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The Effect of Gamma Irradiation on the Ion Exchange Properties of Caesium-Selective Ammonium Phosphomolybdate-Polyacrylonitrile (AMP-PAN) Composites under Spent Fuel Recycling Conditions

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Abstract: The caesium radioisotopes ^{134}Cs, ^{135}Cs, and ^{137}Cs are highly problematic medium-lived species produced during nuclear fission, due to their high radioactivity and environmental mobility. While many ion exchange materials can readily isolate Cs^+ ions from neutral or basic aqueous solutions, only ammonium phosphomolybdate (AMP) functions effectively in acidic conditions, removing caesium even down to trace levels. Composites of AMP in a porous polymeric support such as polyacrylonitrile (PAN) can be used to selectively remove Cs^+ ions from acidic aqueous decontamination liquors as well as other liquid wastes, and are promising for the isolation of Cs^+ isotopes in spent fuel reprocessing. While both AMP and PAN have demonstrable acid stability, and PAN has known resistance to gamma radiation, AMP-PAN composites have received only a limited analysis of their physiochemical and ion exchange performance following irradiation. In this publication, we explore the effect of high levels of gamma irradiation on the ion exchange properties of AMP and AMP-PAN as a Cs^+-selective adsorbent under spent fuel dissolver liquor concentrations and acidity. We demonstrate no significant reduction in performance with respect to uptake kinetics or capacity upon irradiation, abiding by the same absorption mechanism observed in the established literature.

Keywords: AMP-PAN; ion-exchange; composites; chromatographic separation; fission product; caesium; spent fuel reprocessing; waste management; radiation effects

1. Introduction

Nuclear power will be essential to meet the targets of the Paris agreement, reducing carbon emissions to prevent the further warming of planet Earth [1]. However, nuclear fission reactions generate hazardous medium- and long-lived radionuclide by-products [2]. Some of these, including the radioisotopes of Cs ($^{134}Cs - t_{1/2} = 2.1$ y; $^{135}Cs - t_{1/2} = 2.3$ My; and ^{137}Cs; $t_{1/2} = 30.2$ y) [2,3], are difficult to selectively isolate and are environmentally mobile [4–6], leading to concerns about their long-term storage and disposal.

While many natural materials (such as clay) and synthetic ones (such as hexacyanoferrates and various phosphates) can selectively remove and retain Cs^+ ions from aqueous solutions at neutral or basic pH values, few of these operate well in acidic media [7–14], with the exception of ammonium

phosphomolybdate (AMP, $(NH_4)_3PMo_{12}O_{40}$) [15–18]. AMP, a finely powdered material, is often used as a porous composite in a polyacrylonitrile matrix (PAN) to facilitate column processing [17–20]. It has been demonstrated to effectively remove Cs^+ down to trace levels from decontamination liquors [19] and tank wastes [21], and is theorised to be an effective heterogeneous Cs^+ absorber for spent-fuel recycling liquors [22], even in the presence of high concentrations of other alkali metals [23]. Both AMP and PAN are known to be radiation- and acid-resistant, but to our knowledge, little research has investigated the ion exchange properties of this or similar composites after exposure to high levels of gamma radiation [13,16,18,19]. While Sebesta et al. [18] undertook a preliminary investigation into the effects of γ radiation up to 1 MGy on AMP-PAN, the adsorption conditions used were reminiscent of those found in wastes: low (1 M) acidity and minimal (50 μM) Cs^+ concentration. The works of Rao et al. [24] and later Narasimharao et al. [25] explored the effect of up to 200 MGy β^- irradiation on AMP with no negative effects on ion exchange performance observed at 2 MGy exposure, but at 100 MGy and above, the effect of radiation severely was found to diminish the desired action of AMP [25].

In previous work [22], we proposed a sequential, continuous chromatographic approach to spent fuel recycling for the safe and ready removal and disposal of problematic radionuclides, eliminating a significant proportion of heat-generating species from process waste streams. We have recently proven the efficacy of this proposed method by demonstrating the ability of AMP-PAN to selectively sequester Cs^+ from 250 times this concentration of Ce^{4+} (as a U surrogate) in 3 M nitric acid [26]. Developing upon this idea, in this publication, we explore the effect of 100 kGy gamma irradiation on the Cs^+-specific ion exchange performance of AMP and AMP-PAN under the acidity and Cs^+ concentrations found in spent fuel recycling with respect to capacity, rate of uptake, and absorption mechanism.

