Sorption study of $\text{Sr}^{2+}$, $\text{Co}^{2+}$ and $\text{Pb}^{2+}$ Ions from Aqueous Waste Solutions using Hydroxyapatite Formed into Soil

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ABSTRACT

Sorption of $\text{Sr}^{2+}$, $\text{Co}^{2+}$ and $\text{Pb}^{2+}$ from aqueous waste solution on six hydroxyapatite (HAP) samples was studied. Formation of in situ apatite barriers in soil using water soluble reagents for sequestering $\text{Sr}^{2+}$, $\text{Co}^{2+}$ and $\text{Pb}^{2+}$ ions from their aqueous waste solutions as an application for HAP uses is of high interest. This technique is based on injecting a solution of calcium citrate and sodium phosphate into the soil to form insoluble calcium phosphates that transform into apatite. Both batch and column techniques were used. A synthetic mixed waste solution of $\text{Sr}^{2+}$,$\text{Co}^{2+}$ and $\text{Pb}^{2+}$ ions is percolated from up to down into the sorbent column at constant flow rate. The obtained data show that the HAP barrier formed in the soil has a high efficiency for sequestering the studied metal ions from the aqueous solutions. The maximum capacity of HAP to $\text{Sr}^{2+}$, $\text{Co}^{2+}$ and $\text{Pb}^{2+}$ is about 530 mg g$^{-1}$, 375 mg g$^{-1}$ and 590 mg g$^{-1}$, respectively. Therefore, it is recommended to inject HAP into the soil under any tanks of liquid waste in order to work as a barrier to protect the environment from the hazardous radionuclides or heavy metals present in the tank, in case of any leakage from the tank.

Key Words: Sorption/ Aqueous Waste Solutions/ Hydroxyapatite/ $\text{Sr}^{2+}$, $\text{Co}^{2+}$ and $\text{Pb}^{2+}$ Ions.

INTRODUCTION

The peaceful application of radionuclides in research institutes, hospitals and industries generates aqueous waste solutions. The waste solutions should be treated to remove the hazard isotopes prior to control discharge to the environment. The treatment should reduce the quantities of radioactive contaminants to a level which allows safe discharge according to national and international regulations. A common method of removing heavy metals from wastewater has been to mix them with sewage, where conventional primary, secondary and tertiary treatment would then remove heavy metals$^{(1)}$. Several solids have been used as new adsorbents such as, activated carbons$^{(2)}$, wool$^{(3)}$, polymers$^{(4,5)}$, silicas$^{(6)}$, zeolites$^{(7,8)}$, clays$^{(9,10)}$, and fishbone apatite$^{(11)}$. It is well recognized the importance of apatite, derived from animals, as a sorbent$^{(12)}$. The contamination of water with toxic heavy metal ions is a complex problem. The removal of this contamination has received much attention in recent years. From an environmental protection point of view, heavy metal ions should be removed at the source in order to avoid pollution of natural waters and subsequent metal accumulation within the food chain$^{(13)}$. The mechanism of cadmium uptake by synthetic hydroxyapatite (HAP: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) from aqueous solution was investigated by David Marchat$^{(14)}$. The aim of the present work is to study the possibility of the injection of soluble reagents which react with each other to form hydroxyapatite into soil and study the efficiency of the injected hydroxyapatite in the removal of $\text{Sr}^{2+}$, $\text{Co}^{2+}$ and $\text{Pb}^{2+}$ ions from their waste solutions.
EXPERIMENTAL

Chemicals and instruments

All chemicals utilized in this work were of analytical grade purity and were used without further purification. The main chemicals and reagents are given in Table (1). Bi-distilled water was used for preparing aqueous solutions and washing glassware. A distillator of type AquaMatic AWC-4D, Hamilton Co., made in Germany, was used to producing bi-distilled water. An analytical balance of type AB204-S, Mettler Toledo, made in U.K, was used for the measurement of the pH values of different solutions used in this study. An Atomic Absorption Spectrophotometer of type Thermo Jarrell Ash, AA-scan 4, made in USA, was used for the determination of the metal ion concentration in different solutions. A water bath of type (Shaker Bath SBS30, Sturat Scientific) made in U.K, as well as a heater/stirrer thermix stirrer of type (RCT BASIC 120M, KIKA LABORTE-CHNIK) made in Germany, a chamber furnace of type (UAF 16/10, Lenton Furnaces) made in England, and mortar grinder of type (Mortar Grinder RM100, Retsch) made in Germany, all these wares were used for the preparation of hydroxyapatite. A mechanical shaker of type (SK-300, Lab Companion) made in Korea, was used for mixing of the two phases through the sorption experiments.

