

DECONTAMINATED RADIOACTIVE WATER FROM RADIONUCLIDES BY MAGNETIC NONOPARTICLES

Asia H. Al-Mashhadani¹, Zain Abidin A. Hassen²

Abstract: There are many studies have confirmed that water was contaminated with radioactive cesium (¹³⁷Cs), this radionuclide was needed to be separated from contaminated water. There are many methods were used to separated radioactive ¹³⁷Cs from water. The goal of this research was to study the capacity of the Prussian blue material by applied external magnetic field for the ¹³⁷Cs separation from water. This goal was achieved by preparing magnetic poly (diallyldimethylammonium chloride)-coated Fe_3O_4 (PDDA- Fe_3O_4) nanoparticles. The results showed that Fe_3O_4 /PDDA nanocomposites have excellent future using as a carrier for bonding with ¹³⁷Cs particles i.e. decreasing the concentration of ¹³⁷Cs in contaminated water. The concentration of radioactive ¹³⁷Cs in water was measured by gamma spectroscopy using HPGe detector. The magnetic material was studied using scanning electronic microscope (SEM), Fourier-transform infrared (FTIR) and X-ray diffraction (XRD).
Keywords: Contamination, ¹³⁷Cs, magnetic nanoparticles.

I. INTRODUCTION

Radioactive cesium (¹³⁷Cs) removal has become an emerging issue after the Fukushima Daiichi Nuclear Power Plant Disaster [1]. Thus, radioactive cesium due to its high radioactivity and relatively long half-life time (30.2 years) is a significant component of nuclear wastes and nuclear fallout [2]. The cesium is water-soluble and behaves similarly to potassium and sodium in the biological behavior profile. Additionally, a high dose of radioactive ¹³⁷Cs can induce medullar dystrophy and disorders of reproductive function [3]. Moreover, it can cause a number of negative health effects, including carcinoma of the liver, kidney, bladder, renal functions, cardiovascular disease and gastrointestinal distress [4]. Prussian blue, known as ferric (III) hexacyanoferrate(II), is a pigment of dark blue color and was one of the first synthetic dyes. Prussian blue is a complex composed of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot X\text{H}_2\text{O}$ ($X = 14-16$) with a cubic face-centered lattice structure[5]. Prussian blue is known as a low-cost adsorbent, which has a high selectivity for cesium, including a high stability, high conductivity, biocompatibility, size controllability and easy surface functionalization for decomposition[6]. Furthermore, Prussian blue is a typical FDA-approved drug used in clinics for the safe treatment of radioactive exposure [7]. Additionally, magnetic nanoparticles can be easily separated from a treated solution by the simple application of either a permanent or electro magnet and have made it possible to

¹ Department of Physics, College of Science, Baghdad University

² Department of Physics, College of Science, Baghdad University

utilize several advantages of the sorbent without the typical difficulty associated with the separation of nanoparticles from solution[8,9]. In this study, modified Prussian blue, including Fe_2O_3 magnetic nanoparticles, was synthesized and characterized by Fourier-transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

II. EXPERIMENTAL SECTION

2.1. Chemicals

All chemicals used in this work were of analytical reagent grade. Deionized water was used throughout the study. Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), potassium hexacyanoferrate(II) trihydrate ($\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$), poly(diallyldimethylammonium chloride) (PDDA) solution (20 wt%, MW 400,000~500,000), ammonium hydroxide (NH_4OH) and hydrochloric acid (HCl), radioactive cesium chloride (^{137}Cs).