2. Materials and Methods

2.1. Materials, AMP-PAN Composite Preparation and Characterisation

Ammonium phosphomolybdate (AMP, $(NH_4)_3PMo_{12}O_{40}$, Merck, NJ, USA), polyacrylonitrile (PAN, molecular weight 80,000, Merck, NJ, USA), Tween 80 (Merck, NJ, USA), dimethyl sulfoxide (DMSO, Merck, NJ, USA), caesium nitrate, (Merck, NJ, USA) and nitric acid (Merck, NJ, USA) were obtained as reagent grade precursors and used as procured with no further purification required. Deionised water (>18 MΩ/cm) was used for all experiments.

A 70% (by weight) composite of AMP contained within a porous support substrate of PAN (henceforth referred to as AMP-PAN) was prepared using the well-established method of Park et al., with minor modifications as noted [27]. A measurement of 200 mL of DMSO was heated to 50 °C in a water bath with overhead stirring at 250 rpm, and mixed with 0.8 g of Tween 80. To this was added 28 g of AMP powder. The mixture was stirred at 50 °C for 1 h to fully disperse the AMP, forming a homogenous yellow-green suspension. Then 12 g of PAN was added to this suspension over about 10 min and the mixture was maintained at 50 °C with stirring for 6 h to fully dissolve the PAN. The mixture was then sprayed with compressed air into a large excess of deionised water through a confined jet nebuliser [28] (rather than dropwise addition under gravity as per Park's work [27]), forming 2–3 mm sized, spherical, porous beads of AMP-PAN. The spheres were left in the water overnight and subsequently washed three times with a large excess of deionised water, allowing 30 min for equilibration each time. The washed beads were then sieved and air-dried at 60 °C for 24 h. Optical images were recorded using a Sony Xperia XA1 (Sony Ltd. Tokyo, Japan) equipped with an Sony Exmor RS 23 MPixel sensor and a Sony 24 mm wide-angle f2.0 lens under ambient lighting. Surface areas were determined using the Brunauer–Emmett–Teller (BET) model at 77 K using nitrogen absorption (Micrometrics ASAP2020Plus, Nocross, GA, USA), with accuracy checked against an alumina standard. Scanning electron microscopy (SEM) was conducted under high vacuum using an FEI Quanta 200 scanning electron microscope (Hilsboro, OR, USA) equipped with an EDAX Sapphire Si(Li) elemental analyser (Mahwah, NJ, USA). Fourier Transform Infra-Red (FTIR) analysis was conducted using a Thermo Scientific Nicolet iS5 spectrometer (Waltham, MA, USA) equipped with an ATR diamond lens, recorded in the absorption mode.

2.2. Irradiation

Dry AMP powder and AMP-PAN were both irradiated in sealed vials with gamma radiation (1.173 MeV and 1.333 MeV) at a rate of 60 Gy/min, to an exposure of 100 kGy using a using a Foss Therapy 812-self-shielded ^{60}Co irradiation source located at the Dalton Cumbrian Facility, Whitehaven, UK.

2.3. Ion Exchange Performance

The ion exchange performance was measured as follows: 0.175 g of AMP or 0.25 g of AMP-PAN was exposed to 25 mL of 5.0 (665 ppm) or 10.0 mM (1330 ppm) Cs^+ solution in 3 M nitric acid, replicating the range of Cs^+ concentrations and the acidity of spent fuel recycling liquors. Aliquots were taken after 10, 20, 30, 60, 180, 360, and 1440 min and analysed for Cs^+ concentration by ICP-MS using a Thermo Fisher X-Series analyser. Triplicate analysis was performed for all ICP-MS samples with average standard deviations from $\sigma = 0.001$ to 0.047.

