Chapter 5

CeVO$_4$ based adsorbents

*Mo-substituted CeVO$_4$ oxides: Potential sorbents and Insight into solid solution formation*  
**Jerina Majeed**, Vinita Grover, Jayshree Ramkumar, K. Bhattacharyya and A. K. Tyagi  
*Dalton Transactions (Communicated)*
5.1. Introduction:

ABO$_4$ class of compounds (A: lanthanide ion, including Sc and Y), in particular orthovanadates and orthophosphates, have been the subject of continued research due to the interesting physical properties exhibited by these compounds [74, 81, 340-342]. The REVO$_4$ compounds exhibit three structural types viz. tetragonal scheelite and zircon-type [68] and monoclinic monazite-type [69]. Cerium(III) orthovanadate (CeVO$_4$), which according to phase diagrams is located at the boundary of zircon and monazite types, exhibit three polymorphic forms with the pseudo-octahedral -like structure of tetragonal scheelite (occurring naturally in calcium tungstate) in addition to the known zircon and monazite type forms. The compound exhibits unique electronic [71-73], optical [71-75], magnetic [71-75], catalytic [74, 75], and luminescent [74, 75] properties. They are also used as sensors and electrode in electrochromic devices [74, 77]. Lanthanide orthovanadates also used as catalyst and exhibit selective oxidative dehydrogenation of propane to propene [343]. Recently, they have been examined as potential photocatalysts for the degradation of dyes and organics [344]. Due to interesting physical features depicted by REVO$_4$, many studies have been dedicated to structural changes observed in this system using various diffraction and spectroscopic techniques [345, 346]. However, most of the studies on cerium vanadate have focused on A-site substitution. Out of few studies performed on B-site substituted CeVO$_4$, one was by Hirano et al. [347] on Tb(V$_{1-x}$P$_x$)O$_4$ systems wherein ‘V$^{5+}$’ was isovalently substituted by P$^{5+}$. To the best of the knowledge, there has been no structural study reported on substituted CeVO$_4$ with aliovalent substitution at B-site. It has been reported, that A-site substitution in CeVO$_4$ brings about
variation (depending on relative ionic radii of host and guest) in CeVO\textsubscript{4} lattice but does not affect the VO\textsubscript{4} tetrahedra. With this background, it is worth exploring the effect of substituting V\textsuperscript{5+} with a moiety possessing differently charged anion, on the structure of CeVO\textsubscript{4} and the possible solid solution formation mechanism adopted by the lattice to maintain the local charge neutrality.

The presence of lead in water has been a big menace in the present times. Pb(II) has got severe health implications involving immune disorders \cite{348}. In fact, among inventory of priority heavy metal pollutants in ground water system set by most of the Environmental Protection Agencies, lead (Pb) is most challenging with high toxicity and carcinogenicity. There has always been a pressing need to circumvent this problem and various procedures have been implemented for the same. Development of an appropriately efficient sorbent which is also cost effective is hence very significant. There have been several examples wherein nanomaterials have been shown to exhibit superior sorption behavior \cite{349}. From some of the earlier studies done in the group, it has been illustrated that nanomaterials can be employed as efficient sorbents for removal of lead and various toxic species through formation of inner-sphere complex with contaminants \cite{350-352}. Some of the nanomaterials have also been explored for separation of radionuclides also \cite{353}.

In view of above information, the present work endeavors to explore the synthesis of Mo- doped CeVO\textsubscript{4} system, Ce(V\textsubscript{1-x}Mo\textsubscript{x})O\textsubscript{4} \((0.0 \leq x \leq 0.4)\). An exhaustive study which probes the solid solution formation mechanism based on X-ray diffraction (XRD) and spectroscopic techniques like Raman and X-ray photoelectron spectroscopy is presented.
The system has also been subjected to microscopic studies. To the best of our knowledge this is a new system and it has not been explored for its sorption properties. Hence, pure CeVO$_4$ and Mo-substituted CeVO$_4$ were explored as potential sorbents for Pb(II) ions. This entails investigating their sorption capacities and modeling of sorption behavior and kinetics.