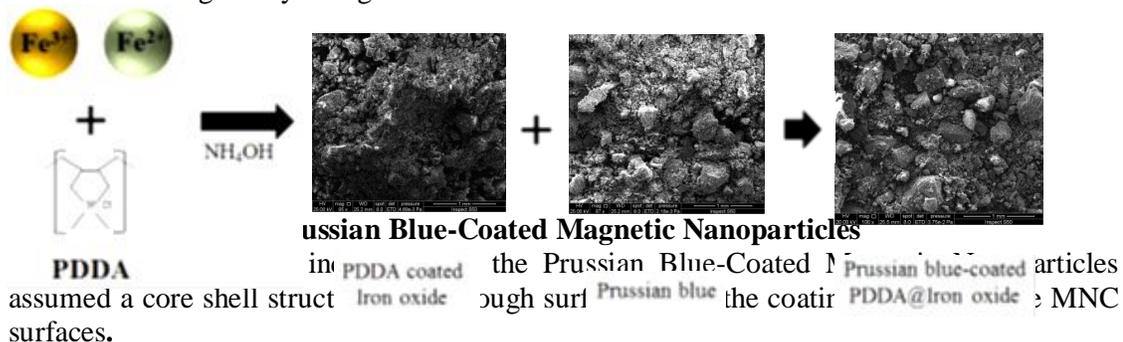
2.2. Preparation of Prussian blue Coated-PDDA@Iron Oxide Nanoparticles

Heating deoxygenate (20 ml) solution containing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.16 g), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.8 g) and PDDA to 80 °C. Subsequently, rapidly NH_4OH was added to the heated solution, which was left to stir for another 1 h. After cooling to room temperature, the formed PDDA- Fe_3O_4 NPs were isolated with the help of a magnetic field and washed three times with deionized water. Additionally, these were dried at room temperature. Finally, purified PDDA-coated iron oxide nanoparticles (PDDA@Iron oxide) were obtained. PDDA@Iron oxide (0.1 g) was dispersed in 10 mL of deionized water, and 0.01 M HCl were added to adjust the pH to 6.0. Prussian blue (0.3 g), the pH of which ranges from 2.4 to 2.7, was dispersed in 10 mL of deionized water, to which 0.01 M NaOH was added to adjust the pH to 6.0.

III. RESULTS AND DISCUSSION

3.1. Synthesis of Prussian Blue-Coated Magnetic Nanoparticles

The surface of a coated iron oxide nanoparticle, was coated by Prussian blue. In this case, the PDDA@Iron oxide nanoparticles can act as nucleation sites for the precipitated Prussian blue, resulting in the coating of the Prussian blue on to the PDDA@Iron oxide nanoparticle surface. Synthetic procedures for Prussian blue-coated magnetic nanoparticles are presented in Figure 1. The scheme represents that the adsorbents are composed largely of negatively-charged Prussian blue with a smaller amount of positively-charged PDDA@Iron oxide and that the surface area of the positively-charged PDDA@Iron oxide nanoparticles is entirely covered with negatively-charged Prussian blue.



FTIR spectra indicate that the peaks of bands at 2800 cm^{-1} and 1900 cm^{-1} of Prussian blue-coated PDDA@Iron oxide as shown in Fig (2)