Distribution coefficients (K_d, mL/g) were calculated according to Equation (1) [29], where C_0 and C_e are the starting and equilibrated concentrations of Cs^+, respectively (ppm), V is the volume of liquor contacted with the adsorbent (25 mL), and m is the mass of adsorbent used (0.175 or 0.25 g for AMP and AMP-PAN, respectively) [29]:

$$Kd = ((C0 - Ce)/Ce).V/m. \tag{1}$$

Kinetic analysis was performed by comparing the acquired adsorption data to Langmuir and Freundlich isotherms. These require the calculation of q_e (equilibrium absorption, mg/g), according to Equation (2) [29]:

$$q_e = (C_0 - C_e).V/m. \tag{2}$$

The Langmuir and Freundlich isotherms are expressed as Equations (3a) and (4a) [29]. Rearranging these equations give straight line plots for pseudo-first-order Langmuir (Equation (3b)) or second-order Langmuir or Freundlich (Equations (3c) or (4b)) processes [29]. Q^0 and K_l are the Langmuir constants for absorption capacity (mg/g) and energy of adsorption (L/g), and K_f and n are the Freundlich constant (mg/g) and the adsorption intensity constant, respectively [29–31].

$$q_e = (Q^0.K_L.C_e)/(1 + K_L.C_e) \tag{3a}$$

$$1/q_e = 1/Q^0 + (1/K_l.Q^0.C_e) \tag{3b}$$

$$C_e/q_e = 1/K_l.Q^0 + C_e/Q^o \tag{3c}$$

$$q_e = K_f.C_e^{1/n} \tag{4a}$$

$$\log q_e = \log K_f + 1/n.\log C \tag{4b}$$

3. Results and Discussion

3.1. Overview

A thorough investigation with respect to the effect of gamma irradiation on the physiochemical properties of AMP and AMP-PAN, and the likely mechanism of this process, is underway and will be published separately in due course. The most profound visible effect we observe following irradiation, however, is a marked colour change (AMP from yellow to green, AMP-PAN from lime green to dark green, as shown in Figure 1), reminiscent of the literature references [18,24,25], and theorised as a result of Mo^{VI} to Mo^V reduction [24,25], which is reversible upon immersion in 3 M HNO_3 [25]. Preliminary results suggest a reduction in the porosity of the AMP-PAN composite and a decrease in thermal stability above 120 °C, but this does not affect the material at intended operational temperatures (<100 °C) when sequestering Cs^+ in spent fuel recycling. For reference, the AMP-PAN beads used here possess a BET surface area of 21.56 m^2/g and an average pore diameter of 5.24 nm, comparable to our previous work [26]. The porous cross-section of a bisected AMP-PAN

bead is shown in Figure 1, showing that the structure of our dissected bead is comparable with all previously published information [13,20,27], given the identical preparative route. The use of a confined-jet nebuliser serves merely to decrease the size of the beads formed, increasing absorptive efficiency [28]. The FTIR spectrum of our produced AMP-PAN (Figure 2) matches those of prior literature references [27].

AMP adsorbs caesium ions from aqueous solution by exchange with the ammonium ions in the crystal structure (phosphomolybdate anion pictured in Figure 1)—as per Equation (5), where $0 \leq x \leq 3$—through pores in the crystal structure [25]. Caesium phosphomolybdate ($Cs_3[PMo_{12}O_{40}]$, CsMP, $x = 3$) can be prepared synthetically and has been studied [32], although in ion exchange environments only about two thirds of the NH_4^+ ions in AMP ($x = 2$) are typically replaced with Cs^+ [15,33]. The theoretical capacity of AMP is 220 mg/g Cs at $x = 3$.