5.2. Results and discussions

5.2.1. Characterization of adsorbent

All the nominal compositions synthesized in Ce(V$_{1-x}$Mo$_x$)O$_4$ (0.0 ≤ x ≤ 0.5) system were characterized by powder X-ray diffraction (XRD). The XRD patterns observed for the nominal compositions Ce(V$_{1-x}$Mo$_x$)O$_4$ (0.0 ≤ x ≤ 0.5) are shown in Figure 5.1. The XRD pattern for pure CeVO$_4$ matched well with that reported in the literature (JCPDS-PDF file No. 84-1457) and indicates well crystallized structure. It possesses tetragonal symmetry (SG: I4$_1$/amd) and the lattice parameters were calculated (by Powderx) to be: a= b= 7.336 Å, c= 6.472 Å, which are in good agreement with that reported in the literature for bulk CeVO$_4$. It is observed (Figure 5.1) that upto 40 mol% substitution of Mo$^{6+}$ into CeVO$_4$ lattice, similar XRD patterns were obtained and on further increasing the Mo$^{6+}$-content to 50 mol%, a small and broad impurity peak centered at 2θ~ 28 ° could be observed. This implies that 40 mol% is the solubility limit of Mo in CeVO$_4$ under present experimental conditions, retaining the zircon-type crystal structure. Also, the peak broadening decreases on successive Mo-substitution. Hence, the particle size of CeVO$_4$ increases on substituting Mo$^{6+}$ (Table 5.1). The XRD patterns of various nominal
compositions in Ce(V_{1-x}Mo_x)O_4 (0.0 \leq x \leq 0.4) are refined and the refined lattice parameters are shown in Table 5.1.

Figure 5.1: XRD pattern as synthesized (a) CeVO_4, (b) 5 \% Mo-CeVO_4, (c) 10 \% Mo-CeVO_4, (d) 20 \% Mo-CeVO_4 (e) 40 \% Mo-CeVO_4 and (f) 50 \% Mo-CeVO_4 nanoparticles.

It is also interesting to note that initially upon 5 mol\% Mo substitution in CeVO_4 lattice, there is no shift in peak positions and then there is a slight peak shift to higher angle side in the XRD patterns on subsequent Mo-substitutions up to 40 mol\%. This implies that the cell parameters initially do not change and then decrease slightly. The ionic radii of V^{5+} and Mo^{6+} are 0.355 and 0.42 Å, respectively [354]. If it is assumed that Mo is substituting V^{5+} as Mo^{6+}, it predicts an increase in lattice parameter of the solid solution formed by substituting Mo^{6+} in CeVO_4.
Table 5.1: Lattice parameters and unit cell volume of as synthesized 
\(\text{Ce(V}_{1-x}\text{Mo}_x\text{O}_4\) (0.0 ≤ x ≤ 0.4) samples.}

<table>
<thead>
<tr>
<th>Sample Ce(V(_{1-x})Mo(_x))O(_4)</th>
<th>Structure</th>
<th>A (Å)</th>
<th>c (Å)</th>
<th>Volume (Å(^3))</th>
<th>Crystallite size from Scherrer equation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.0</td>
<td>zircon</td>
<td>7.354</td>
<td>6.483</td>
<td>350.609</td>
<td>10</td>
</tr>
<tr>
<td>x=0.05</td>
<td>zircon</td>
<td>7.352</td>
<td>6.482</td>
<td>350.364</td>
<td>15</td>
</tr>
<tr>
<td>x=0.1</td>
<td>zircon</td>
<td>7.344</td>
<td>6.464</td>
<td>348.632</td>
<td>12</td>
</tr>
<tr>
<td>x=0.2</td>
<td>zircon</td>
<td>7.303</td>
<td>6.470</td>
<td>345.069</td>
<td>16</td>
</tr>
<tr>
<td>x=0.4</td>
<td>zircon</td>
<td>7.305</td>
<td>6.455</td>
<td>344.458</td>
<td>20</td>
</tr>
</tbody>
</table>

This is indeed surprising because, 40 mol% substitution is large enough amount to be manifested as the increase in lattice parameters of the solid solutions (Table 5.1) if the lattice is same as the parent compound and Mo is getting substituted in the lattice. This result is in contrast to that reported by Porta et al. [355] who could observe an increase in lattice parameters in Mo-doped cerium vanadate solid solutions. Hence, it becomes absolutely essential here to confirm whether the increasing amount of Mo is indeed getting substituted in CeVO\(_4\), by an alternate technique.

The X-ray fluorescence studies performed on all the nominal compositions (Figure 5.2) show that there is a definite increase in the Mo-content in corroboration with nominal compositions. Hence, this observation along with absence of any other Mo-containing phase in the XRD patterns, upto 40 mol% substitution, confirms, that even
though significantly small and opposite shift in peaks of the diffraction patterns (and consequently the lattice parameters) is observed in contrast to that expected, an increasing amount of Mo is indeed getting substituted in these compositions. The Mo doped CeVO$_4$ samples will be denoted as CVM henceforth.