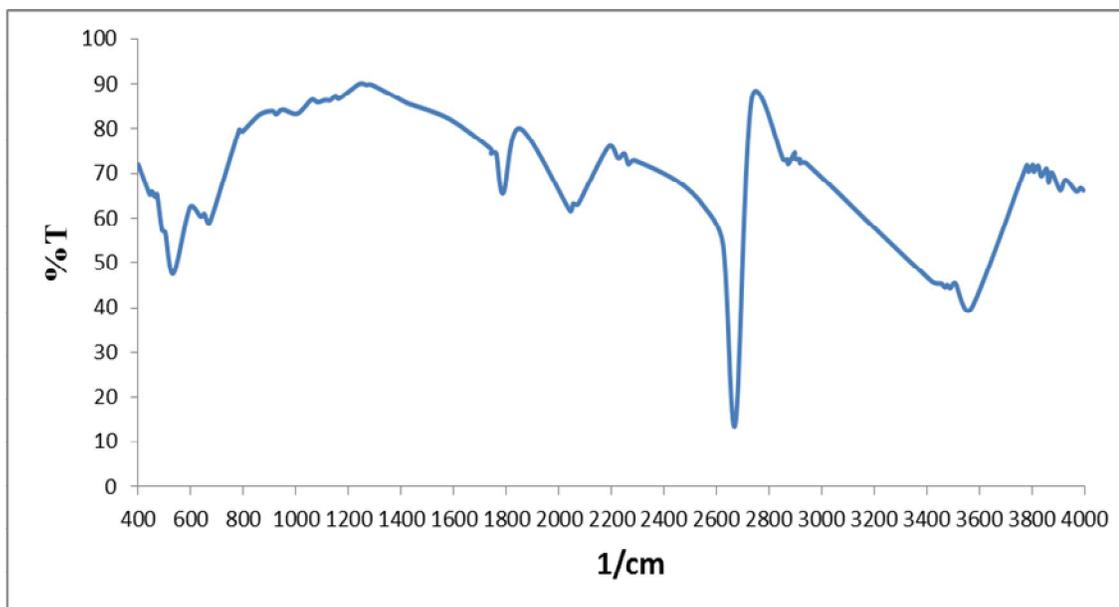


Fig (2): Fourier-transform infrared (FTIR) spectra of Prussian blue-coated PDDA@Iron oxide

Prussian Blue-Coated Magnetic Nanoparticles at 31.14 in good agreement with the characteristic peaks of Prussian blue-coated PDDA@Iron oxide Fourier transform infrared spectroscopy (FTIR) analysis using the attenuated total reflection (ATR) mode also revealed the successful coating of Prussian blue-coated PDDA@Iron oxide on the MNC surfaces. A new strong absorption peak corresponding to the cyanide group (-CN) stretching vibration appeared at 2200 and 1000 cm^{-1} in FTIR spectra of Prussian Blue-Coated Magnetic Nanoparticles, indicating the formation of PB (Fig. 2).

Fig. 3 shows the XRD patterns of Prussian blue displays a strong peak notably at $2\theta = 31.140^\circ$

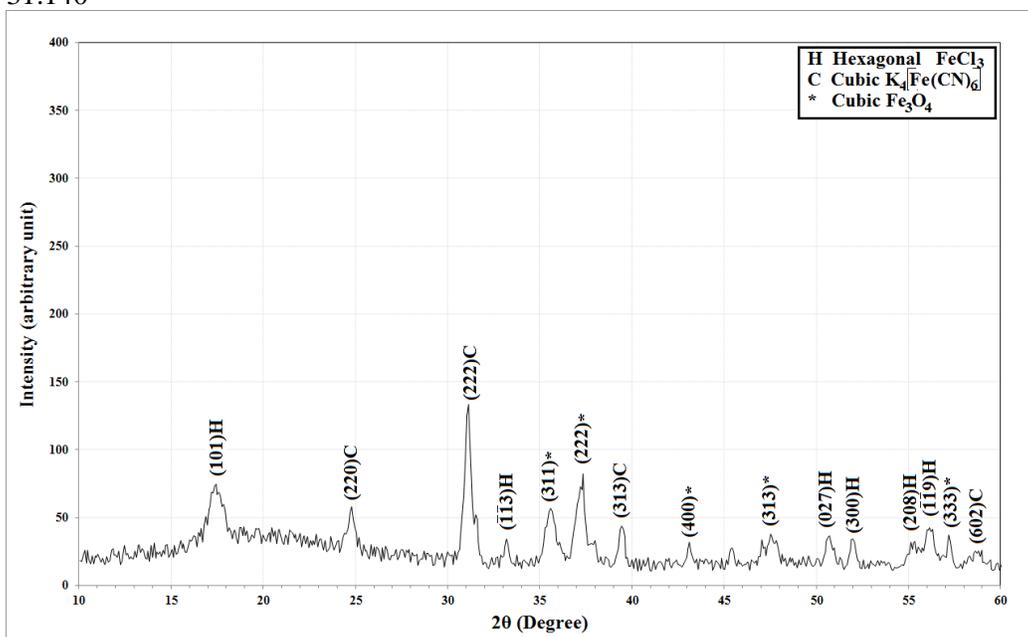


Fig (3): X-ray diffraction (XRD) peaks of Prussian blue-coated PDDA@Iron oxide

The XRD patterns obtained from Prussian Blue-Coated Magnetic Nanoparticles are shown in Fig. 3. Comparison with the XRD patterns obtained from the MNC revealed that four new diffraction peaks were observed in all Prussian blue-coated magnetic nanoparticles. Energy dispersive x-ray (EDX) spectrum of Prussian blue-coated PDDA@Iron oxide particles which show the elemental analysis of the Prussian blue-coated PDDA@Iron oxide revealed the presence of Ru, Cl, C, N, Co, in and Fe. As expected from the chemical formula, the elemental contents of Fe, Cl and Ru were higher as shown in Figure 4