$$(NH_4)_3[PMo_{12}O_{40}]_{(s)} + xCs^+_{(aq)} \rightarrow (NH_4)_{3-x}Cs_x[PMo_{12}O_{40}]_{(s)} + xNH_4^+_{(aq)} \qquad (5)$$
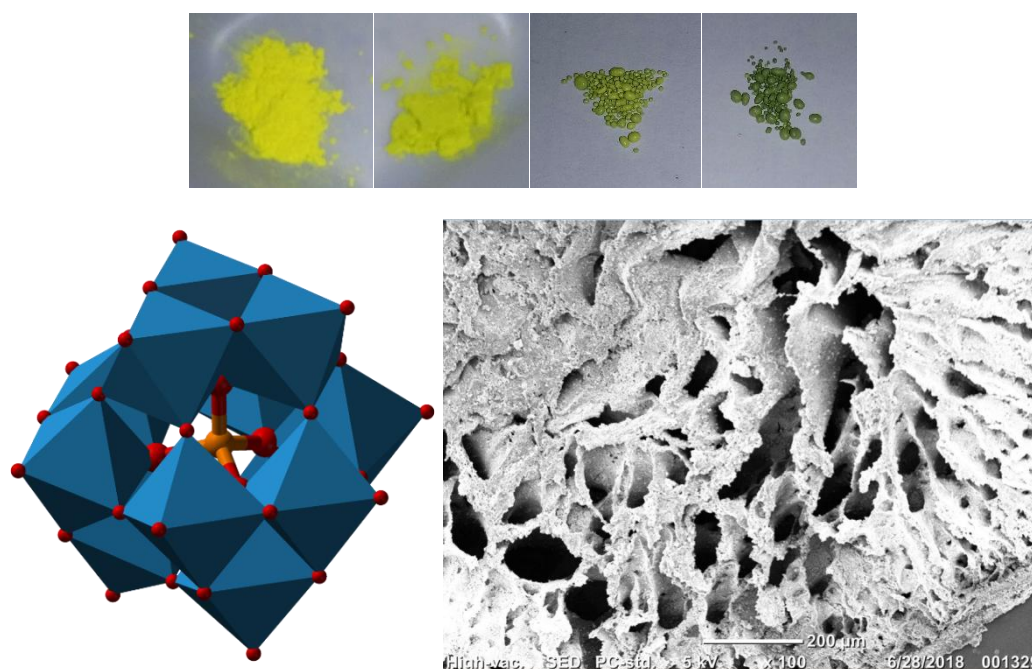

Figure 1. Top: The observed colour changes of ammonium phosphomolybdate (AMP) powder (left two images) and AMP-polyacrylonitrile (PAN) beads (right two images) upon 100 kGy γ irradiation. Below, left: Keggin structure of the phosphomolybdate anion ($PMo_{12}O_{40}^{3-}$). MoO_6 octahedra: blue; P: orange; O: red [22]. Open source image: Wikimedia commons; right: SEM micrograph of bisected virgin AMP-PAN bead.
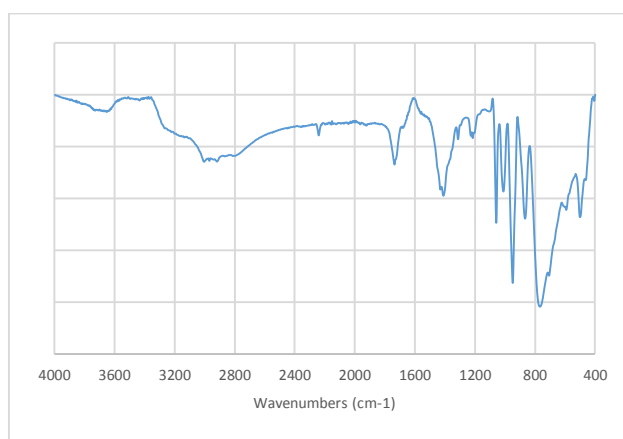

Figure 2. FTIR absorption spectrum of AMP-PAN beads.

3.2. Ion Exchange Performance

We explored the rate of uptake and capacity of Cs^{+} for virgin and irradiated AMP and AMP-PAN using two different Cs^{+} concentrations in 3 M HNO$_3$: 5.0 and 10.0 mM, replicating the acidity [34] and Cs^{+} concentration [22] for spent fuel recycling of the present and future and higher-burnup fuels, respectively. The observed Cs^{+} uptake is shown as capacity as a function of time in Figure 3A–D, and the associated distribution coefficients (K$_d$) of each sample after 24 h are shown in Figure 4.

The uptake of Cs^{+} by AMP (Figure 3A,B) is rapid, achieving near complete uptake (>98%) within 10 min, independent of the Cs^{+} concentration initially present. The capacity is proportional to the concentration of Cs present in the solution, reaching near the theoretical maxima for AMP: 5.0 mM, 94.9 mg/g; and 10 mM, 189.9 mg/g. Irradiation has no discernible effect on either the rate of uptake or capacity by AMP.

