

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 Kd values as summerised in table 2, were obtained by the formula

$$Kd = \frac{I-F}{F} \times \frac{V}{W}$$

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.

Degradation of dyes

Aqueous solution of MO, MB, CV and CR (20ml, 10ppm) were equilibrated separately with 200mg of CeAsMo for 24 hours at 30°C. The sample solutions were then filtered and centrifuged to remove the catalyst. Absorbance was recorded before and after equilibrium with a UV-Visible diffuse reflectance spectrophotometer. The removed ion exchangers from each of the dye solutions after equilibrium were collected and dried. Absorbance was recorded for these samples and compared with that of pure CeAsMo to endeavor the catalytic ability of the new exchanger for the degradation of these dyes.

3. RESULT AND DISCUSSION

Samples of cerium(IV) arsenomolybdate of various composition have been synthesized but CeAsMo5 obtained as bright yellow solid having maximum ion exchange capacity, 2.19meqg^{-1} was selected for detailed studies (table 1). The composition of CeAsMo5 was found as Ce: As: Mo:: 1.8:1:1.4.

Table 1. Synthesis and properties of various samples of exchanger

Sample	Volume ratio	P^H	Appearance (colour)	Ion exchange capacity for Na^+(meq/g)
CeAsMo1	1:1:1	1	Orange	0.95
CeAsMo2	1:1:2	1	Orange	1.64
CeAsMo3	1:2:1	1	Bright yellow	1.65
CeAsMo4	1:2:3	1	Bright yellow	1.71
CeAsMo5	1:3:2	1	Bright yellow	2.19
CeAsMo6	2:3:1	1	Orange	1.30

FTIR spectra (fig. 1) shows broad band in the region ~3341cm^{-1} attributed to symmetric and asymmetric –OH stretching, (Davis 1963; Nakamoto 1963) while band at ~1622cm^{-1} is due to H-O-H bending. A peak in the region 809cm^{-1} is attributed to metal oxygen vibrations (Miller et al. 1952; Socrates 1980). A band at 1310 cm^{-1} is due to the presence of ($AsO4)^{3-}$and the sharp intense peak around ~1384 cm^{-1} may be due to the presence of δ(AsOH).

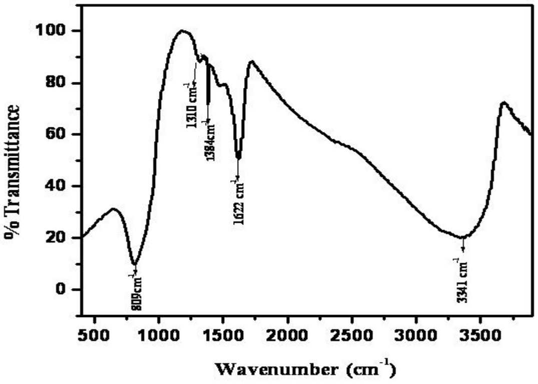

Fig 1. FTIR spectrum of CeAsMo.

The X-ray diffraction spectrum (fig.2) of cation exchanger cerium (IV) arsenomolybdate shows a number of peaks at different 2r values. The analysis of these signal peaks supports towards its semi crystalline nature (Suzuki 2002).

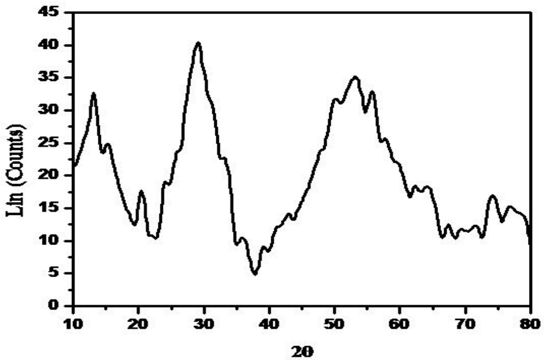

Fig. 2. XRD of CeAsMo

The TG of CeAsMo (fig 3) shows a sharp weight loss up to 170°C , attributed to the loss of moisture and hydrated water and the weight loss observed from 260-345°C due to condensation of exchangeable hydroxyl groups take place which is the usual behavior of inorganic ion exchangers (Qureshi et al. 1973; Rawat et al. 1975) and a continuous weight loss in the temperature range 465-800°C is due to decomposition of the material to the corresponding oxide.