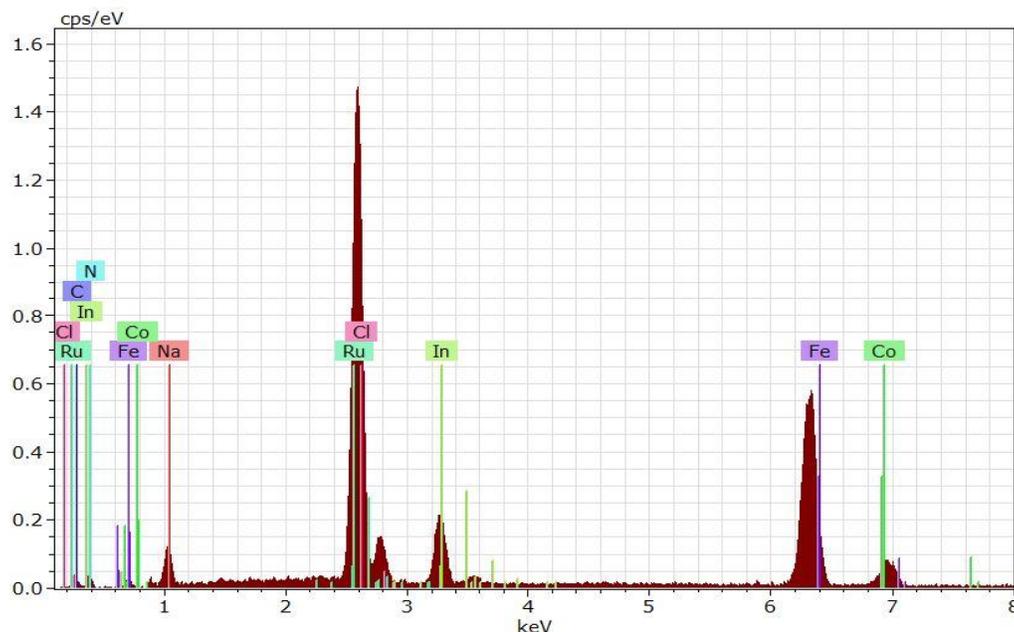


Fig (4): Energy dispersive X-ray (EDX) spectrum of Prussian blue-coated PDDA@Iron oxide

Prussian blue, and especially potassium iron ferrocyanide, can be obtained through a reaction between hexacyanoferrate ions and ferric ions if an excess of potassium hexacyanoferrate is used as the starting reagent. After the reaction between the Prussian Blue-Coated Magnetic Nanoparticles and potassium hexacyanoferrate, the aqueous solution turned a dark blue, indicating the formation of Prussian blue. As the concentration of potassium hexacyanoferrate increased from 0.5 mg to 2 mg, the color of Prussian Blue-Coated Magnetic Nanoparticles solution changed from dark blue to blue due to an increase in PB formation on the surface of Prussian Blue-Coated Magnetic Nanoparticles.

3.2. Removal of Radioactive Cesium

Because the natural background counts in deionized water were below the detection limit of the gamma counter (0.0067 ppb as Cs ions). Therefore deionized water was contaminated by different values of ^{137}Cs radionuclides as shown in Fig.5. Then mass of Prussian blue-coated PDDA@Iron oxide added to contaminated waters then this solution exposed to permanent magnet and the decontaminated water were measured (Fig. 5A and B). It was found that the radioactivities of the water for ^{137}Cs were reduced significantly and removal efficiency was 96%. as shown (Fig.5C).