The Cs capacity of AMP-PAN composites (Figure 3C,D) is similarly proportional to the Cs^{+} concentration used. Uptakes at both Cs^{+} concentrations are rapid, as per AMP, reaching a maximum within 10 min of exposure for both virgin and irradiated AMP-PAN samples; the theoretical maxima of capacity (5.0 mM, 66.3 mg/g; 10 mM, 132.8 mg/g) is approached. As the AMP-PAN composite is 70% by weight AMP, the resulting capacities are therefore 70% lower than those of AMP. The slight increase in the Cs^{+} capacity of AMP induced by β^- irradiation reported by Rao et al. [24,25] was not observed here.

Due to the sensitivity of Equation (1) (for the calculation of distribution coefficients) at near complete Cs^{+}, small variations in the observed uptake result in significant variations in the value of the distribution coefficient (K$_d$). At complete (100%) uptake, K$_d$ = ∞. Figure 4 highlights the affinity of AMP for Cs^{+} is maintained [30] across the range of concentrations tested, with irradiation having a negligible impact on the uptakes.
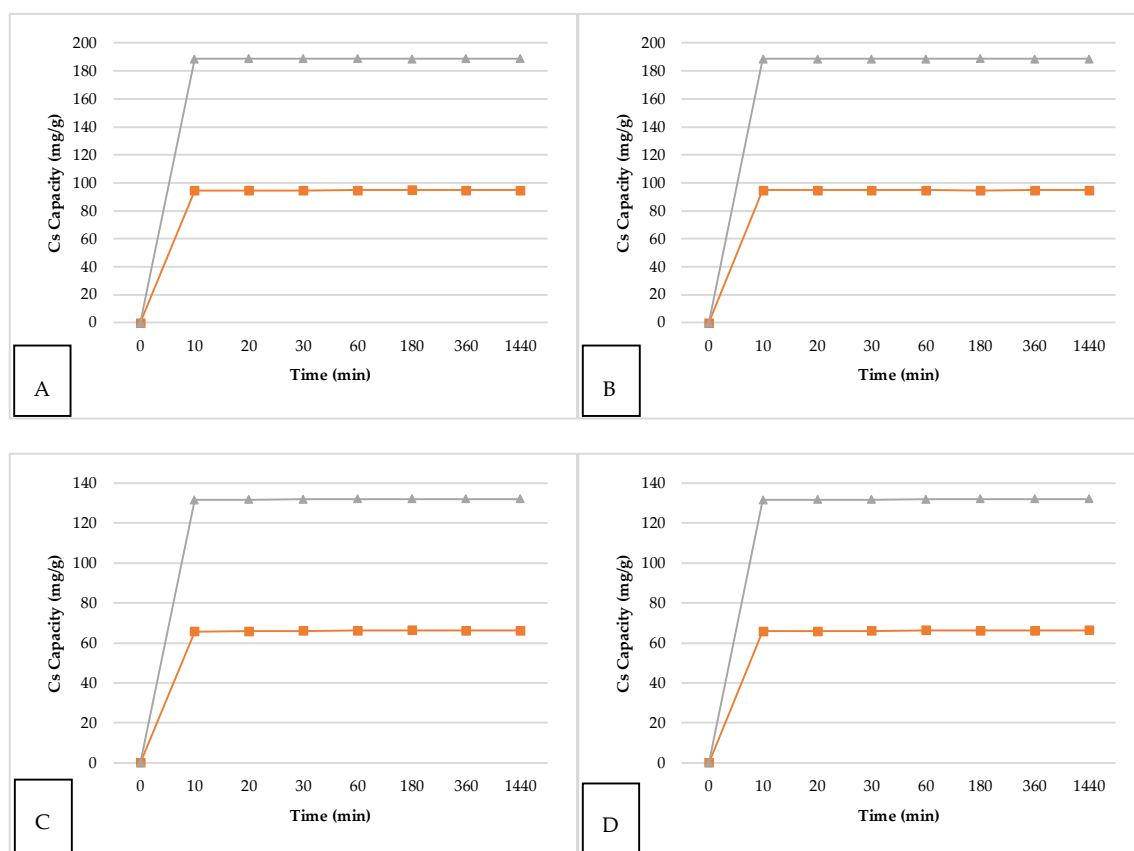