Table (1): Chemicals and reagents used in this work.

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Formula</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt nitrate</td>
<td>Co(NO₃)₂·6H₂O</td>
<td>WINLAB</td>
</tr>
<tr>
<td>Strontium chloride</td>
<td>SrCl₂·6H₂O</td>
<td>Merck</td>
</tr>
<tr>
<td>Lead nitrate Hydrochloric</td>
<td>Pb(NO₃)₂</td>
<td>WINLAB</td>
</tr>
<tr>
<td>acid</td>
<td>HCl</td>
<td>Riedel-de Haen</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>Ca(OH)₂</td>
<td>BDH</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>GCC diagnostic</td>
</tr>
<tr>
<td>Ammonia solution</td>
<td>NH₃</td>
<td>BDH</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>KNO₃</td>
<td>Adwic</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>KOH</td>
<td>Adwic</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃</td>
<td>GCC diagnostic</td>
</tr>
</tbody>
</table>

Samples

Six hydroxyapatite samples were used. Three samples were chemically synthesized apatite; the first one was dried at 100 °C (has annotation Synth100), the second was dried at 500 °C (has annotation Synth500) and the third was dried at 700 °C (has annotation Synth700). Two samples of natural cow bone derived apatite; the first was natural cow bone apatite (has annotation Nbone); raw bone, and the second was natural cow bone apatite after treatment and burning at 700 °C (has annotation Nbone700). A six sample was commercial apatite supplied from Bio-Rad Co. USA (Bio-Rad).

Adsorbate

The stable salts of Sr²⁺, Co²⁺ and Pb²⁺ ions used in this study was prepared by dissolving a certain amount of their ion salts in distilled water. Initial pH of solutions was adjusted by the addition of 0.1M HNO₃ or 0.1M NaOH. The concentration of Sr²⁺, Co²⁺ and Pb²⁺ metal ions were determined using Atomic Absorption Spectrometrically method.
Sorption of Sr\(^{2+}\), Co\(^{2+}\) and Pb\(^{2+}\) from waste solution by the HAP samples using batch technique

Sorption of a mixture of Sr\(^{2+}\), Co\(^{2+}\) and Pb\(^{2+}\) from aqueous waste solution on each HAP samples was studied using the batch technique. The synthetic waste solution was prepared by incorporating an appropriate volume of each stock solution (100 ppm) of the investigated metal ions into 1000 ml distilled water to prepare a solution with concentration 10 ppm for each metal ion. Suspensions containing 0.2 g of each hydroxyapatite samples and 40 ml of the synthetic mixed waste solution were shaken for 2 hrs, then filtered and analyzed to determine each metal ion concentration. The primary experiments show that these parameters are suitable to have good distribution with an error not more than ± 1.1%. The obtained data were presented in the form of uptake percent (%) using the following formula:

\[
\text{Uptake percent } \% = \left( \frac{C_o - C_e}{C_o} \right) \times 100
\]

Where,

- \(C_o\): is the initial metal ion concentration in the aqueous phase, (mg/l).
- \(C_e\): is the metal ion concentration in the aqueous phase at equilibrium time, (mg/l).

The sorption process of the investigated metal ions by hydroxyapatite samples were clearly found to be affected by contact time and hydrogen ion concentration.

Formation of in-situ apatite as barriers in soil using water soluble reagents for sequestering Sr\(^{2+}\), Co\(^{2+}\) and Pb\(^{2+}\) ions using column technique as an application

The formation of in-situ apatite barrier in the soil is based on injecting a solution of calcium citrate and sodium phosphate into the soil. As the citrate is biodegraded, calcium is gradually released and immediately reacts with the phosphate to form insoluble calcium phosphates that transform into apatite\(^{15}\).