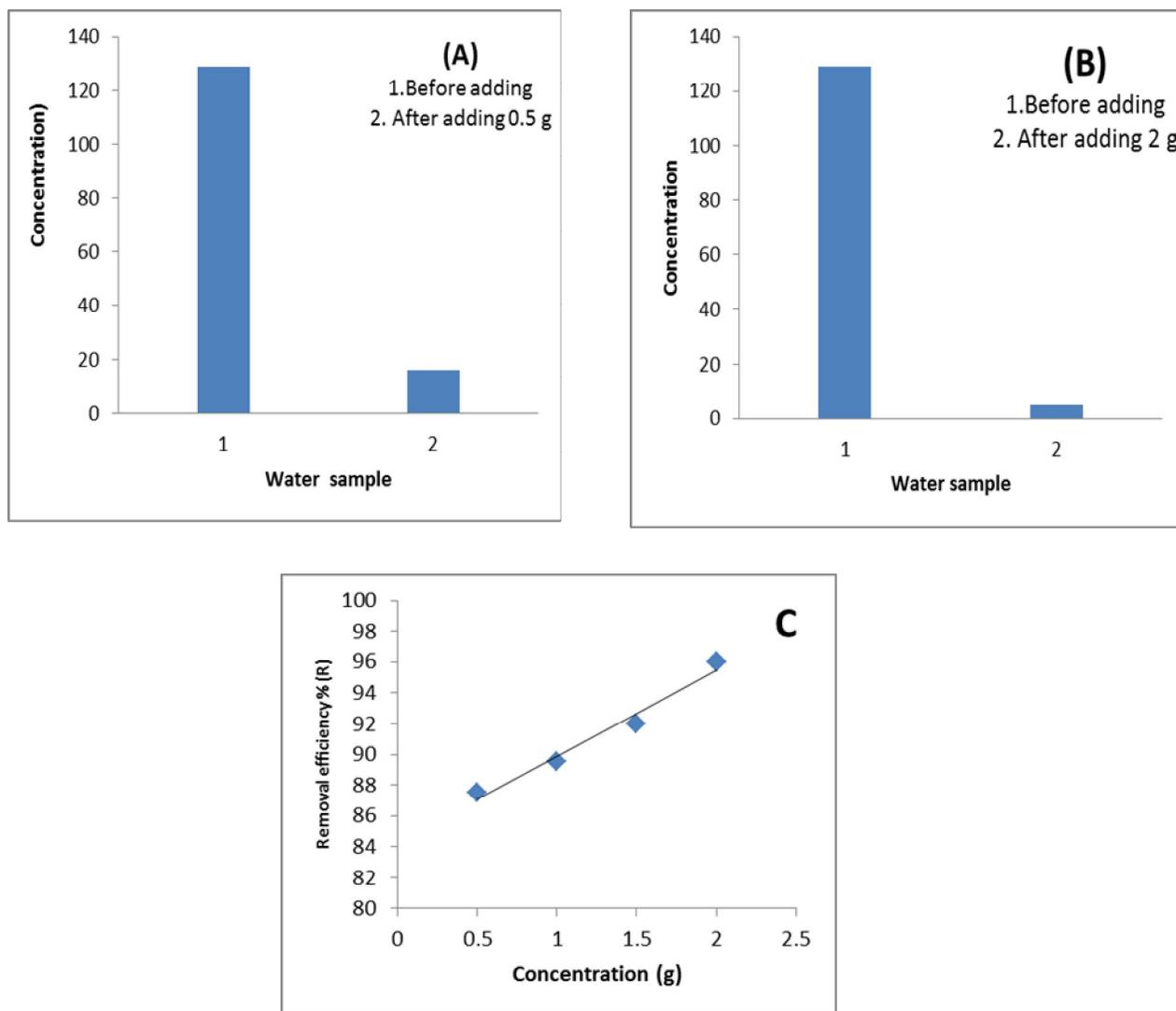


Fig (5) : The relation between the Removal efficiency (R) and concentration of of Prussian blue-coated PDDA@Iron oxide

IV. CONCLUSIONS

Prussian blue-functionalized magnetic nanoclusters with selective adsorption toward Cs and a high K value of 33,471 ml/g were successfully fabricated for the removal of radioactive cesium from water and rapid magnetic separation of the adsorbent. Furthermore, Prussian Blue-Coated Magnetic Nanoparticles displayed excellent removal efficiency for Cs-137 from contaminated water, with more than 98. %. Therefore, Prussian blue-functionalized magnetic nanoclusters demonstrated good potential for the treatment of Cs-137 contaminated water.

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