ABSTRACT

Hydroxyapatite (HAp) has been investigated for the removal of heavy metals in environmental application. However, little is known about the influences of surface modifications of the HAp. In this paper nano- HAp - polyvinyl alcohol (PVAL) gel was synthesized under pH control and the formed gel was used for removing nickel ions. The influence of nickel ions on the surface of HAp was studied. Reaction mechanisms were followed by ICP-MS and discussed via continuous variations method (CVM), mole ratio method (MRM) and slope-ratio method (SRM). The formed gel with nickel ions was characterized by various methods including UV, FTIR, XRD, and SEM. The ICP-MS was used to analyze the supernatant solution to confirm the presence of Ca and/or Ni ions. The nickel ions were found to reduce the degree of crystallinity of the synthesized HAp phase. The present results indicate that nickel ions were completely adsorbed on the HAp structure with its anion. The validation of the nature of HAp gel as chelating agent, or complex formation as well as physical sorption was discussed.
INTRODUCTION

There has been an increasing concern over the discharge of heavy metals into the environment and there are several methods for heavy metal removal from wastewaters [1-3]. In particular, chemical stabilization is one of the methods of reducing the leachability of heavy metals in waste materials, with forming new, less soluble mineral phases that are more stable in the environment [4]. Hydroxyapatite (HAp) Ca\(_{10}\)(OH)\(_2\)(PO\(_4\))\(_6\) is an ideal material for long-term containment of contaminants because of its low water solubility (K_{sp}<10^{-40}), high stability under reducing and oxidizing conditions and over a wide temperature range, availability, and low cost. It is well documented that HAp strongly sorbs uranium and many other radionuclides and heavy metals [5-8]. HAp has been investigated as a potential agent to treat heavy metal–contaminated soils, sediments, wastes, and wastewater, especially in the cases of Pb, Cd, Zn, and U [9-10]. HAp is an economical and natural source of phosphate, which has a high removal capacity for divalent heavy metal ions [11].

In this work an inexpensive and simple technique was used for the synthesis of HAp gel by using, polyvinyl alcohol (PVAL) as the polymeric carrier for Ca\(^{2+}\) under pH control. HAp gel was prepared in polymeric media (polymer matrix) without any chemical interaction between organic–inorganic interface. Also the Metal ion–ligand complex based polymer precursors, which are very suitable for complex mixed oxide systems and as complexing agent to keep homogeneous distribution of metal ions through the matrix [12]. This was reported to result the formation of HAp in nanoscale [13]. The advantages of this technique are low processing temperature, molecular level homogeneity, improved purity, morphology, texture, and wide scope for tailor made compound.

UV, FTIR, XRD, SEM and ICP-MS tools were used to evaluate and confirm the nature and role of HAp-PVAL nano composite gel towards Ni ions removal and sought mechanisms.

EXPERIMENTAL

1-Chemicals

The chemicals used are calcium nitrate tetrahydrate (Ca(NO\(_3\))\(_2\).4H\(_2\)O, Mwt. 236.15g/mole, Merk, Germany), di ammonium hydrogen ortho phosphate (anhydrous (NH\(_4\))\(_2\)HPO\(_4\), 132.06g/mole, S.D. Fine Chem.Ltd. Mumbai), poly vinyl alcohol (PVAL) (Mwt. \(\approx\)160000 g/mole), Nickel Chloride hexahydrate, (NiCl\(_2\) 6H\(_2\)O, Mwt.237.7g/mole,Spectroscopy BDH, England) and ammonium hydroxide (NH\(_4\)OH, Mwt. 35.5g/mole, May & Baker, England). They were used in the experimental work without further purification.

2-The preparation of HAp-PVAL gel:

Nano hydroxyapatite was prepared described by S. Nayar and Sinhal [13,14]. A 5% PVAL was prepared in 1-L flat bottom flask (dissolved in deionized water) while stirring and heated at 80°C for 30 min. After complete dissolution of PVAL, calcium nitrate (Ca(NO\(_3\))\(_2\).4H\(_2\)O) was added while stirring and heating until complete dissolution. Finally diammonium hydrogen ortho phosphate((NH\(_4\))\(_2\)HPO\(_4\) ) solution
was added to the mixture with Ca/P atomic ratio 1.67 while stirring and heating at 80°C, under pH controlled at 8 using ammonium hydroxide until the gel was formed.

