

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

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## Abstract

Super paramagnetic maghemite  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles (average diameter of  $\sim 10$  nm) are applied for the selective binding of radioactive strontium-85 using 4,4'(5')- di-(t-butyl)dicyclo-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  $\text{Sr}^{2+}$  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  $\text{Fe}_2\text{O}_3$  and is generally made in single crystals smaller than  $1 \mu\text{m}$ . The crystal structure of  $\gamma\text{-Fe}_2\text{O}_3$  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  $\gamma\text{-Fe}_2\text{O}_3$

MNPs are super paramagnetic and do not have a magnetic memory to aggregate after the external magnetic field is withdrawn.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 to 18-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  $\text{Sr}^{2+}$  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

(Revolutionary Science RS- 102), and sonication was done using a sonication apparatus (Branson 2510). Temperatures were regulated using a digital water bath (VWR 89032-214). IR spectra were acquired using a spectrometer (Varian 100 FTIR). Radiation measurements were made using a radiation tester (Triathler multilabel tester) in gamma counting mode for the detection of radiation from Sr-85 in a sample using a NaI detector. Particle size measurements were done using a Brookhaven Instruments Nano DLS analyzer. Nano imaging analysis was performed by scanning electron microscopy (SEM) on a Tescan Vega-II XMU VPSEM system and by electron transmission microscopy (TEM) on a FEI Tecnai G2 F20 TEM system.

### Synthesis of magnetic nanoparticles

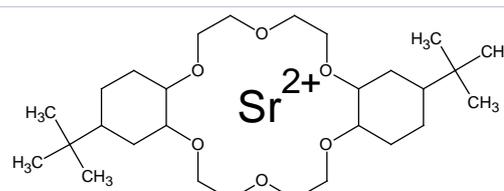
Nanoparticles of ferromagnetic iron oxide were synthesized from co-precipitation of ferrous ( $\text{Fe}^{2+}$ ) and ferric ( $\text{Fe}^{3+}$ ) ions in sodium hydroxide solution [12]. A molar ratio of  $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$  was prepared by dissolving 1.625 g of  $\text{FeCl}_3$  and 1.0 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  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  $\text{Fe}^{2+}/\text{Fe}^{3+}$  to the NaOH solution. The reaction was carried out under a gentle stream of He. The solution was stirred for 30 min once all the Fe solution was added. The resultant colloidal solution was centrifuged at 10,000 rpm 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.

### 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 15mL 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, 2'-azobisisobutyronitrile (AIBN). The contents were sonicated for 10 min (40 kHz, 5.71 L, 103 Watts) at room temperature followed by bubbling of  $\text{N}_2$  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.

The crown ether, 4, 4' (5')-di-(t-butyl)dicyclo-hexano)-18-crown-6 (DtBuCH18C6), was used as a chelating agent for selective uptake of  $\text{Sr}^{2+}$  [11], as illustrated in Figure 1. This crown ether was impregnated onto the P (AMPS/DVB)-coated MNPs following Horwitz's procedure [13] by mixing 20 mg of crown ether (1 M crown ether solution in 1-octanol) and 15 mg of coated MNPs. The contents were sonicated for 30 min and the solvent was evaporated. FTIR analysis was used to confirm successful impregnation of crown ether onto the polymer-coated MNPs.

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



**Figure 1:** 4,4' (5')-di-(t-butyl)dicyclo-hexano)-18-crown-6 binding to  $\text{Sr}^{2+}$ .

0.4 mL DDW and 0.1mL 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.

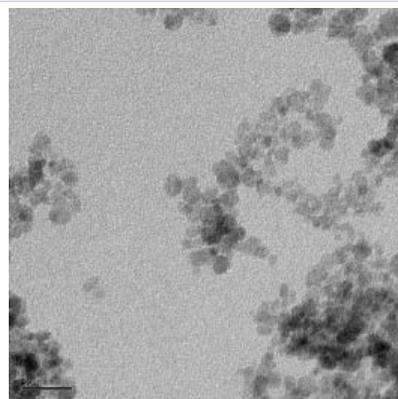
### Results and Discussions

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 ( $\gamma\text{-Fe}_2\text{O}_3$ ) was confirmed by FTIR analysis. Figure 3 shows the IR spectrum of MNPs. The broad OH peak at 3300-3500  $\text{cm}^{-1}$  indicates presence of surface bound hydroxyl groups coming from residual solvent, as suggested in literature [15]. The broad peak at 575  $\text{cm}^{-1}$  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 $\text{Sr}^{2+}$ 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-