![Graph showing Mo content in various Ce(V$_{1-x}$Mo$_x$)O$_4$ samples](image)

**Figure 5.2:** Trend in Mo-content observed in various Ce(V$_{1-x}$Mo$_x$)O$_4$ (0.0 ≤ x ≤ 0.4) samples as obtained by EDXRF analysis.

A series of Raman spectra were recorded on all the nominal compositions (Figure 5.3(a)). CeVO$_4$, which exists in zircon structure, is supposed to exhibit 12 active Raman modes. Out of 12 Raman modes expected for this system, 9 modes have been observed. The main modes of CeVO$_4$ which are observed are 118, 142, 218, 260, 370, 446, 771, 784 and 845 cm$^{-1}$. The spectrum is dominated by the Raman band at 845 cm$^{-1}$ which is assigned to vanadate symmetric stretching ($\nu_1$), and at 771 cm$^{-1}$ to the anti-symmetric stretching of vanadate. The other major bands at 444 and 368 cm$^{-1}$ can be ascribed to bending deformations of the vanadate group. The modes observed at lower wave numbers
like 118 cm$^{-1}$, 220 cm$^{-1}$ are due to external rotations, translations etc. A careful observation of Figure 5.3(a) shows that the Raman spectra of all the Mo-substituted CeVO$_4$ are qualitatively similar to pure, undoped CeVO$_4$ which suggests the structural similarities between all the nominal compositions in the present CVM system. The Raman bands are clearly broadened, which can be ascribed to nano-size as well as the randomization introduced by hetero-ion (Mo) substitution in the lattice (Figure 5.3(a)). It is noticeable that with increase in Mo-content, there is a progressive red-shift in the frequencies of the symmetric (845 cm$^{-1}$) and asymmetric stretch (769 cm$^{-1}$) of BO$_4$ (B: V, Mo) groups (Figure 5.3(b), (c)). The red shift can be explained by increase in average cationic size on substituting V by larger Mo and hence the increased B-O bond length. This leads to decrease in the force constant and hence the observed red shift in the stretching frequencies (symmetric, asymmetric stretch) of B-O bond. In addition to the support provided by XRF for Mo-substitution in CeVO$_4$ lattice, the shift in Raman mode frequencies is also a valid proof of the substitution of Mo into CeVO$_4$ lattice.

However, the bending Raman modes do not show similar and consistent trend. The substitution of Mo in place of V, will lead to irregularities in BO$_4$ tetrahedra which are otherwise regular in zircon structure. The bending of distorted polyhedral groups requires higher energy. In zircon structure, as mentioned earlier, the BO$_4$ - tetrahedra share edge with AO$_8$ dodecahedra. The substitution of a higher charged cation (Mo$^{6+}$) in place of V$^{5+}$ should raise the energy of bending vibrations, for it may bring higher charged positive cations closer (across the edge) and hence require greater energy. Now, there are two competing factors operating here which are (i) decrease in force constant
due to higher size of Mo-ion which should lead to red shift and (ii) increase in bending vibrational energies which should result in blue shift. As a consequence of these two opposing factors, the modes ascribed to the bending vibrations (260-455 cm\(^{-1}\)) do not show a consistent trend. The symmetric bending vibration at 368 cm\(^{-1}\) is almost constant whereas, the asymmetric bending vibration at 445 cm\(^{-1}\) shows blue shift initially and then shows red shift in subsequent compositions with increase in Mo content.

**Figure 5.3:** (A): Raman spectra of as synthesized (a) CeVO\(_4\), (b) 5% Mo-CeVO\(_4\), (c) 10% Mo-CeVO\(_4\), (d) 20% Mo-CeVO\(_4\) and (e) 40% Mo-CeVO\(_4\) nanoparticles, (B): Shift in symmetric (845 cm\(^{-1}\)) stretch and (C) asymmetric stretch (769 cm\(^{-1}\)) of VO\(_4\) groups in all the Ce(V\(_{1-x}\)Mo\(_x\))O\(_4\) samples.