3-Influence of nickel ions on the formed HAp gel:
A 5 ml of 0.1 M NiCl₂ 6H₂O (spectroscopy) was prepared in deionized water, after then, 1 ml of HAP- gel was added to the prepared solution. The proper mechanism of reaction between HAp gel and nickel chloride was studied and validation of complex formation or chemical reaction or physical sorption were also investigated accordingly;

a) The formation of complex-ion (HAp gel / Ni ions) was studied using UV-Spectrophotometer (UV-160A- SHIMADZU) to monitor continuous variation method CVM, molar ratio method MRM and slop ratio method SRM [15]. The three procedures are briefed as follows:

(i) Continuous variations method (CVM) by plotting the volume of ratio (HAp gel/ HAp gel + NiCl₂) against the absorbance as follows:

<table>
<thead>
<tr>
<th>Volume of HAp gel (ml)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of 0.1M NiCl₂ (ml)</td>
<td>7</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

(ii) The mole-ratio method (MRM): a series of solutions were prepared in which the metal (Ni as chloride) was kept constant while that of the others varied and the absorbance is plotted against the volume fraction of one reactant as follows:

<table>
<thead>
<tr>
<th>Volume of HAp gel (ml)</th>
<th>0.2</th>
<th>0.5</th>
<th>1</th>
<th>1.5</th>
<th>2</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of 0.1M NiCl₂ (ml)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Volume of H₂O (ml)</td>
<td>5.8</td>
<td>5.5</td>
<td>5</td>
<td>4.5</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

(iii) The slope-ratio method (SRM) is useful for single complex formation as in the present case. The ratio of metal (Ni as chloride) to HAp gel was plotted against its absorbance as follows:

<table>
<thead>
<tr>
<th>Volume of HAp gel (ml)</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of 0.1M NiCl₂ (ml)</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Volume of H₂O (ml)</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

b) The presence of Ca and Ni ions in the supernatant solution of HAp gel and NiCl₂ was analyzed by inductively coupled plasma mass spectrometry ICP-MS (HP4500).

c) The structure, morphology of HAp gel/NiCl₂ were investigated using SEM (Phillips – XL30) equipped with EDAX for cations detection and distribution while x-ray diffractometer (Philips PW 1390) and FTIR (Mattson infinity series) were employed for crystallinity and structure confirmation validation.
RESULTS AND DISCUSSION

UV spectra chart for NiCl₂ and upon loaded to HAp is illustrated in Fig. 1. It is to be observed that the green color of NiCl₂ has disappeared considered as confirmation for complexation process with gel.

The continuous variation method (CVM), Fig 2a illustrate that the contact point of the two lines is at 0.5 which mean that the best results for complex formation was obtained by adding equal volumes of metal (Ni as nickel chloride) to the chelating agent (HAp gel). This is confirmed also by mole-ratio method (MRM), Fig 2b where the absorbance versus volume ratios of the reactants show two straight lines of different slopes that intersect at a volume ratio unity. The slope ratio method (SRM), Fig 2c, plotting the ratio of Nickel chloride to HAp gel against its absorbance, where straight lines obtained with slope of $A_{\text{Ni}}=0.1002$ for NiCl₂ and $A_{\text{HAp}}=0.0906$ for HAp gel. The combining ratio between two lines $A_{\text{HAp}} / A_{\text{Ni}}$ is unity. This result is in complete agreement with the CVM and MRM since the ratio of HAp gel to NiCl₂ is equal i.e. 1:1 volume ratio. Consequently HAp gel / 0.1M NiCl₂.6H₂O should be added with equal volumes for complete reaction. Therefore 1 ml of HAp gel (of HAp concentration 20ppm) should be added to 1 ml of 0.1 M NiCl₂ 6H₂O (containing 6 ppm Ni²⁺). The concentration corresponding to the combination ratio in the complex HAp gel/ Ni²⁺ is 3.3.

Therefore, when HAp gel is added to 0.1M NiCl₂.6H₂O at equal volumes complete complex formation is obtained and when the gel settled the solution turns clear. The supernatant liquid was analyzed by ICP-MS for detection of Ni and Ca ions, results of which showed no detection of Ca or Ni ions which mean that the Ni ions are trapped in HAp gel or reacted with it, and no ion exchange occurred since there is no Ca ions in the supernatant liquid.

To reveal the role of HAp gel, a 100ml of HAP-gel were added to 100ml of 0.1M NiCl₂, after settling the solution became clear and the supernatant liquid was separated. The formed gel was dried at 100°C for 24h. Visually outer layer of the dried sample had green color while the inner heart reserved white color which means that the nickel chloride of green color absorbed on the HAp gel surface. The difference in color appeared clearly in the morphological analysis of the dried sample Fig 3 a1. The morphology of HAp Fig3b1 clearly show developed with crystal edges compared to that containing nickel chloride Fig3 a3 proving that the nickel chloride reduced the gel crystallinity. When compared with the parent HAp/PVAL composite aggregation and grain boundaries turning it eventually to a diffused morphology, Fig3a4.

