Cerium (IV) Arsenovanadate – A Reusable And Highly Efficient Ion Exchange Material For The Recovery of Cobalt, Lead And Manganese From Aqueous Solutions

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ABSTRACT

A new inorganic cation exchanger Cerium(IV) arsenovanadate (CeAsV) has been synthesized by co-precipitation method under different experimental conditions. Ion exchange material synthesized at pH 1.0 shows an ion exchange capacity 1.25 meq/g for Na^+ ions. Instrumental techniques like XRD, FT-IR, TGA, SEM, EDS and UV-Vis DRS were used to elaborate the structural aspects. Its thermal and chemical stabilities, pH titration curve, and distribution coefficients towards different metal ions were studied systematically. Distribution studies showed that the selectivity of the exchanger towards various metal ions was in the order $Co^{2+}> Pb^{2+} > Mn^{2+}>Cd^{2+}> Bi^{3+}> Cu^{2+}> Zn^{2+}> Mg^{2+}> Hg^{2+} > Ni^{2+}$. The differential selectivity of metal ions on CeAsV has been utilised for some important binary separations such as Co^{2+}-Hg^{2+}, Co^{2+}-Ni^{2+}, Co^{2+}-Mg^{2+} and Co^{2+}-Zn^{2+}. The analytical applications of new exchanger were explored by the recovery of Co^{2+}, Pb^{2+} and Mn^{2+} metal ions from synthetic wastewater on the column of CeAsV. Effects of pH on uptake of these metal ions on CeAsV also studied to regulate the settings for column operations.

Keywords: Ion exchange material, Ion exchange capacity, Distribution coefficients, Binary separations etc.

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INTRODUCTION

Here we report a novel, efficient, stable, and reusable inorganic cation exchanger for the separation and removal of toxic heavy metals from water. Heavy metals are the largest class of contaminants and also the most difficult to treat. Toxic metal compounds coming to the earth's surface contaminate surface and underground water in trace amounts. One of the important problems caused by this is the accumulation of toxic metals in food structures. The contaminated food can cause poisoning in humans and animals. It is, therefore, essential to remove heavy metals from wastewater before release due to the property of upsetting ecological quality and being unsafe to human health.

In recent years, inorganic cation exchangers gained great attention to remove heavy metals from water and wastewater. A selective elimination of target contaminants in the trace concentration range is exclusively

possible by means of ion exchangers [1 – 3]. Several effective inorganic ion exchangers are available nowadays for industrial scale applications. The inorganic ion exchangers based on three components have been found to show relative increased ion exchange capacity (IEC) and selectivity [4 – 5]. In the present study we prepared a three component inorganic cation exchanger, Cerium(IV) arsenovanadate for the separations of heavy metals from binary systems and removal and recovery of toxic metal ions from polluted water.

MATERIALS AND METHODS

Reagents and Chemicals*:* Ammonium ceric nitrate (E.Merck), Sodium vanadate (E.Merk) and sodium arsenate (Loba Chemie, India) were used for the synthesis of the exchanger. All other reagents and chemicals used were of analytical grade.

Instrumentation*:* ELICO L1613 pH meter was used for pH measurements and an electric thermostat oven was used for heating the sample at various temperatures. UV-Vis DR 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 ion exchange material*:* Different samples were precipitated by adding a mixture of 0.05M sodium sodium vanadate and 0.05M sodium arsenate solution to 0.05M ammonium ceric nitrate solution with continuous stirring in different volume ratios (table 1). The desired pH was adjusted by adding dilute HNO_3. The precipitates were kept in the mother liquors for 24 h at room temperature. The precipitates of different samples were filtered. After filtration continuous washing of all the samples was done to remove excess acid, with distilled water. pH of the effluents was checked with the help of pH paper. When the effluent becomes neutral, precipitates were assumed to be free from excess acid. Now these samples were kept in an oven at $40\pm1^{o}C$ for drying. The dried granules were converted into the H^+ form by keeping them immersed with HNO_3 (1.0M) for 24h with occasional shaking and intermittently replacing the supernatant liquid with fresh acid. The material thus obtained was then washed with demineralised water to remove the excess acid before drying finally at $40\pm1^{o}C$ and sieved to obtain particles of size 60-100 mesh.
Properties like ion exchange capacity (IEC), chemical resistivity and pH titration studies, distribution studies and effect of temperature on IEC were carried out as reported earlier [6].