According to the general principle of preservation of local charge neutrality in case of substitutional solid solutions, the aliovalent substitution of V\(^{5+}\) by higher charged Mo\(^{6+}\) should either create an anion excess or cation vacancies for maintaining local charge neutrality. A similar study on Bi(Mo\(_{1-x}\)V)O\(_4\) has shown, that among these two options, cation vacancies at Bi\(^{3+}\)-site are preferred over anion excess [356]. In this present
system, the electro-neutrality can also be maintained by change in oxidation states of cations. This is possible at B-site, wherein both Mo and V (which are known to exist in variable oxidation states) can adopt lower oxidation states to maintain charge neutrality. However, the reduction of V$^{5+}$ and Mo$^{6+}$ to lower oxidation states should again lead to increase in the average cationic size because lower valent states are known to have larger ionic radii than higher valent in the similar co-ordination. This should also then result in increase in the lattice parameters in contrast to what is actually observed.

Thus, X-ray diffraction, X-ray fluorescence and Raman studies, quite evidently support the formation of substitutional solid solutions by replacement of V by Mo in CeVO$_4$. However, the lattice parameter trend is indeed intriguing. Also, there is no signature of any secondary phase Ce(V$_{1-x}$Mo$_x$)O$_4$ ($0.0 \leq x \leq 0.4$) system and the major phase appears to be same.

The XPS studies were performed on the representative nominal compositions in Ce(V$_{1-x}$Mo$_x$)O$_4$ ($0.0 \leq x \leq 0.4$). The Ce$^{4+}$ 3d spectra of Ce(V$_{1-x}$Mo$_x$)O$_4$ ($0.0 \leq x \leq 0.4$) system are shown in Figure 5.4. The Ce- XPS spectra shows, the splitting due to R-S [357] coupling (Figure 5.4) and the peaks Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ can be identified. The individual 3d peaks also show splitting which indicates the presence of both Ce$^{4+}$ and Ce$^{3+}$ in pure CeVO$_4$[68] Certain satellite peaks at (884.1–884.6 eV), (887.6–888.1 eV) and (896.4–897.1 eV) and at (902.9–903.4 eV), (906.0–906.3 eV), (915.1–915.3 eV) are also observed which have been attributed to interaction between Ce-4f and O-2p states [358].
Figure 5.4: Ce-3d XPS spectra for (a) CeVO$_4$, (b) 5% Mo-CeVO$_4$, (c) 10% Mo-CeVO$_4$, (d) 20% Mo-CeVO$_4$ and (e) 40% Mo-CeVO$_4$ nanoparticles.

On substituting Mo$^{6+}$, it is observed that both the splitting of 3d peaks as well as intensity of satellite peaks decrease and the trend is continued with subsequent Mo-substitutions. The decrease in splitting of individual 3d peaks with increase in Mo-substitution can be taken as the signature of decrease in amount of Ce$^{4+}$ on increasing Mo$^{4+}$ content (Figure 5.4). This can be explained, since addition of higher charged Mo will tend to decrease the positive charge in the parent lattice in order to maintain the charge neutrality. Further, the decrease in the satellite peaks attributed to interaction between Ce-4f and O-2p states [73], with the subsequent Mo-substitution, suggests a decreased overlap between the Ce and O.
Figure 5.5: (A): Mo-3d XPS spectra for (a) CeVO₄, (b) 5% Mo-CeVO₄, (c) 10% Mo-CeVO₄, (d) 20% Mo-CeVO₄ and (e) 40% Mo-CeVO₄ nanoparticles (B): Mo-3d₅/₂ de-convoluted XPS spectra for the sample 10% Mo-CeVO₄.

The XPS patterns of the Mo-3d for the various nominal compositions are depicted in Figure 5.5(A). The Mo-XPS peaks are not expected in the parent compound. The 5% Mo-substituted sample shows the presence of the XPS peaks at 231.9 and 235.6 eV respectively attributed to 3d₅/₂ and 3d₃/₂ of Mo⁶⁺ [359]. Interestingly, the 10 mol% Mo-substituted sample shows a shoulder at 230.6 eV along with the peak at 231.9 eV which corresponds to Mo⁵⁺ species [359] and this is found to increases with increase in Mo-substitution.

The deconvolution of the shoulder peak corresponding to Mo⁵⁺ and the main peak belonging to Mo⁶⁺ in all the compositions was performed (Figure 5.5) and Mo⁵⁺-contents present in the system as a function of the Mo doping, are tabulated in Table 5.2. Thus, the
presence of both Mo$^{5+}$ and Mo$^{6+}$ peaks, with increase in amount of Mo$^{5+}$ on subsequent Mo-substitutions indicate that the reduction of some amount of Mo$^{6+}$ to Mo$^{5+}$ is playing a major role in maintaining local charge neutrality in the CVM system.