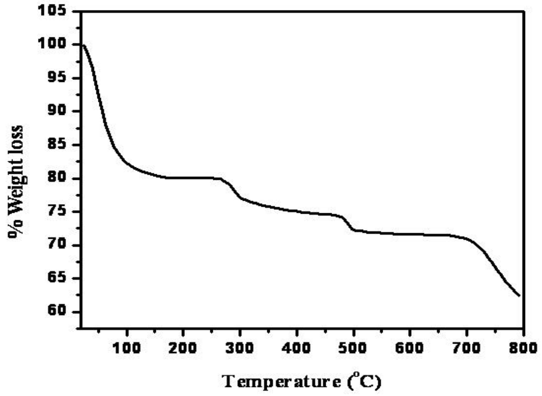

Fig. 3: TGA of CeAsMo

pH titration studies using NaCl/NaOH, KCl/KOH systems show nearly bifunctional behavior indicating two types of ionizing group . The exchange capacity obtained from the curve is in agreement with that obtained by the column method.

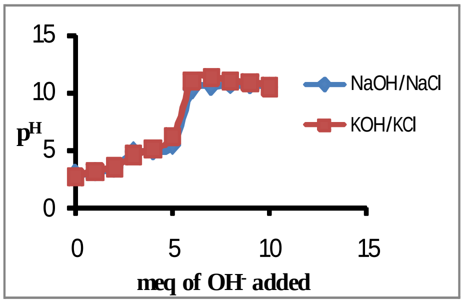

Fig.4: pH Titration curve of CeAsMo

It was observed that on heating at different temperatures for 1h, the ion exchange capacity of the dried sample material was changed as the temperature increased as shown in fig.5. Up to 300°C the material shows prominent ion exchange capacity.

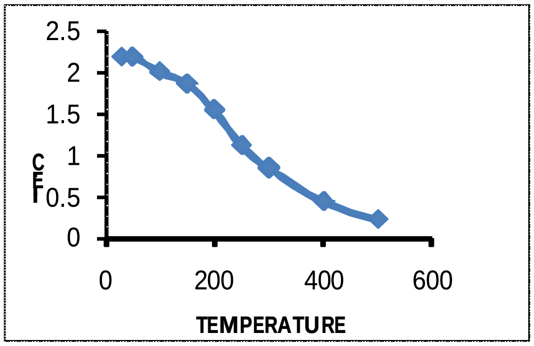

Fig.5: Temperature effect on I.E.C

The distribution studies of metal ions (table 2) show that the exchanger has very high affinity towards Pb^{2+} ions in comparison to other metal ions studied. The selectivity was found to be in the order $Pb^{2+} > Co^{2+} > Cu^{2+} > Mn^{2+} > Bi^{3+} > Cd^{2+} > Mg^{2+} > Zn^{2+} > Ni^{2+} > Ca^{2+} > Hg^{2+}$.

Table 2. Kd values of various metal ions in water.

Metal Ions	Kd
Pb^{2+}	523.08
Co^{2+}	432
Cd^{2+}	112.4
Bi^{3+}	124.7
Ni^{2+}	72.2
Hg^{2+}	NE
Cu^{2+}	168.5
Mn^{2+}	156.1
Mg^{2+}	87.2
Zn^{2+}	78

NE: negligible exchange.

3.1. UV-Visible DRS studies on catalytic activities of CeAsMo for dye degradation

The synthesized CeAsMo cation exchanger was used as the catalyst to study the degradation of MB, MO, CV, and CR in aqueous solution in our work . The spectral changes of the four dye solutions in the presence of CeAsMo catalyst (kept overnight in each dye solutions) were shown in fig.6. Figure illustrates that the original peaks (663nm-MB, 463nm-MO, 590nm-CV and 498nm-CR) for each dye gets disappeared and no new peaks were observed after the catalytic degradation. This implied that the dyes might be fully degraded.

The UV-Visible spectrum of each samples of CeAsMo collected from dye solutions after equilibrium shows close agreement with that of pure sample of CeAsMo (fig.7). It indicated that the ion exchanger play a role of catalyst. So we can conclude that these dyes are catalytically degradable by the newly synthesized cation exchanger CeAsMo. Slight deviations observed in the spectrum of CeAsMo samples from MB may be due to the presence of some strongly adsorbed dye particles on the surface of the exchanger.

(IE-for pure ion exchanger, IE-MB, IE-MO, IE-CV,& IE-CR are for retained exchangers from corresponding dye solutions after degradation.)