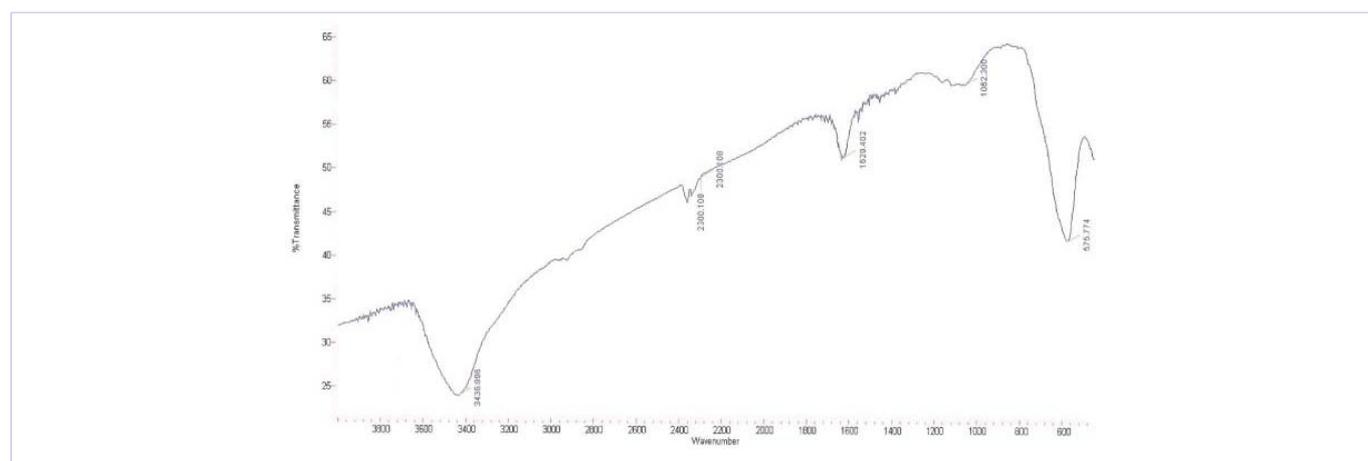
**Figure 2:** Nanoimaging of ferrimagnetic iron oxide nanoparticles by transmission electron microscopy (50-nm scale bar).

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  $\text{cm}^{-1}$  is observed in both spectra. The presence of AMPS is confirmed by the O-H stretch at 3200-3600  $\text{cm}^{-1}$ , C=O stretch at 1701  $\text{cm}^{-1}$  and N-H bend at 1636  $\text{cm}^{-1}$ . The presence of DVB is confirmed by the C=C aromatic stretches in the 1400-1600  $\text{cm}^{-1}$  region [17].

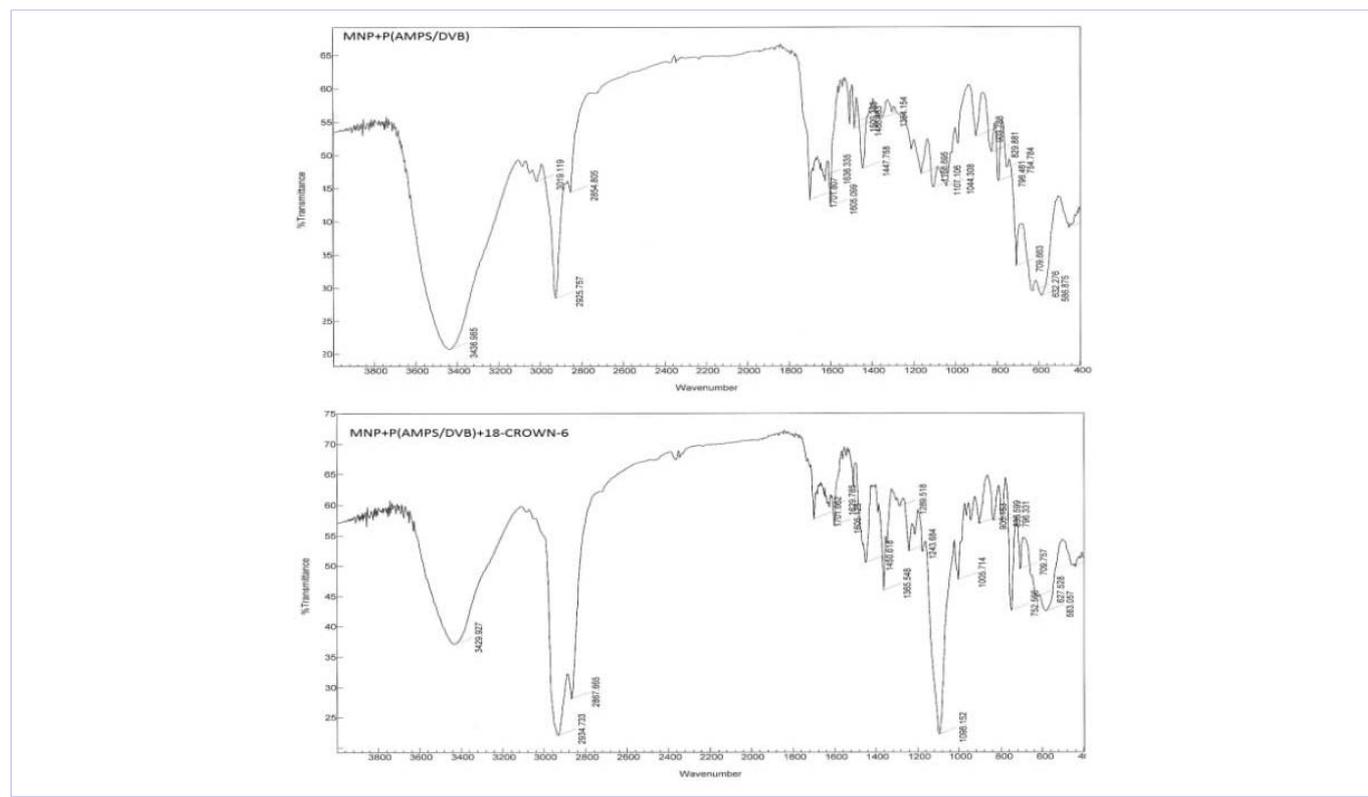
Figure 4B is the FTIR spectrum of 18-crown-6 impregnated P (AMPS/DVB)-coated MNPs. The binding of crown ether to the polymer is suggested to be electrostatic and hydrophobic