Figure 3. Measured Cs^{+} capacities (mg/g) over time (min) for 5.0 mM (orange squares) and 10.0 mM Cs^{+} in virgin AMP (top left, **A**), irradiated AMP (top right, **B**), virgin AMP-PAN (bottom left, **C**), and irradiated AMP-PAN (bottom right, **D**) from 3 M HNO$_3$ solution.
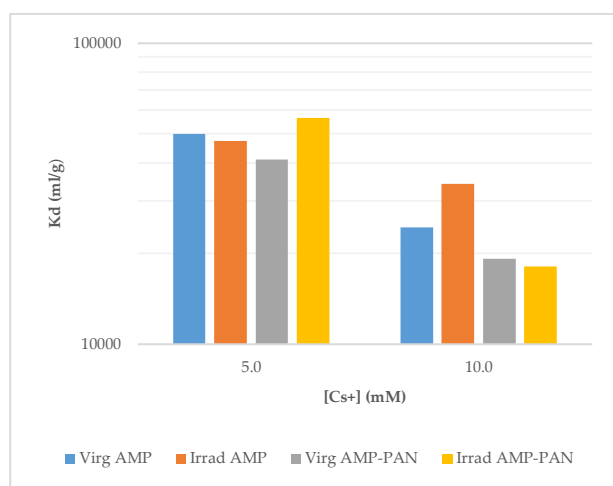
Figure 4. Variation of 24 h exposure Cs^+ K_d values in AMP and AMP-PAN at 5 and 10 mM Cs in 3 M HNO_3. NB: *Y*-axis is logarithmic.

Figure 5A–D show the Langmuir (Equation (3c)) isotherm plots for virgin and irradiated AMP and AMP-PAN exposed to 5.0 and 10.0 mM Cs^+. The isothermal parameters and regression coefficients calculated from this data and the equivalent Freundlich isotherm interpretation [29] are presented in Table 1.
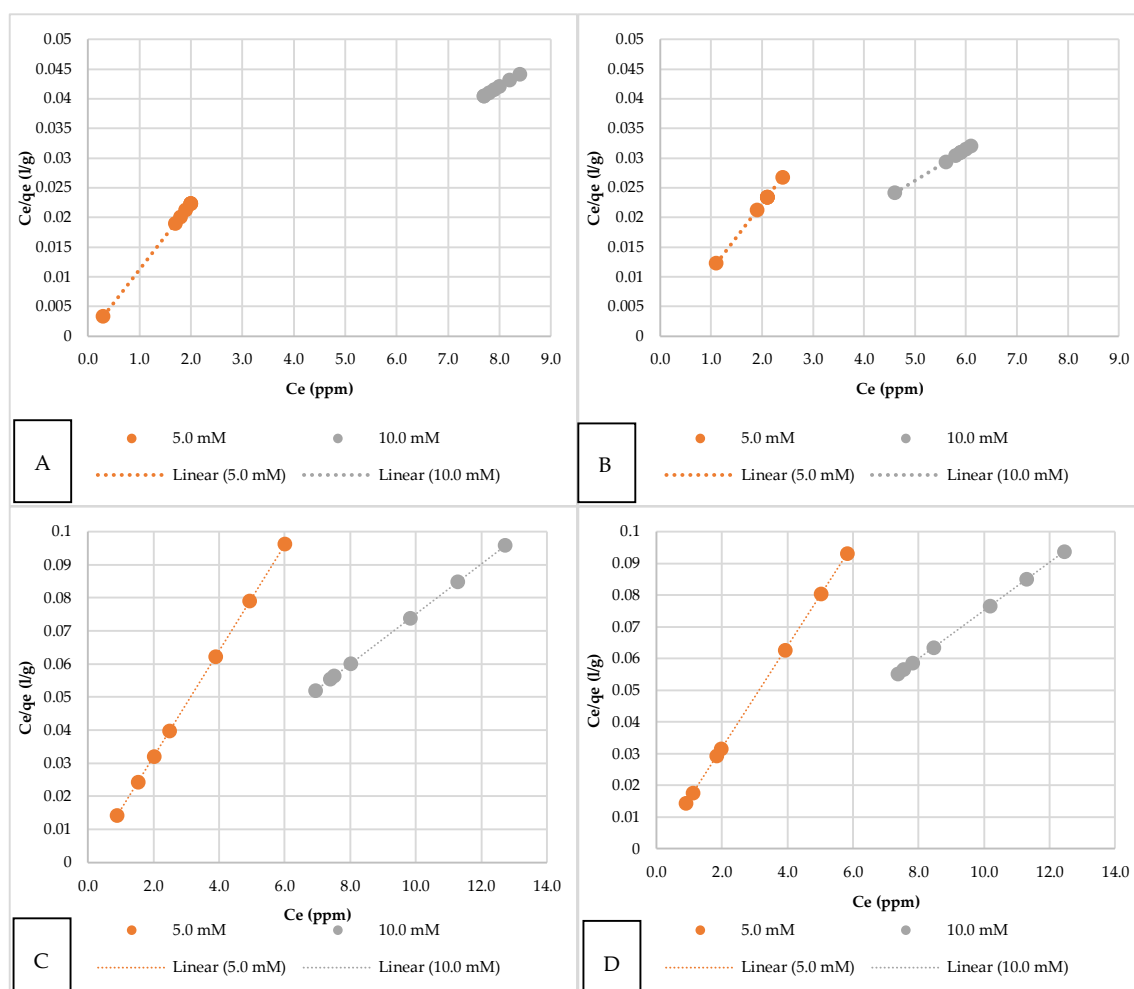