Binary separations: Quantitative binary separation of some metal ions of analytical utility was achieved on the column of Cerium(IV) arsenovanadate (CeAsV) by knowing the effect of electrolyte concentration on distribution coefficients. This was studied by equilibrating known amount of exchanger with metal ions solution in electrolyte of various concentrations (0.1 M, 0.01 M, 0.001 M NH_4NO_3 and HNO_3). The column (30cm x 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 (10ml) 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 0.2ml per minute. The concentration of metal ion in the solution was determined by collecting known volume of effluent at regular intervals. Binary separations were carried out on the column.

Ion exchange recovery of heavy elements from synthetic wastewater: Various samples of synthetic waste water were used by contaminating the water with different metal ions, dyes and other common organic pollutants seen in industrial waste water. Samples of waste water containing Co^{2+}, Pb^{2+} and Mn^{2+} were used separately since the ion exchanger shows high selectivity to these cations. The waste water samples were filtered first to remove suspended particle and then neutralised. The solution was

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decolourised using charcoal. The samples thus obtained were used to separate and recover the heavy metal present in it. The granular cerium(IV) arsenovanadate having greater selectivity towards heavy metals were packed in a column, 100 ml of the sample was passed through the column and repeated 3-4 times using effluent collected at the bottom. This was for the maximum uptake of cations. The flow rate was maintained at 0.2ml min^{-1}. Varying concentrations of NH_4NO_3 and HNO_3 as eluents were used to elute the metal ions completely from the cation exchanger column and then determined titrimetrically with standard EDTA solution.

RESULTS AND DISCUSSION

The result from the sodium ion exchange capacity of various samples of Cerium(IV) arsenovanadate are presented in table 1. The lead in the ion exchange capacity and chemical stability seem to be much higher for sample CeAsV5 and, therefore, this sample was selected for detailed studies.

Table 1: Conditions of synthesis and properties of different samples of Cerium(IV) arsenovanadate.

sample	Molar conc.(M)			Volume mixing ratio	pH	Appearance	I.E.C(meq g^{-1})
	Ce	As	V				
CeAsV1	0.05	0.05	0.05	1:1:1	1	Orange glassy solids.	0.94
CeAsV2	0.05	0.05	0.05	1:2:1	1	Orange glassy solids.	1.13
CeAsV3	0.05	0.05	0.05	1:1:2	1	Orange glassy solids.	1.12
CeAsV4	0.05	0.05	0.05	1:1:3	1	Orange glassy solids.	1.03
CeAsV5	0.05	0.05	0.05	1:3:1	1	Orange glassy solids.	1.25
CeAsV6	0.05	0.05	0.05	1:2:3	1	Orange glassy solids.	1.18

The energy dispersive spectrometry (EDS) was used to identify the elements exist in the prepared sample. The elemental composition of the prepared sample is listed in the table 2 in percentage weight as well as percentage of atomic elements in the sample and its spectral images are given in Figure 1. Composition of the CeAsV was found as Ce: As: V; 5.95: 3.11: 1.