in nature. The C-O stretches at 1365  $\text{cm}^{-1}$  and 1098  $\text{cm}^{-1}$  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  $\text{Sr}^{2+}$  binding tests were carried out by measuring the characteristic gamma emission peak of Sr-85 [Table 2] using



**Figure 3:** FTIR spectrum of synthesized MNPs.



**Figure 4:** FTIR spectra of P (AMPS/DVB)-coated MNPs: (A) without and (B) with 18-crown-6.

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 separating the Sr<sup>2+</sup>- bound particles efficiently. 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 % Sr<sup>2+</sup> uptake accurately. As shown in Table 2, the % Sr<sup>2+</sup> uptake for the 18-crown-6-impregnated P (AMPS/ DVB)-coated MNPs is 66% (± 15%) where as for the non-impregnated P (AMPS/ DVB)-coated MNPs it is 23% (± 10%). Although 81% and 50% bindings seem like a large spread of the individual results, it is regarded as reasonable considering the very low gamma activity of 1-2 Bq remaining in the samples. This statistically significant difference,

**Table 1:** Sample preparation for Sr (II) measurement using Hidex Triathler.

<b>Total sample volume</b>	<b>1 mL</b>
Concentration of MNP+P solution	20 mg/ mL
Amount of MNP+P solution used	0.5 mL
Amount of Sr (II) stock added	0.1 mL
Amount of DDW	0.4 mL
Method of removing particles	Magnetic separation
Equilibration time	10 min

**Table 2:** Results of Sr- 85 radiation measurement.

Description	Gross cpm	B kg cpm	Net cpm	Net cps	Activity (Bq)	% Sr Uptake
Control 1	665	522	105.18	1.75	4.43	
Control 2	679	549	119.18	1.99	5.02	
Control 3	660	573	100.18	1.67	4.22	
average					4.56	
<b>MNPs + P+ crown</b>						
1	580	558	20.18	0.34	0.85	81.34
2	613	555	53.18	0.89	2.24	50.84
3	597	554	37.18	0.62	1.57	65.63
Average						65.94
<b>MNPs + P without crown</b>						
1	656	567	96.18	1.6	4.05	11.09
2	639	564	79.18	1.32	3.34	26.81
3	634	576	74.18	1.24	3.12	31.43
Average						23.11

between 66% (± 15%) and 23% (± 10%), demonstrates the effectiveness of the crown ether used in binding Sr<sup>2+</sup>. It must be noted that DtBuCH18C6 is able to weakly coordinate cations such as K<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>, Y<sup>3+</sup> and Pd<sup>2+</sup> as well as Sr<sup>2+</sup> [19]. Further optimization of sorption conditions is needed to improve the observed sorption efficiency. The uptakes of Sr<sup>2+</sup> by non-crown ether impregnated polymeric MNPs can be explained by the fact that the polymer is anionic (with the sulfonic acid functionality) and can electro statically bind the cation.

Our findings demonstrate the efficiency of DtBuCH18C6 in binding Sr<sup>2+</sup> and the use of magnetism for rapid separation of the hybrid MNPs. Magnetic susceptibility measurements using either Superconducting Quantum Interference Device (SQUID) or a vibrating sample magnetometer can be done to determine the magnetic strength of synthesized MNPs and the subsequent loss (if any) after polymer coatings and crown ether impregnation.

## Conclusion

This work demonstrated the significance of magnetic separation, rather than centrifugation/ filtration, as a rapid, efficient, and energy saving method for sample treatment in analytical applications. The polymeric crown ether hybrid material synthesis was completed successfully as evident from the FTIR spectra. Strontium binding tests successfully showed 66% (± 15%) uptake by the crown ether-bound MNPs, which was superior to only 23% (± 10%) by the non-bound particles. The MNP core made separation (after the binding tests) simple and efficient, requiring only the presence of an external magnetic field. A magnetic separation time of 1-2 min is demonstrably superior to all existing methods of liquid-liquid extraction and extraction chromatography. Further research work would be conducted in developing an automated system for radioactive Sr<sup>2+</sup> determination based on MNPs. A number of works have reported the recent advancement of imprinting methods for crown ethers; [20] they can be readily adapted to expand the applicability of magnetic separation in this rapidly growing field of research.

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