Figure 5. Pseudo-second-order Langmuir isothermal plots for virgin and irradiated AMP (top left and top right, **A**,**B**), and virgin and irradiated AMP-PAN (bottom left and bottom right, **C**,**D**), calculated from the data in Figure 3A–D.

Table 1. Comparison of calculated Langmuir and Freundlich isothermal parameters.

Isotherm	Parameter	AMP		AMP (Ir)		AMP-PAN		AMP-PAN (Ir)	
		5 mM	10 mM	5 mM	10 mM	5 mM	10 mM	5 mM	10 mM
Langmuir	Q_0 (mg/g)	89.28	188.68	89.28	188.68	62.50	131.57	62.50	131.57
	R^2	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Freundlich	K_F (mg/g, 1/n)	89.81	192.83	89.86	192.08	62.95	135.27	62.93	135.30
	R^2	0.990	0.999	0.991	0.999	0.935	0.995	0.952	0.996

As the data presented in Figure 4 demonstrate, the observed uptake of Cs^+ by AMP and AMP-PAN fits the pseudo-second-order Langmuir isotherm with a high regression coefficient (R^2), mirroring the previous work of Mahendra, Herbst, and Ding [20,30,35]. While the regression coefficients (R^2) for the Freundlich isotherm are close to 1, slopes of the lines produced by this method were negative, indicating a poor fit to the technique. Despite this, the calculated Langmuir absorption capacity constants (Q_0) and the Freundlich constants are in close agreement for the AMP and AMP-PAN system, and the Cs^+ concentrations investigated. No variation is observed between the virgin and irradiated material, indicating that irradiation does not negatively affect ion exchange performance, Cs^+ capacity, or the mechanism of uptake. Previous work by ourselves and numerous other researchers has demonstrated the selectivity of AMP-PAN for Cs^+ over other cations, and is thus beyond the scope of the results presented here [15–22,26].

4. Conclusions

In this publication we have demonstrated the effect of high levels (100 kGy) of gamma irradiation on the ion exchange performance of Cs-selective AMP and AMP-PAN composites containing 70% AMP. This level of irradiation thus has little or no effect on the ion exchange properties of both AMP and AMP-PAN. K_d values for Cs^+ at both concentrations tested remained above 10,000 after 24 h. Under the conditions we tested, both AMP and AMP-PAN follow pseudo-second-order absorption kinetics adhering to the Langmuir isotherm, mirroring previous results [20,30,36]. We have thus demonstrated the efficacy of AMP-PAN as a Cs ion exchange composite under the Cs^+ concentrations and acidity of spent fuel dissolver conditions following exposure to significant levels of gamma radiation.

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