Table 5.2: Qualitative estimate of the Mo$^{5+}$ in the Mo-substituted CeVO$_4$ systems.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mo$^{5+}$ (Area under the curve) of 230.8 eV*</th>
<th>Mo$^{6+}$ (Area under the curve) of 232.1 eV*</th>
<th>Mo$^{5+}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>x=0.05</td>
<td>-</td>
<td>552</td>
<td>0</td>
</tr>
<tr>
<td>x=0.1</td>
<td>53</td>
<td>188.5</td>
<td>21</td>
</tr>
<tr>
<td>x=0.2</td>
<td>39</td>
<td>137.21</td>
<td>22</td>
</tr>
<tr>
<td>x=0.4</td>
<td>145</td>
<td>381</td>
<td>27.5</td>
</tr>
</tbody>
</table>

*The area under the curve is found by deconvolution of the Mo 3d$_{5/2}$ peaks using the Origin Software and the area under the curve is calculated after fitting (The chi$^2$ values for each fitting are observed to be greater than 0.989)

There have been reports in literature wherein Mo$^{5+}$ has been observed to occur in 4-fold co-ordination and detected by esr spectroscopy. The XPS spectra of the V in these systems are relatively simpler. The XPS peaks for V2p$_{3/2}$ and 2p$_{1/2}$ are observed at 517.1 and 521.2 eV, respectively (Figure 5.6), consistent with that reported in the literature for V$^{5+}$ [223]. However, the oxidation state of V (i.e. V$^{5+}$/V$^{4+}$ reduction) is not significantly disturbed by Mo-doping unless the substitution is performed at higher concentrations. A small peak at 515.7 eV, corresponding to V$^{4+}$ [359] appears only at 40 mol% Mo-substitution and this shows that the reduction of V is not a significant pathway in the solid solution formation.
Figure 5.6: V-2p XPS spectra for (a) CeVO₄, (b) 5% Mo-CeVO₄, (c) 10% Mo-CeVO₄, (d) 20% Mo-CeVO₄, and (e) 40% Mo-CeVO₄ nanoparticles.

Figure 5.7(A): O-1s XPS spectra for (a) CeVO₄, (b) 5% Mo-CeVO₄, (c) 10% Mo-CeVO₄, (d) 20% Mo-CeVO₄, and (e) 40% Mo-CeVO₄ nanoparticles. (B): O1s de-convoluted XPS spectra for the CeVO₄ sample.
The O-1s XPS spectra for this system are depicted in Figure 5.7(a). In CeVO₄, the O-1s peak is found at 528.7 eV. This O 1s peak is observed to be asymmetric in nature and on deconvolution, (Figure 5.7(b)) it shows two peaks centered at 528.5 eV and 531 eV. The peak at 528.5 can be attributed to the oxygen attached to CeO₈ and VO₄ since these polyhedral share edges. The peak at 531 eV is generally ascribed to O corresponding to that of surface –OH groups [360]. Also, the asymmetry in O 1s peak increases with increase in Mo-substitution. This may be attributed to the O attached to Mo⁵⁺ and Mo⁶⁺ in the system.

The collective assessment of results obtained from all the characterizations gives an insight into the mechanism of solid solution formation in CVM system. All the nominal compositions crystallize in tetragonal zircon phase. The charge compensation subsequent to aliovalent substitution of V⁵⁺ by Mo⁶⁺ is primarily obtained by reduction of some of the Mo⁶⁺ to Mo⁵⁺. However, similar reduction of V⁵⁺ to V⁴⁺ occurs only at higher Mo substitution levels. But since all the Mo⁶⁺ is not converted to Mo⁵⁺ as shown by XPS (Figure 5.5(a)), and the presence of anion excess could not be confirmed using above mentioned techniques, shows that some Ce³⁺ vacancies should occur. Such A-site vacancies were also shown in BiVO₄ based system [356]. The presence of Ce vacancies will not only explain charge neutrality but also the near constancy (slight decrease) of lattice parameters (Table 5.1) despite the substitution of smaller V⁵⁺ by larger Mo⁶⁺ (or Mo⁵⁺ and V⁵⁺) cation. The presence of vacancies is known to cause contraction of the lattice [361] and hence, the dilation of lattice due to increase in average cationic size is probably compensated resulting in observed trend. The Ce-XPS spectra also indicated
decreased interaction between Ce and O on subsequent Mo-substitution which can also be explained on assuming Ce\(^{3+}\) vacancies. Anion excess as the charge compensating mechanism will also lead to lattice expansion due inter-anionic repulsion. It must be mentioned however, that the presence Ce\(^{3+}\) vacancies could not be directly evidenced.