Table 2: Composition of elements in CeAsV

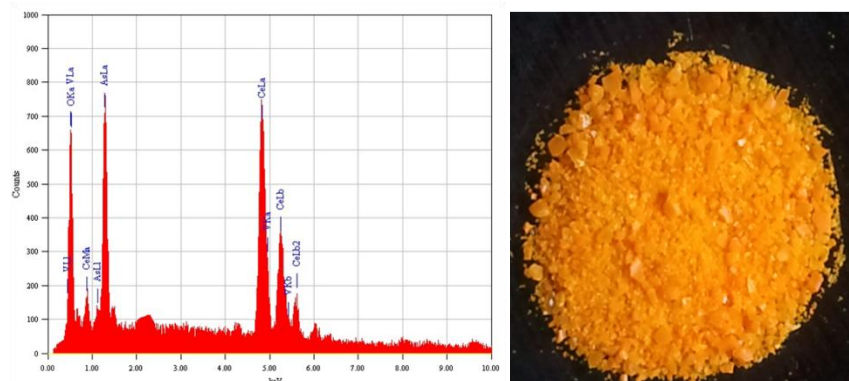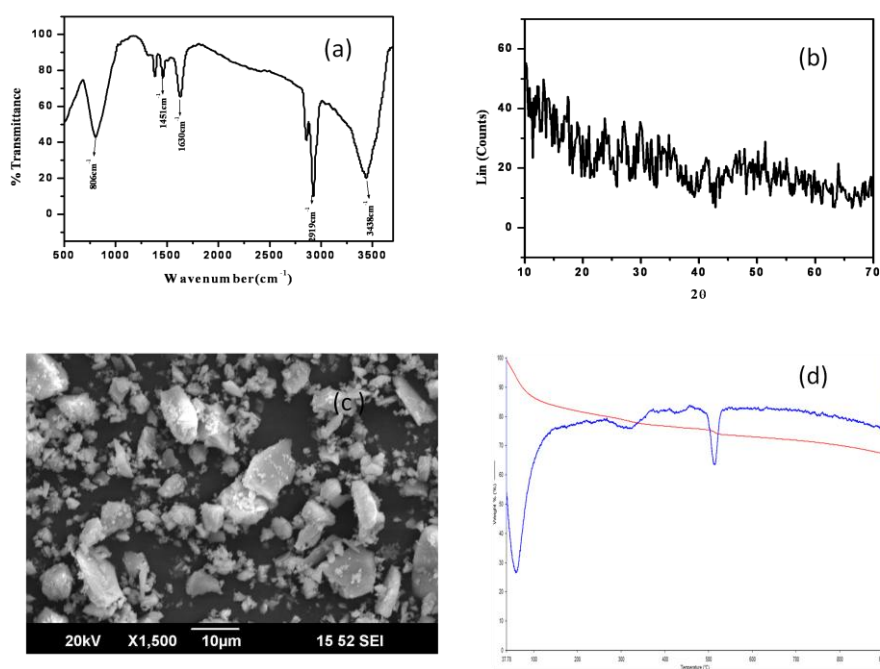| Element	Mass%	Atom%
O	9.11	41.03
As	18.95	18.23
V	4.14	5.86
Ce	67.79	34.87
Totals	100	100

Figure 1: EDS spectrum and picture of CeAsV

Figure 2: (a): FTIR Spectrum, (b): XRD, (c): SEM image and (d): TGA of CeAsV

FTIR spectra (Figure 2: a) shows broad band in the region ~3438 cm^{-1} attributed to symmetric and asymmetric –OH stretching [7] while band at 1630 cm^{-1} is due to H-O-H bending. Sharp band at 1451 cm^{-1} was due to deformation vibrations of metal hydroxyl groups and interstitial water. A peak in the region 806 cm^{-1} is attributed to metal oxygen vibrations [8 – 9].

The TGA of CeAsV (Figure 2: b) indicates the presence of hydrated water which is lost up to 100°C. A gradual weight loss observed up to 300°c is due to the condensation of exchangeable hydroxyl groups which is the usual behavior of inorganic ion exchangers [10 – 11]. After that no sharp change in weight indicates the stability of the compound. The total weight loss up to 800°C is about 27%.

The X-ray diffraction pattern of CeAsV exhibits quite weak peaks, indicating its amorphous form (Figure 2: c). SEM image of CeAsV (Figure 2: d) reveals that the particles having an irregular shape and there is no sign of crystalline structure and these observations strongly support the amorphous nature of the material.

