Magnetic Nanoparticles Impregnated with 18-Crown-6 Ether: Hybrid Material Synthesis for Binding and Detection of Radioactive Strontium

Yacoob Shaikh1, Edward PC Lai1*, Baki Sadi2, and Chunsheng Li2

1Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, ON K1S 5B6, Canada
2Radiation Protection Bureau, Health Canada, 775 Brookfield Road, Ottawa, ON K1A 1C1, Canada

Received: November 10, 2014; Accepted: February 20, 2015; Published: March 04, 2015
*Corresponding author: Edward PC Lai, Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, ON K1S 5B6, Canada, Tel: +613-520-2600; E-mail: edward.lai@carleton.ca

Abstract
Super paramagnetic maghemite γ-Fe₂O₃ nanoparticles (average diameter of ~10 nm) are applied for the selective binding of radioactive strontium-85 using 4,4'(5')- di-(t-butyldicyclo-hexano)-18-crown-6 as a chelating agent. These magnetic nanoparticles offer easy separation once strontium is complexed with the crown ether. Binding test results demonstrate a 65% uptake of Sr²⁺ by gamma radiation measurement.

Introduction
Application of crown ether for selective extraction and determination of radio isotopes of strontium is well established. In the existing methods, the extraction is carried out either by liquid-liquid extraction (adding the crown ether in an organic solvent) or by extraction chromatography (where crown ether is impregnated onto an inert polymeric support). This research utilizes Magnetic Nanoparticles (MNPs) as the primary separation tool for strontium ions in aqueous sample. Magnetic separation has been found to be effective when handling particles on a Nano-size scale (1-10 nm) [1-3]. Magnetic separation is an affordable and efficient alternative to centrifugation and filtration. It overcomes problems such as blocking of filters and allows the handling of large samples. Magnetic separation also allows for accelerated sedimentation of particles when an external field is applied, therefore making separation and purification steps experimentally simple.

Maghemite has the empirical formula of Fe₂O₃ and is generally made in single crystals smaller than 1 μm. The crystal structure of γ-Fe₂O₃ is classified as isometric tetartoidal and is described as a spinel structure with systematic defects in the octahedral cation [4]. MNPs have a wide range of applications in chemistry and medicine. They are used in waste water treatment, [5] magnetic resonance imaging, [6] hyperthermia tumor treatment, [7] DNA separation, [8] and site specific drug delivery [9]. The γ-Fe₂O₃ MNPs are superparamagnetic and do not have a magnetic memory to aggregate after the external magnetic field is withdrawn. These crystallites offer better stability and biocompatibility compared to higher magnetization materials [10]. Their small size allows them to remain in aqueous suspension for prolonged periods.

Given the tremendous analytical potential of MNPs, herein we demonstrate one of its applications in radioactive hazard determination using selective binding of strontium-18 to crown-6 ether. Stable strontium occurs naturally as Sr-88, 87, 86 and 84. Radioactive strontium- 90 (Sr- 90) is a byproduct of nuclear fission of U-235 or Pu-239, which is a highly hazardous isotope with a long half-life and serious human health concerns [11]. Detection of radioactive strontium can be used as an indication of nuclear contamination. To develop the applications of MNPs for Sr-90, we used Sr-85 as a radioactive strontium isotope in our work. Sr-85 is much less hazardous, has a shorter half-life of 65 days and emits gamma radiation.

In this work we describe a novel method of synthesizing hybrid MNPs containing 18-crown-6 ether for selective strontium separation. In order to synthesize this hybrid material, a polymer matrix was needed; the monomer used was 2-acrylamido-2-methylpropanesulfonic acid (AMPS). Divinylbenzene (DVB) was the cross-linker that forms a 3-dimensional matrix with AMPS. This polymer matrix was selected to assist in Sr²⁺ binding onto crown ether. The novelty of our work is that, after the extraction, the radio-strontium can be conveniently isolated from the aqueous phase by application of an external magnetic field. This technology is very promising for automated radioactive waste disposal/ and clean up, remotely, using robotic arms where the amount of radioactivity will be too high to handle by workers in close proximity using the traditional techniques.