The presence of variable oxidation states of same ion (Mo) in the same structure without causing the disruption of CeVO\(_4\) lattice may applications for such materials in redox catalysis.

### 5.2.2. Exploring CVM system as Pb(II) ion sorbents

The framework compounds like vanadates and phosphates are known to show good sorption capacities [353, 362]. There has been report about feasibility of CeVO\(_4\) and Cemolybdate as sorbents [353], however not much detailed work is reported. Also, to the best of the knowledge, this cerium vanado-molybdate system has not been explored as sorbents. Hence, it was attempted to explore the sorption of unwanted, highly toxic Pb(II) ions from aqueous solutions and examine the effect of Mo-substitution on the sorption efficiency. For the sake of clarity, in this section, CeVO\(_4\), CeVO\(_4\) -10 mol % Mo and CeVO\(_4\) -40 mol % Mo will be represented as CV, CVM-1 and CVM-4, respectively.

The sorption behavior of the nanoparticle has tremendous dependence on their morphology. Thus, in order to reveal whether the powder properties and morphology of the pure and Mo substituted CV nanopowders are conducive to sorption, the samples were subjected to electron microscopic studies. The representative transmission electron micrograph of the as-prepared CeVO\(_4\) nanopowders is shown in Figure 5.8(a). The
formation of spherical particles of dimension 60-70 nm is easily discernible from the micrographs.

![Tem image](image.png)

Figure 5.8: (a) TEM image of as synthesized CeVO₄ nanoparticle, (b) enlarged view of HR-TEM image of CeVO₄ nanoparticle.

Interestingly, a detailed HR-TEM (Figure 5.8(b)) reveals that each nano-sphere is composed of numerous nanocrystals (average size ~ 10-20nm) self-aggregated to form highly porous 3D spherical structures. This is also consistent with the particle size obtained from X-ray line broadening. The particles are fairly homogeneous and not very agglomerated. The pore shapes are observed to be irregular and the pore sizes are also not uniform.

In order to investigate the specific area and the porosity behavior of CV and Mo-substituted CV nano-assemblies, the N₂ adsorption-desorption isotherm were measured. The N₂ isotherm (Figure 5.9(A)) displays the typical Type IV curve with a H₃ type hysteresis loop.
Figure 5.9(A): N$_2$ adsorption-desorption isotherm and (B): t-plot analysis of CV, CVM-1 and CVM-4 nanoparticles.

Figure 5.10: BET surface area analysis of pure and doped CeVO$_4$

In order to obtain more information on surface area and porosity, the Braunauer-Emmet-Teller (BET) surface area measurement and t-plot analysis were also carried out [363]. The t-plots showing the quantity of nitrogen adsorbed Q (mmol/g) at different P/Po values as a function of thickness of adsorbed gas, for pure and Mo substituted CV are shown in Figure 5.9(B). The experimental values are found to be in good agreement with the Harkins and Jura equation [337]. It must be noted that in the t-plot, the straight line
passing through the data points corresponding to the thickness of 0.35-0.46 nm does not pass through origin for any of these samples. This signifies the porous natures of the samples [364]. Also, the positive intercepts (on y-axis) in these t-plots suggest the presence of micropores for the Mo-substituted CeVO₄ samples. This peculiar behavior, attributable to micropores, was however found to be absent in the case of pure CeVO₄.

The deviation from linearity in the region of higher t values in the t-plot signifies the mesoporous nature of the materials. The BET surface area plots of pure and doped CeVO₄ are shown in Figure 5.10. The specific surface areas of CV, CVM-1 and CVM-4 were determined as 76, 86 and 147 m²/g, respectively, and the corresponding pore volumes (at P/Pₒ = 0.9960) are 0.42, 0.20 and 0.25 cm³/g, respectively.