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pH titration of Cerium (IV) arsenovanadate was performed by the method of Topp and Pepper[12]. The pH titration curve shows that the ion exchange material releases H^+ ions easily on addition of NaCl solution to the system in neutral medium. The titration curve shows two inflexion points indicating that CeAsV behaves as bifunctional ion exchanger. The titration curves with added salts are shown in figure 3. The curve in the presence of sodium salt was slightly different from that in the presence of potassium salt. The exchange capacity obtained from the curve is in agreement with that obtained by the column method.
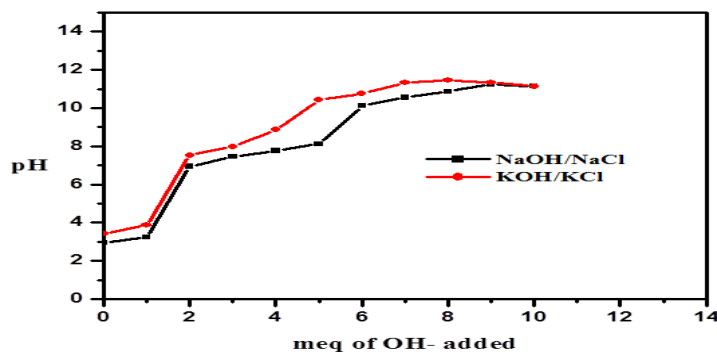

Figure 3: pH titration curve

It was observed that on heating the material at different temperatures, the ion exchange capacity of the dried sample material were changed as the temperature increased as shown in figure 4.
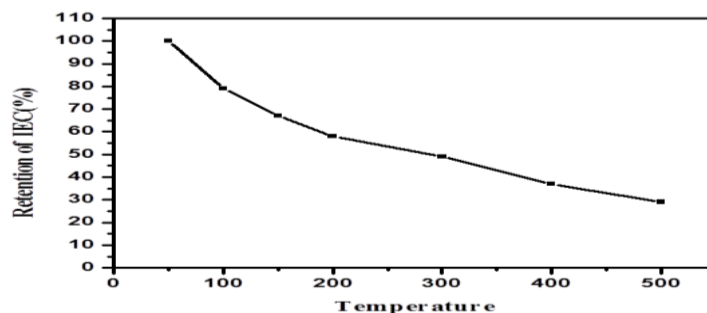

Figure 4: Effect of temperature on IEC

Distribution studies of various metal ions were carried out with the sample. It is evident from data in table 3 that the material is selective for Co^{2+}, Pb^{2+} and Mn^{2+} ions. The selectivity was found to be in the order $Co^{2+}> Pb^{2+} > Mn^{2+}> Cd^{2+}> Bi3^+> Cu^{2+}> Zn^{2+}> Mg^{2+}> Hg^{2+} > Ni^{2+}$.

Table 3: Distribution coefficients in water and other electrolytes

| Cations	Distribution coefficients (K_d)						
	DMW	HNO$_3$			NH$_4$NO$_3$		
		0.001M	0.01M	0.1M	0.001M	0.01M	0.1M
Bi^{3+}	76.80	47.67	18.65	2.34	51.56	21.02	3.12
Ca^{2+}	32.14	10.34	1.43	NS	11.87	2.81	NS
Cd^{2+}	85.20	50.43	21.43	5.21	58.98	25.64	6.54
Co^{2+}	222.00	103.54	38.34	10.70	118.98	41.07	11.23
Cu^{2+}	37.2	10.43	2.54	NS	11.21	3.67	NS
Hg^{2+}	13.26	NS	NS	NS	NS	NS	NS
Mg^{2+}	20.67	6.16	NS	NS	7.64	NS	NS
Mn^{2+}	102.84	64.76	21.98	8.88	70.87	26.78	9.56
Ni^{2+}	5.10	NS	NS	NS	NS	NS	NS
Pb^{2+}	120.00	74.32	27.76	9.87	81.34	32.11	10.41
Zn^{2+}	26.34	7.76	NS	NS	8.09	NS	NS

NS: No sorption

APPLICATIONS

Binary separations using CeAsV : The separation potential of the material has been established by achieving some analytically difficult binary separations of metal ions such as Co^{2+} - Ni^{2+}, Co^{2+} - Hg^{2+}, Co^{2+}- Mg^{2+} and Co^{2+} - Zn^{2+} on its column. The significant features of these separations are summarized in table 4. The separations are somewhat sharp and recovery is quantitative and reproducible. The separation was based on sequential elution of ions through the column using different eluting agents such as NH_4NO_3 and HNO_3. The sequential elution of ions from the column depends upon the stability of metal-eluting ligand (eluent). The weakly retained metal ions get eluted first, followed by stronger one. The efficiency of separation and eluents used for the same were also shown in table 4.