Materials and Methods

Materials
All chemical reagents were purchased from commercial sources. Centrifugation was performed using a micro centrifuge
Synthesis of magnetic nanoparticles

Nanoparticles of ferromagnetic iron oxide were synthesized from co-precipitation of ferrous (Fe\(^{2+}\)) and ferric (Fe\(^{3+}\)) ions in sodium hydroxide solution [12]. A molar ratio of Fe\(^{2+}/Fe^{3+} = 0.5\) was prepared by dissolving 1.625 g of FeCl\(_3\) and 1.0 g of FeCl\(_2\)\(\cdot\)4H\(_2\)O in 15 mL of aqueous HCl (12.5 mL DDW (distilled de ionized water) and 2.5 mL of 1 M HCl). This solution was added drop wise into 25 mL of 1 M NaOH under vigorous magnetic stirring. The solution turned black upon addition of Fe\(^{2+}/Fe^{3+} = 0.5\) ions. The reaction was carried out under a gentle stream of N\(_2\) gas for 15 min. The reaction flask was placed in a 60°C water bath for 24 hrs. This resulted in a dark suspension of MNPs. In order to confirm successful coating of the MNPs by the polymer, FTIR analysis was done.

Synthesis of crown ether-impregnated P (AMPS/DVB)-coated MNPs and strontium binding tests

Synthesized MNPs in water were separated by applying an external magnetic field and decanting the supernatant. MNPs were then suspended in 15 mL of methanol under mechanical stirring. The following compounds were added in order: 0.0590 g of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 0.450 mL of divinylbenzene (DVB) and 0.0082 g of 2',0.0590 g of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), 0.450 mL of divinylbenzene (DVB) and 0.0082 g of 2,-azobisisobutyronitrile (AIBN). The contents were sonicated for 30 min and the supernatant was removed. The MNPs were washed with DDW five times or more until the pH was 6.0. They were stored in 125 mL of DDW at 5°C for further coatings.

Strontium binding tests were done on the crown ether-impregnated polymer-coated MNPs as well as the non-impregnated ones. The dried particles were suspended in a 50:50 MeOH: DDW mixture, and 0.5 mL of this solution was mixed with 0.4 mL DDW and 0.1 mL of stable Sr (II) stock solution (0.5 ppm), giving a total sample volume of 1 mL [Table 1] shows a summary of sample preparation for Sr (II) measurement using Hidex Triathler multilabel radiation tester.

Characterization of particles

Transmission Electron Microscopy (TEM) was used to characterize the MNPs on a FEI Tecnai G2 F20 microscope operating at 200 kV. It offered a point resolution of 0.27 nm and a magnification ranging from 21 x to 700,000 x.

Results and Discussions

The magnetic-field-assisted separation efficiency and transferability of the synthesized MNPs was determined using an automated magnetic particle transfer workstation. Transmission electron microscopy in Figure 2 showed spherical nanoparticles that averaged 10 nm in diameter [14].

Successful synthesis of MNPs (γ-Fe\(_2\)O\(_3\)) was confirmed by FTIR analysis. Figure 3 shows the IR spectrum of MNPs. The broad OH peak at 3300-3500 cm\(^{-1}\) indicates presence of surface bound hydroxyl groups coming from residual solvent, as suggested in literature [15]. The broad peak at 575 cm\(^{-1}\) indicates that the iron oxide phase is maghemite [16]. Upon visual inspection of the synthesized MNPs, they appeared pitch black, indicating they were not oxidized to rust.

Strontium binding tests were done on the crown ether-impregnated polymer-coated MNPs as well as the non-impregnated ones. The dried particles were suspended in a 50:50 MeOH: DDW mixture, and 0.5 mL of this solution was mixed with 0.4 mL DDW and 0.1 mL of stable Sr (II) stock solution (0.5 ppm), giving a total sample volume of 1 mL [Table 1] shows a summary of sample preparation for Sr (II) measurement using Hidex Triathler multilabel radiation tester.

Characterization of particles

Transmission Electron Microscopy (TEM) was used to characterize the MNPs on a FEI Tecnai G2 F20 microscope operating at 200 kV. It offered a point resolution of 0.27 nm and a magnification ranging from 21 x to 700,000 x.

Results and Discussions

The magnetic-field-assisted separation efficiency and transferability of the synthesized MNPs was determined using an automated magnetic particle transfer workstation. Transmission electron microscopy in Figure 2 showed spherical nanoparticles that averaged 10 nm in diameter [14].

Successful synthesis of MNPs (γ-Fe\(_2\)O\(_3\)) was confirmed by FTIR analysis. Figure 3 shows the IR spectrum of MNPs. The broad OH peak at 3300-3500 cm\(^{-1}\) indicates presence of surface bound hydroxyl groups coming from residual solvent, as suggested in literature [15]. The broad peak at 575 cm\(^{-1}\) indicates that the iron oxide phase is maghemite [16]. Upon visual inspection of the synthesized MNPs, they appeared pitch black, indicating they were not oxidized to rust.