Properties of the studied soil

The soil sample used in these experiments was collected from the site of Inshas at depth of 5 m. Physical and chemical analyses were performed (Table 2&3) at the Central Lab for Elemental & Isotopic Analysis, Nuclear Research Center, Atomic Energy Authority, Egypt. Mineralogical analysis using X-ray diffraction technique was performed (Table 4) at the Nuclear Materials Authority, Egypt.

Preparation of the working solutions

As shown in Figure (1), two bottles were used for the preparation of the solutions; the first bottle containing 40 mM calcium chloride and 100 mM sodium citrate at pH 8.4, the bottle must be kept away from light, because the formed Ca-citrates break down after 2 hrs if exposed to light. The second bottle contained 30 mM sodium hydrogen phosphate, 15 mM ammonium nitrate and other nutrients at pH 8.4. The other nutrients are FeCl\(_3\), Na\(_2\)SO\(_4\), NaCl, MgCl\(_2\), MnCl\(_2\) and KNO\(_3\). 0.5 g of each one of the nutrients is poured in one liter bi-distilled water, 5 ml added from this stock to the second bottle\(^{15}\).

The injection process

25 ml of each of the two bottles were mixed and adjusted to pH 8.4 then injected into the studied soil sample (420 g in weight and 10 cm in height) contained in column made from polyacrylic acid with 50 cm length and 7.62 cm diameter and keep it for two weeks.
Table (2): Physical properties of the studied soil sample.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>1.52</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.81</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.215</td>
</tr>
<tr>
<td>Particle Size</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>90.0 %</td>
</tr>
<tr>
<td>Silt</td>
<td>8.0 %</td>
</tr>
<tr>
<td>Clay</td>
<td>2.0 %</td>
</tr>
</tbody>
</table>

Table (3): Chemical analysis of the studied soil.

<table>
<thead>
<tr>
<th>Metal Oxides</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>54.20</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.50</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.13</td>
</tr>
<tr>
<td>FeO</td>
<td>0.10</td>
</tr>
<tr>
<td>MnO</td>
<td>0.22</td>
</tr>
<tr>
<td>MgO</td>
<td>1.55</td>
</tr>
<tr>
<td>CaO</td>
<td>20.20</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.32</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.31</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.61</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.10</td>
</tr>
<tr>
<td>L.O.I (mainly CO$_2$)</td>
<td>16.54</td>
</tr>
<tr>
<td>Total</td>
<td>99.78</td>
</tr>
</tbody>
</table>

Table (4): Mineralogical analysis of the studied soil.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>Minor</td>
</tr>
<tr>
<td>Calcite</td>
<td>Com</td>
</tr>
<tr>
<td>Quartz</td>
<td>Mod</td>
</tr>
</tbody>
</table>

Sequestering the investigated metal ions

A synthetic mixed waste solution with concentration 10 ppm of each of Sr$^{2+}$, Co$^{2+}$ and Pb$^{2+}$ ions were percolated from up to down into the sorbent column at constant flow rate of 3 ml/min. Great care was taken to avoid of any air bubbles within the sorbent bed. The effluents were collected from the bottom of the column in small fractions (5 ml) for analysis. The experiment was continued until the selected sorbet concentration percolating from the column was approximately the same as the feed solution. The breakthrough curve was plotted as the sorbet concentrations of the effluent solution vs. effluent volume.
RESULT AND DISCUSSION

Effect of contact time on sorption of of Sr$^{2+}$, Co$^{2+}$ and Pb$^{2+}$ by hydroxyapatite