Table 4: Binary separations of metal ions using CeAsV

Separations achieved	$\alpha = K_{d1}/K_{d2}$	Eluent	Metal ion (mg)		Efficiency (%)
			Loaded	Eluted	
Co^{2+}- Ni^{2+}	43.53	0.01M NH_4NO_3(Ni)	1.40	1.35	96.42
		1M HNO_3+0.1M NH_4NO_3(Co)	1.52	1.24	81.57
Co^{2+}- Hg^{2+}	16.74	0. 01M NH_4NO_3(Hg)	4.92	4.63	94.11
		1M HNO_3+0.1M NH_4NO_3(Co)	1.52	1.31	86.18
Co^{2+} - Mg^{2+}	10.74	0.01M NH_4NO_3(Mg)	1.34	1.25	93.28
		1M HNO_3+0.1M NH_4NO_3(Co)	1.52	1.43	94.07
Co^{2+} - Zn^{2+}	7.14	0.01M NH_4NO_3(Zn)	1.62	1.46	90.12
		0.5MHNO_3+0.1MNH_4NO_3(Co)	1.52	1.49	98.03

Ion exchange recovery of Co^{2+}, Pb^{2+} and Mn^{2+} metal ions from waste water on CeAsV : Based on the granular nature of the synthesized Cerium(IV) arsenovanadate and its affinity towards Co^{2+} ,$Pb^{2+}$and Mn^{2+} ions, column experiments were carried out to examine the possible removal of these hazardous cations from their aqueous waste solution at proper pH. Figure 5 shows the effect of pH on distribution of these cations on CeAsV. The maximum sorption for Co^{2+}, $Pb^{2+}$and Mn^{2+} was at pH 6.0, pH 4.0 and pH 3.0 respectively. The decrease of sorption of Co^{2+}, Pb^{2+} and Mn^{2+} ions on CeAsV with the higher pH is associated with the dissociation of surface hydroxy group of CeAsV. Low sorption of metal ions was observed below pH 2.0 which may possibly owing to weak exchange of H^+ ions with the cations in highly acidic solutions.
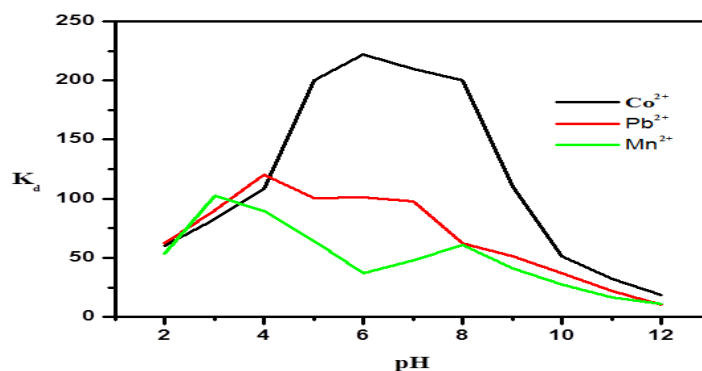
Figure 5: Effect of pH on K_d values of metal ions

For the recovery of metal ions, the regeneration solution 1M HNO_3, is allowed to flow through the CeAsV exchange column drop by drop for 4 hrs. HNO_3 removes the cations adsorbed during the cycle and converts the inorganic ion exchange material to the hydrogen form for the next cycle. This solution is collected in the bottom and the metal ion is recovered from the collected effluents.