The microstructure HAp/PVAL/NiCl₂ composite analyzed by EDAX shown in Fig 4a where the presences of Ni²⁺, Cl are detected. It is also important to note the height intensity of oxygen and detected at 0.523 KeV compared to the parent HAp gel Fig 4 b has increased, which mean that the Ni²⁺ and its cation Cl were chelated in HAp gel structure. The analysis of the surface dark spots which appeared in the SEM Fig 3 a2 by using the EDAX unit reverted more content of nickel chloride than the other parts of the sample and oxygen content increase in the sample containing NiCl₂ Fig4a.

As the Ca/P ratio in the parent HAp/PVAL composite gel is 1.88 compared to that of HAp/PVAL/NiCl₂ is 2.39 is described as mainly due to the presence of Ni.
Mineral structure:

The characteristic XRD pattern of HAp (main peak d=2.81 Å and secondary peaks at d=2.78 Å, d=2.72 Å) [16] still exist Fig5b with a small shift due to the presence of nickel chloride Fig 5a; (d=2.80 to 2.82 & d=2.76 to 2.78 & d=2.71 to 2.74). It is to be noticed that the presence of nickel chloride didn’t change the crystal structure of HAp. The width of the main XRD pattern characteristic to HAp at d= 2.81 changed from 2θ (31-33), Fig 5b to (30-35), Fig5a d, proved decreased crystallinity of HAp while the pattern of NiCl₂ didn't appear. The decrease of the peaks intensity is mainly due to reduced content of the HAp concentration, Fig5a.

HAp IR spectra characteristic bands are at 630 and 3570 cm⁻¹ that belong to the vibration of hydroxyl OH and bands at 1036, 1091 and 963 cm⁻¹ for phosphate PO₄³⁻ stretching vibration, while the bands at 603 and 565 cm⁻¹ from phosphate bending vibration [17-19]. The peak at 2071 cm⁻¹ stands for –CH₂ asymmetric bending of PVAL [13]. The FTIR analysis of HAp gel dried at 100°C for 24h and HAp gel with nickel chloride Fig6 proves that the OH⁻ at 3570 cm⁻¹ has disappeared while the of OH⁻ at 630 cm⁻¹ has decreased. The increase of oxygen content is detected by EDAX analysis refers to the broadening of OH⁻ at 630 cm⁻¹ proving the change of HAp structure confirmed by XRD Fig 5a. The broadening of characteristic bands of PO₄³⁻ at 1091 and 1036 cm⁻¹ compared to the sharp beak of HAp could be due to the decrease of the crystallinity of HAp by the presence of nickel chloride results of which are matched with XRD analysis.

CONCLUSION

Nano-Hydroxyapatite (HAp) - polyvinyl alcohol (PVAL) was synthesized and tested as of prospective chelating agent of some transition metals. The nano-composite gel successfully removed nickel chloride from its solution. The nickel ions were completely chelated and intervened with the gel reducing the degree of HAp crystallinity as being completely adsorbed on the HAp structure with its anion. The formed HAp gel can be used, accordingly in the environmental application of removal of nickel ions from waste water.

REFERENCES


Figure 1: The UV spectrum of

a) 0.1 M NiCl$_2$.6 H$_2$O and b) 5 ml of 0.1 M NiCl$_2$.6 H$_2$O with 1 ml of HAp gel(complex).
Fig. 2: The spectrophotometric analysis of complex formation HAp gel / 0.1 M of NiCl₂ 6 H₂O by three different methods: a) Continuous variation method (CVM), b) Mole ratio method (MRM), and c) Slope ratio method (SRM).
Fig. 3: The SEM of a) HAp gel with 0.1 M of NiCl$_2$·6 H$_2$O dried at 100°C for 24 h and b) HAp gel dried at same conditions.
Fig. 4: The EDAX analysis of a) HAp gel with 0.1 M of NiCl₂·6 H₂O dried at 100°C for 24 h and b) HAp gel dried at same conditions.
Fig. 5: The XRD pattern of a) HAp gel / 0.1 M of NiCl₂ 6 H₂O dried at 60°C for 24h and b) HAp gel dried at same conditions.
Fig. 6: IR spectrum bands of a) HAp gel dried at 100°C for 24 h and b) HAp gel with 0.1 M of NiCl₂ 6 H₂O dried at same conditions.