Effect of contact time on sorption of Sr$^{2+}$, Co$^{2+}$ and Pb$^{2+}$ by different hydroxyapatite samples at room temperature (25±1 °C) from solutions of pH 6.2 is shown in Figures (2, 3, 4). From these figures it is clear that the equilibrium is attained within 1.5 hours. The uptake percent of the investigated metal ions increases with time to reach a saturation level depending on the chemistry of the element and the nature of the hydroxyapatite samples. It is clear that the uptake percent of Sr$^{2+}$ ions on the Synth100, Synth500, Synth700, Nbone700, Nbone and Bio-Rad samples is found to be 90 %, 94 %, 86.8 %, 85 %, 82 % and 53 %, respectively. For Co$^{2+}$ ions the uptake percent is found to be 87 %, 88 %, 60 %, 88 %, 82 % and 53.6 %, respectively. For Pb$^{2+}$ ions the uptake percent is found to be 75 %, 88 %, 53.5 %, 98 %, 85 %, and 53.6 %, respectively. The obtained data show that all hydroxyapatite samples can be considered as an efficient sorbent for Sr$^{2+}$, Co$^{2+}$ and Pb$^{2+}$. These data are in good agreement with that published by Smiciklas and Mouflih (16-17).

Effect of hydrogen ion concentration (pH) on sorption of of Sr$^{2+}$, Co$^{2+}$ and Pb$^{2+}$ by hydroxyapatite

The hydrogen ion concentration (pH) is one of the most important factors that influencing the sorption process of the metal ions from its aqueous solutions. The effect of hydrogen ion concentration on sorption of the Sr$^{2+}$, Co$^{2+}$ and Pb$^{2+}$ ions onto the investigated hydroxyapatite samples was studied.
and the uptake percent of the investigated metal ion plotted as a function of the pH value shown in Figures (5, 6, 7 and 8). It was observed that the uptake percent of the investigated metal ions onto the hydroxyapatite samples were slightly affected by the different initial pH value within certain range, while out this range it was highly affected. This is may be due to that the hydroxyapatite samples exhibits amphoteric properties and act as a buffer in a wide pH range from (~4 to ~9). This means that for all values of initial pH in this range, the final pH is the same and very close to the pH_{pzc} of each hydroxyapatite sample. The buffering characteristics of hydroxyapatite samples are the result of the acid-base reactions of the reactive surface sites. According to Wu et al. (18) the reactions responsible for the surface properties of HAP in aqueous solutions are:

\[ =\text{PO}^- + \text{H}^+ \rightarrow =\text{POH}^0 \]  
\[ =\text{CaOH}_2^+ \rightarrow =\text{CaOH}^0 + \text{H}^+ \]  

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Fig. (2): Effect of contact time on sorption of Sr\(^{2+}\) by HAP samples.  
Fig. (3): Effect of contact time on sorption of Co\(^{2+}\) by HAP samples.  
Fig. (4): Effect of contact time on sorption of Pb\(^{2+}\) by HAP samples.
In the range of the lower initial pH values (below pH\text{PZC}) consumption of protons from the solution by the protonation of the surface =PO? and =CaOH\text{o} groups results in increase of a final pH value. The positively charged =CaOH\text{z+} and neutral =POH\text{o} sites prevail on HAP surface in acidic solutions, making surface charge of HAP in this pH region positive. On the other hand, final pH decrease takes place in the range of higher initial pH (above pH\text{PZC}) due to OH\text{-} consumption via deprotonation of surface =CaOH\text{z+} and =POH\text{o} sites. Thus neutral =CaOH\text{o} and negatively charged =PO? species predominate in alkaline solutions, causing HAP surface to become negatively charged in alkaline solutions. If a specific cation sorption occurs, pH\text{PZC} is slightly shifted to the lower values\textsuperscript{(16)}. The maximum uptake of strontium by HAP samples occurs at pH value equals 10. These results are in good agreement with that reported by Smiciklas et al\textsuperscript{(16)}. The optimum removal value of Co\textsuperscript{2+} ions from the solutions is occurred at the final pH of the solution from ~8 to ~10, which in agreements with that reported by Smiciklas et al\textsuperscript{(17)}. While in case of Pb\textsuperscript{2+}, the uptake percent of the metal ion was not affected for the initial pH range (~3 - ~6.5), and the final pH is the same and the sorption of lead is constant within this pH range. These data are in accordance with the data obtained by Aklil et al\textsuperscript{(19)}. Formation of in situ apatite as barriers in soil for sequestering Sr\textsuperscript{2+}, Co\textsuperscript{2+} and Pb\textsuperscript{2+} ions using column technique as an application