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The details of column experiments were summarized in table 5. It is apparent from data in table that the material is efficient for the removal of Co^{2+}, Pb^{2+} and Mn^{2+} ions from waste water. It has been found that the recovery of Co^{2+} and Pb^{2+} ions using the material is 93.4% and 90.2% respectively and the results reveals that CeAsV could be reused successfully for the effective removal of Co^{2+} and Pb^{2+} ions. Although the adsorption of Mn^{2+} ions from waste water using the cation exchange column is significant, its recovery from the surface of CeAsV becomes more difficult with HNO_3 as eluent. Here we can also observe that the color of the exchange column changes from orange to deep brown (almost black). Earlier works from our laboratory have been reported that this is due the oxidation of diffused Mn^{2+} ions to higher oxidation states by Ce^{4+}(Ce^{3+}/Ce^{4+} redox potential=1.61) and other oxidizing species present in cerium based ion exchange material[13]. Since the Mn^{2+} ion exchanged material is stable towards acids, the material after use can be regenerated with hydrogen peroxide (redox potential 0.682) to retain its color and can be used for the next cycle.

Table 5: Sorption and recovery of metal ions on CeAsV

Metal ions	Co^{2+}	Pb^{2+}	Mn^{2+}
pH	6.0	4.0	3.0
Sorption on CeAsV (%)	94.2	92.8	91.6
Recovery by 1M HNO_3(%)	93.4	90.2	4.1

The figure 6 shows UV-Vis DR spectra of pure samples of CeAsV and metal ion exchanged samples. In the spectra the intensity of absorption in the visible region is increased compared to pure CeAsV. The spectra show unusual absorbing ability for visible light which can be observed in the color of the samples.
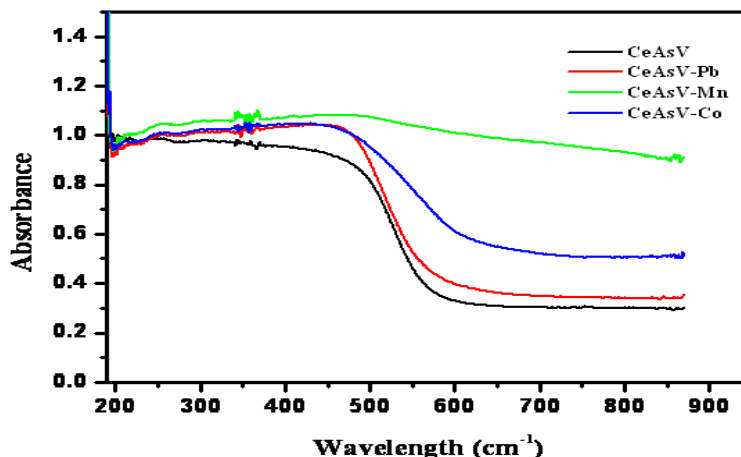

Figure 6: UV-Vis DR spectrum of CeAsV and metal ions exchanged samples.

UV-Vis DRS measurement can be used as a distinctive technique for knowing the surface coordination and the interaction of metal ions on ion exchange material. It may also give information regarding electronic states of metal ion species; here we can suppose that there is no electronic interaction between the exchanged Co and Pb ions. Hence these exchanged metal ions can be eluted quickly from the column of exchanger. The spectra of the Mn exchanged samples shows higher absorption intensity contrast to pure samples of CeAsV, which shows more amount of Mn^{4+} in it as expected due to the oxidation of Mn^{2+} by cerium based ion exchange material [14]. So the samples are stable to acids which indicate the interaction of metal ion with the exchanger is strong.

CONCLUSIONS

CeAsV exhibits good ion exchange characteristics, thermal stability and chemical resistivity. It showed a good efficiency in the removal of Co^{2+}, Pb^{2+} and Mn^{2+} metal ions from waste water. The enhanced adsorption of Co^{2+}, Pb^{2+} and Mn^{2+} metal ions in aqueous solution over the CeAsV surface is highest at pH 6.0, 4.0 and 3.0 respectively. High sorption and desorption of metal ions makes this method valuable and feasible for decontamination of waste solutions.

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