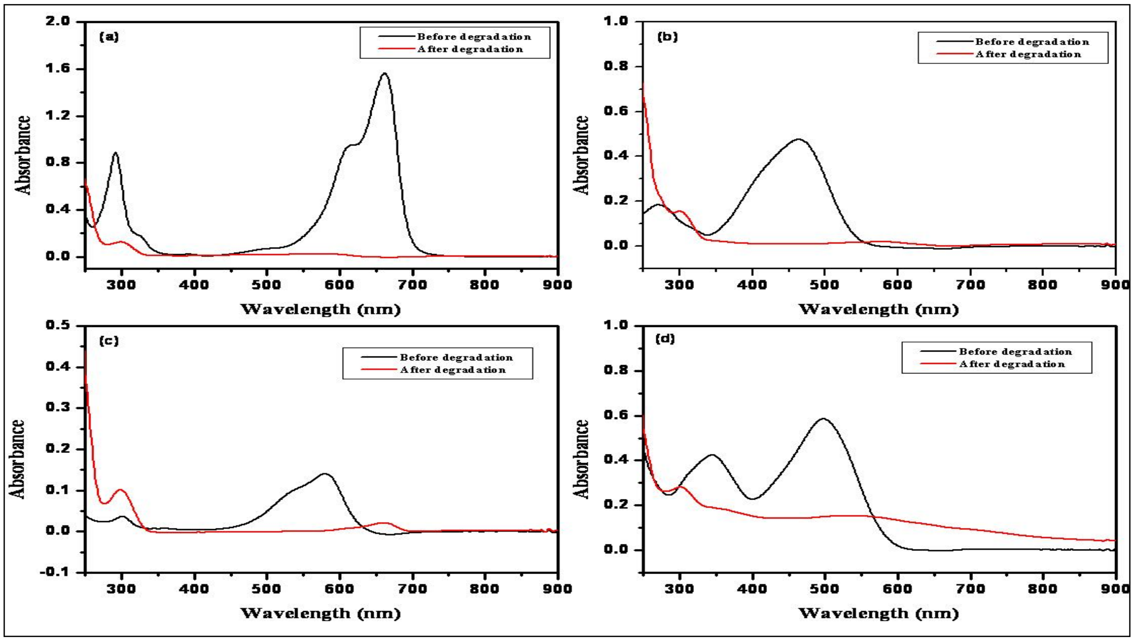

Fig. 6 UV-Visible DR spectrum of (a) MB, (b) MO, (c) CV and (d) CR

from corresponding dye solutions after degradation.)

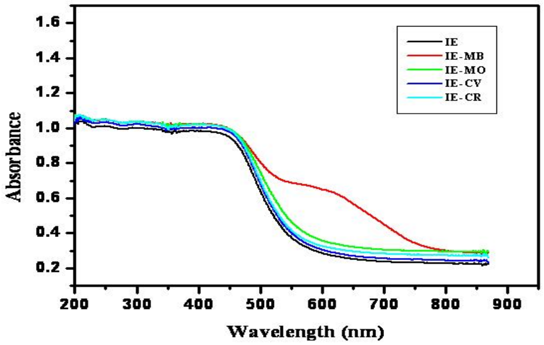

Fig. 7: UV-DRS Spectrum of solid exchangers.

The degradation efficiency of the exchanger towards various dye solutions are shown in fig.8. The dye degradation capability of the cation exchanger may be attributed to the electron exchange property of Ce (Imbihl et al. 1995; Ivanova 2009; Reuter et al. 2003; Trovarelli 2002) and the oxidizingcharacter of the exchanger (Preetha et al. 2012). The efficiency of the exchanger towards the removal of MB, MO, CV and CR from aqueous solution indicates its promising use in waste water treatment for the removal of these dyes**.**

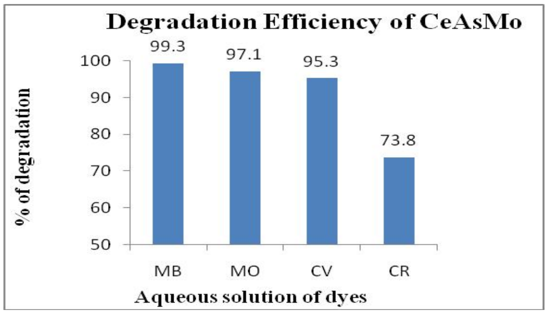

Fig. 8: Degradation percentage of various dye solutions using CeAsMo.

4. CONCLUSION

The inorganic cation exchanger CeAsMo posses' good ion exchange capacity, and is a stable ion exchanger. CeAsMo can be used as catalyst for the degradation of MB, MO, CV and CR in aqueous solutions. In addition the catalyst can be recycled thrice without any loss in its capacity and efficiency. All these properties make it an ideal catalyst for the treatment of industrial waste water containing dyes.

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