The experiments show that the hydroxyapatite samples have good affinity to sequestering the investigated metal ions from their aqueous waste solutions. However, the placement of solid apatite into soil to form a barrier relies on extensive excavation or high pressure injection, both of which exposes workers to safety hazards and is very costly\textsuperscript{(20)}. In this study, a novel technique for placement of apatite barriers for sequestering heavy metals ions is discussed. The process is based on injecting a solution of calcium citrate and sodium phosphate into the soil, and apatite is expected to form as a thin film on the soil particles\textsuperscript{(15)}. Because citrate forms strong complexes with calcium\textsuperscript{(21)}, it prevents the calcium from immediately reacting with the phosphate before it can be injected into the soil. However once injected, citrate is easily metabolized by microorganisms\textsuperscript{(22)}. As the citrate is biodegraded, calcium is gradually released and reacts with phosphate to form insoluble calcium phosphates. At pH 7 - 9 and in the presence of fluoride, conditions are most favorable for the reaction of calcium and phosphate to form apatite\textsuperscript{(15)}.

The soil used in this experiment was collected from the site of the Inshas at depth of 5m. The chemical, physical and mineralogical analyses of this soil are given in Tables (2, 3 and 4). After formation of HAP inside the soil contained in the column, the synthetic mixed waste solution of 10 ppm for each metal ion and pH 6.2 is percolated through the column down flow by descending mode. In column operation, expression of breakthrough capacity is used for the filter capacity. It is defined as the amount of ions taken up quantitatively by the column under the condition in question i.e., the number of mg.g\textsuperscript{-1} which is retained without any leakage observed. The breakthrough capacity is always lower than the total capacity of the column and is dependent upon a number of different variables, such as particle size, filtration rate and composition of solution.

The experimental results are shown in Figure (8). This figure shows the concentration of the effluent solute as a function of effluent volume. It is clear that the effluent solutions are initially sorbet free until a certain point (the break through point) is attained when the sorbet in the effluent at concentrations which increase with the increase of the effluent until a maximum is reached at which the sorbent samples are fully loaded. From this Figure it is clear that the HAP barrier formed in the soil have a high efficiency for sequestering the selected metal ions from the aqueous solutions. The following equation was used for the calculation of the sorption capacity of the sorbent in the column\textsuperscript{(22, 23)}.

\[ Q = (V_{50\%} - V) \frac{C_o}{m} \quad \text{..................} \quad (2) \]
Fig. (5): Effect of initial pH on sorption of Sr$^{2+}$ by HAP samples.

Fig. (6): Effect of contact time on sorption of Co$^{2+}$ by HAP samples.

Fig. (7): Effect of initial pH on sorption of Pb$^{2+}$ by HAP samples.
Fig. (8): Breakthrough curve for sequestering the investigated metal ions by HAP barrier in soil.

Where:
- \( Q \): is the sorption capacity in mg g\(^{-1}\).
- \( C_0 \): is the initial concentration in mg L\(^{-1}\).
- \( V_{50\%} \): is the average breakthrough volume representing at \((C/C_0)_{50\%}\)
- \( V \): is the volume void of sorbat in mL.
- \( m \): is the mass of a sorbent (g).

The maximum capacity of HAP to Sr\(^{2+}\), Co\(^{2+}\) and Pb\(^{2+}\) is about 530 mg g\(^{-1}\), 375 mg g\(^{-1}\) and 590 mg g\(^{-1}\), respectively. Therefore, the hydroxyapatite (HAP) may inject into the soil under any tanks of liquid waste in order to work as a barrier to protect the environment from hazardous radionuclides or heavy metals in case of any leakage from the tank. Figure (9) shows a simulation of HAP barrier formed under a leakage tank containing radioactive waste.

Fig. (9): Example of an insitu formed apatite barrier under a leaking waste tank.
CONCLUSION

The in-situ hydroxyapatite (HAP) barrier formed in the injected soil have a high efficiency for sequestering Sr$^{2+}$, Co$^{2+}$ and Pb$^{2+}$ ions from the aqueous waste solutions. Therefore, HAP can inject into the soil under any tanks containing liquid waste in order to work as a barrier to protect the environment from the radionuclides or hazardous heavy metals present in the tank in case of any leakage from the tank.

Acknowledgment

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