The sorption efficiencies of cerium vanadate and 40mol% molybdenum substituted cerium vanadate (CVM-4) with respect to lead ions were investigated. For a Pb(II) sorbent, to be used for potable water, it is much more relevant to evaluate its sorption efficiency in near neutral solution. Hence, the entire investigation was carried out at pH ~ 6-7. The studies were performed by equilibrating a known concentration of lead solution (10 or 100 ppm) maintained at pH 6-7 with 0.1 g of the sorbent for a period of 1 h. It was shown that both CV and CVM-4 are efficient sorbents and more than 99% uptake was exhibited for the initial concentrations of Pb(II) as 10 and 100 ppm. (Figure 5.11(A), inset). In order to investigate the effect of initial concentration of Pb(II) ions on the uptake behavior, different initial concentrations of Pb(II) varying from 10-100 mg/L were used at room temperature with vigorous stirring for 1 h. The equilibrium sorption capacity sharply reached the saturation point, showing ~100% uptake, regardless of the
initial concentration (Figure 5.11(A)). Thus, Mo-substituted CeVO₄ is an efficient sorbent in all concentrations ranging from 10-100 mg/L.

Figure 5.11(A): Effect of initial concentration of Pb (10-100 mg/L) metal ion on sorption behavior of CVM-4, (B): equilibration period on the amount of lead ion taken up and inset of (A): shows uptake by both the nanosorbents (pure CV and CVM-4).

However, since the BET analysis indicated the presence of micro and mesopores in Mo-substituted systems, it was considered worthwhile to analyse the effect of introduction of such features brought about by Mo-substitution on the sorption behavior of CeVO₄. Hence, the kinetics of sorption of Pb(II) ions by both pure and substituted CeVO₄ was investigated. The results of kinetic studies are shown in Figure 5.11(B) wherein it was found that CeVO₄ could show fast uptake of Pb(II), with 100% uptake achieved in 1 h. However, in comparison, the Mo-substituted CeVO₄ could depict the same uptake in less than 10 min. Thus, even though both CV and CVM-4 exhibited complete uptake of Pb(II) ions, CVM-4 demonstrated exceptionally fast kinetics in
comparison to pure CV. This shows that the presence of molybdate anion framework has an immensely favorable effect on sorption kinetics of cerium vanadate lattice.

Since, CVM-4 exhibited better kinetics, so in order to further investigate the mechanism of sorption process on the samples; the data obtained were fitted to both equilibrium and kinetic modelling using different models. One of the most important characteristics of an adsorbent is the amount of adsorbate it can accumulate, which can be calculated from the adsorption isotherms. Adsorption isotherms are constant–temperature equilibrium relationship between the amount of adsorbate per unit of adsorbent \( q_e \) and its equilibrium solution concentration \( C_e \).

Herein, the sorption data for Pb(II) uptake on CVM-4 were fitted with the fundamental models of Langmuir [227], Freundlich [229] using the linearized equations for these isotherms and the fittings are shown in Figure 5.12 and Figure 5.13, respectively. The Langmuir model considers that the sorption occurs only at specific homogeneous sites i.e. it takes the monolayer adsorption. On the other Freundlich adsorption isotherm, works on the consideration of multilayer adsorption on a non-homogeneous surface. It further assumes that the adsorption sites are having an exponential distribution with respect to heat of adsorption.

The fitted results of these isotherms are presented in Table 5.3. On the basis of correlation coefficient values, the sorption of Pb(II) can be best described by Freundlich isotherm model which implies that adsorption of Pb(II) on CVM-4 is a multilayer sorption process. The high capacity can be explained by the fact that sorption is not restricted to monolayer. The value of \( 1/n \) which reveals information about the nature of
sorption taking place (physisorption/chemisorption) is found to lie between 0-1 thus indicating the chemisorption process.

Figure 5.12: Equilibrium modeling using Langmuir isotherm for sorption of Pb(II) ions on CVM-4.

Figure 5.13: Equilibrium modeling using Freundlich isotherm for sorption of Pb(II) ions on CVM-4 nanoparticles.
Table 5.3: Parameters calculated from the linearized equations of different equilibrium models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_0$ (mg/g)</td>
<td>$b$</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>1995.2</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

The sorption data was also fitted to Dubinin–Radushkevich model [232], from which the energy of sorption was found to be $> 8$ kJ/mol which lies in the range required for chemisorption process [365]. Using Freundlich model, it can also be confirmed that the process is a favourable given by the value of $n$ which lies between 1 to 10. The Langmuir model, even though not the best fit here, showed the sorption capacity to be quite high.

Two types of kinetic modeling were performed to throw light on the kinetics and the order of Pb(II) adsorption process on CVM-4, the pseudo-first-order [233] ($k_1$, min$^{-1}$) model and the pseudo-second-order model [235] ($k_2$, g mg$^{-1}$ min$^{-1}$).