MNPs + P (AMPS/DVB) + crown ether for Sr\(^{2+}\) binding

Next, MNPs were coated with poly-2-acrylamido-2-methylpropanesulfonic acid-co-divinylbenzene, P (AMPS/DVB). This polymer showed successful incorporation of 4, 4', (5')-di-(t-
butyl dicyclohexano)-18-crown-6. The FTIR spectrum in [Figure 4A] confirms the polymerization of P (AMPS/DVB). The presence of maghemite Fe-O stretches at 632-586 cm⁻¹ is observed in both spectra. The presence of AMPS is confirmed by the O-H stretch at 3200-3600 cm⁻¹, C=O stretch at 1701 cm⁻¹ and N-H bend at 1636 cm⁻¹. The presence of DVB is confirmed by the C=C aromatic stretches in the 1400-1600 cm⁻¹ region [17].

Figure 4B is the FTIR spectrum of 18-crown-6 impregnated P (AMPS/DVB)-coated MNPs. The binding of crown ether to the polymer is suggested to be electrostatic and hydrophobic in nature. The C-O stretches at 1365 cm⁻¹ and 1098 cm⁻¹ confirm the presence of 18-crown-6. The 18-crown-6 impregnated P (AMPS/DVB)-coated MNPs had no magnetic memory. When an external magnetic field was applied, the particles in suspension would aggregate towards the magnet. Once the magnetic field was removed, the particles would readily disperse to form a suspension again.

Upon confirmation of successful crown ether complexation, the Sr²⁺ binding tests were carried out by measuring the characteristic gamma emission peak of Sr-85 [Table 2] using...
Magnetic Nanoparticles Impregnated with 18-Crown-6 Ether: Hybrid Material Synthesis for Binding and Detection of Radioactive Strontium

A-Hidex Triathler multi-label tester. The measurements made were in counts per minute (cpm) which were then converted to counts per second (cps). The calculation for activity was done using a conversion factor which was predetermined by standard calibrations. Strontium uptake is measured in terms of % Sr uptake, calculated by taking the percent difference between the sample activity after binding and the control activity before binding.

Although the binding tests had previously been done in the absence of MNPs [18], the major significance of MNP was in binding Sr²⁺ ions. This was done by placing the sample container in a magnetic field with separation time being 1-2 min. This separation was necessary for measuring the activity of supernatant solution to determine the % Sr²⁺ uptake accurately. As shown in Table 2, the % Sr²⁺ uptake for the 18-crown-6-impregnated P (AMPS/ DVB)-coated MNPs is 66% (± 15%) whereas for the non-impregnated P (AMPS/ DVB)-coated MNPs it is 23% (± 10%). Although 81% and 50% bindings for Binding and Detection of Radioactive Strontium

Table 2: Results of Sr-85 radiation measurement.

<table>
<thead>
<tr>
<th>Description</th>
<th>Gross cpm</th>
<th>B kg cpm</th>
<th>Net cpm</th>
<th>Activity (Bq)</th>
<th>% Sr Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control 1</td>
<td>665</td>
<td>522</td>
<td>105.18</td>
<td>1.75</td>
<td>4.43</td>
</tr>
<tr>
<td>Control 2</td>
<td>679</td>
<td>549</td>
<td>119.18</td>
<td>1.99</td>
<td>5.02</td>
</tr>
<tr>
<td>Control 3</td>
<td>660</td>
<td>573</td>
<td>100.18</td>
<td>1.67</td>
<td>4.22</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.56</td>
</tr>
<tr>
<td>MNPs + P+ crown</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>580</td>
<td>558</td>
<td>20.18</td>
<td>0.34</td>
<td>0.85</td>
</tr>
<tr>
<td>2</td>
<td>613</td>
<td>555</td>
<td>53.18</td>
<td>0.89</td>
<td>2.24</td>
</tr>
<tr>
<td>3</td>
<td>597</td>
<td>554</td>
<td>37.18</td>
<td>0.62</td>
<td>1.57</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>65.63</td>
</tr>
<tr>
<td>MNPs + P without crown</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>656</td>
<td>567</td>
<td>96.18</td>
<td>1.6</td>
<td>4.05</td>
</tr>
<tr>
<td>2</td>
<td>639</td>
<td>564</td>
<td>79.18</td>
<td>1.32</td>
<td>3.34</td>
</tr>
<tr>
<td>3</td>
<td>634</td>
<td>576</td>
<td>74.18</td>
<td>1.24</td>
<td>3.12</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>31.43</td>
</tr>
</tbody>
</table>