$q_t$ is the adsorption amount (mg g$^{-1}$) at time $t$ and $q_e$ is the adsorption capacity at equilibrium (mg g$^{-1}$), the $k_2$ can be calculated from the plot of log ($q_e$ vs $q_t$) against $t$, the $k_2$ can be calculated from the slope and intercept of the plots of $t/q_t$ against $t$. The results of kinetic modeling are summarized in Table 5.4. The sorption data was found to fit well to the pseudo-second-order kinetic model. This suggests a chemisorption process as the rate
limiting step (Figure 5.14). The equilibrium amount taken up, $q_e$, was calculated to be ~100 mg/g for both cerium vanadate and CVM-4, from the model fitting. The $q_e$ is very high for CVM-4.

![Graph showing adsorption kinetics](image)

Figure 5.14: Kinetic modeling using Ho and Mackay Pseudo-second order rate equation for both CV and CVM-4 nanoparticles.

Table 5.4: Parameters calculated from the linearized equation of second order kinetic model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$q_e$ (experimental)</th>
<th>$q_e$ (calculated)</th>
<th>$K_{2ads} \times 10^{-2}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td>100</td>
<td>109.4</td>
<td>0.196</td>
<td>0.9949</td>
</tr>
<tr>
<td>CVM-4</td>
<td>100</td>
<td>102.5</td>
<td>1.4</td>
<td>0.9991</td>
</tr>
</tbody>
</table>
The $q_e$ values for Pb(II) sorption observed in the present study are compared with those reported for some reported systems in Table 5.5[366-370]. It should also be noted that this is very much in agreement with experimentally determined capacity. In order to gain an insight into the rate determining step of the sorption process, Weber–Morris model was employed [237] and the fitted data is shown in Figure 5.15.

**Figure 5.15: Kinetic modeling using Webber Morris model for CV and CVM-4.**

The sorption, in general, can be defined by three steps, the mass transfer to surface of sorbent, diffusion of the sorbate through the boundary and finally the adsorption-desorption equilibrium. This corresponds to linear regression in three regions in the Weber Morris fitted plot as shown in Figure 5.15. The ratio of the slopes of these regions gives information about the rate determining step. Thus, it shows that external mass transfer to the surface of the sorbent (here CVM-4) that controls the rate of the sorption
process. This, even in the chemisorption, that is taking place here, it is the mass transfer to sorbent sites which is the rate determining step.

Table 5.5: Comparison of Pb(II) uptake with that reported for different materials.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Pb(II) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide nanoparticles</td>
<td>36.0</td>
<td>[366]</td>
</tr>
<tr>
<td>Al₂O₃-supported iron oxide</td>
<td>28.98</td>
<td>[367]</td>
</tr>
<tr>
<td>Manganese oxide–carbon nanotube</td>
<td>26.24</td>
<td>[368]</td>
</tr>
<tr>
<td>Urchin like Ni–P microstructure</td>
<td>39</td>
<td>[369]</td>
</tr>
<tr>
<td>Flower-like titanium phosphate</td>
<td>550</td>
<td>[370]</td>
</tr>
<tr>
<td>Hierarchical cerium molybdo-vanadate</td>
<td>100 (40 mol% Mo)</td>
<td>Present study</td>
</tr>
</tbody>
</table>

5.3. Summary

In summary, zircon-type Mo-substituted CeVO₄ solid solutions were synthesized by co-precipitation method. The system was extensively characterized using X-ray diffraction, X-ray fluorescence, Raman spectroscopy and X-ray photoelectron spectroscopy. The solid solution formation mechanism is proposed which involves reduction of Mo⁶⁺ to Mo⁵⁺ accompanied by Ce³⁺ vacancies. The particle size increased on Mo-substitution with concomitant increase in surface area as well which can be attributed to the presence of mesopores as shown by the N₂-adsorption-desorption isotherms. The
hierarchical morphology coupled with the mesoporous structure showed efficient uptake of Pb(II) ions by CeVO₄. Introduction of hetero-Mo network improved the uptake kinetics by five times wherein 100 mg/L of Pb(II) uptake was exhibited in 10 min. The adsorption equilibrium isotherm showed best fit to Freundlich model. The isotherm analysis and kinetic modeling revealed the process to be a favorable chemisorption phenomenon following pseudo-second order kinetics. The study brings forth highly promising Pb(II) ion sorbents in a hitherto unexplored cerium molydovanadate system.

Further to ease the use of nanosorbents and ease of separation, it was felt worthwhile to use magnetic nanosorbents which will be discussed in the next chapter.