



Linear and Non Linear Recognition for the Sorption of ^{60}Co and $^{152+154}\text{Eu}$ Radionuclides onto Bio CuO Nanocomposite

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Abstract

A novel nanocomposite was prepared by hybridizing polyacrylic acid/maleic acid with nano copper oxide (PAACMA/CuO) for the sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) radionuclides from an aqueous solution. Nano-CuO was biochemically produced by hydrolysing its salt in the presence of the *Aspergillus terreus* fungus. The PAACMA/CuO nanocomposite was characterized using a variety of analytical techniques. The optimum sorption conditions (pH 4.5 for ^{60}Co and pH 3.53 for $^{152+154}\text{Eu}$, 24 h of equilibrium time at 20 °C) were applied. The kinetic mechanism of the sorption reaction was controlled by pseudo second order based on residual charts, coefficient of determination (R^2), and corrected Akaike information Criterion (AIC_c). The sorption reaction mechanism was controlled by Langmuir model for linear regression using the coefficient of determination and the Dubinin-Radushkevich D-R model for the AIC_c and residual plots error functions. The reaction mechanism throughout non-linear regression was controlled by the D-R model due to the coefficient of determination, AIC_c , and residual charts. The PAACMA/CuO nanocomposite had a mono-layer adsorption capacity of 11.04 mg g⁻¹ for Co (II) and 21.54 mg g⁻¹ for Eu (III). According to desorption studies, Co (II) and Eu (III) could be recovered by 0.1 mol L⁻¹ EDTA with efficiencies 55.46% and 95.044%, respectively. According to thermodynamic studies, the sorption of Co (II) and Eu (III) on the prepared composite was endothermic and spontaneous.

Keywords Nano CuO biosynthesize · Polyacrylic acid/maleic acid/CuO nano composite · ^{60}Co and $^{152+154}\text{Eu}$ radionuclides · Sorption · Linear and non linear regression

Introduction

The global expansion of nuclear energy applications in fields such as agriculture, industry, nuclear medicine, nuclear weapons, nuclear research, and others has disrupted the environmental balance as radioactive residues for these applications have increased. Scientists [1–4] are working hard to find a solution to this growing problem. Radioactive isotopes like ^{60}Co and $^{152+154}\text{Eu}$ are hazardous to humans due to their prolonged half-lives of 5.3 and 8.8 years, respectively. They are pollutants, and they cause

significant harm to the environment and to human health [5]. ^{60}Co can cause skin burns, acute radiation sickness, and even death at extremely high doses. $^{152+154}\text{Eu}$ has been associated to cancers of the liver and/or bones [6]. A number of techniques for removing radionuclides from waste water have been developed such as coagulation, precipitation, sorption, ion exchange, membrane technique [7], and solvent extraction [8]. The most effective method determined by the waste treatment cost and methodology. Metal oxides, including iron oxide [9–11], activated aluminium oxide [12, 13], titanium oxide [14, 15], manganese oxide [16, 17], and zirconium-magnesium binary oxide [18, 19], have attracted a lot of attention as sorbents.

Yılmaz D et al. [20] found that nanomaterials offered a wide range of possibilities for producing the newest radioactive wastewater decontamination technology [21]. However, the toxicity features and expansive analysis requirements in addition to the need of skilled human resources hinder the actual/specific application of these nanomaterials [22]. The

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use of natural resource which named as green chemistry can solve most of these limitations [22].

Aspergillus terreus is a fungus that can produce extracellular or intracellular nanoparticles [23] through metabolic activity that bio-reduces or aggregates complex metal ions that do not dissolve into colloidal particles.

Dispersing nanoparticles in polymer matrices can enhance a variety of chemical properties, including thermal stability, electric conductivity, hydrophilicity, and the transition of chemical properties from “bulk” matrix-controlled criteria to interphase or “surface” dominated characteristics [24]. Maleic acid combined with polyacrylic acid (PAACMA) has superior adsorption capabilities for copper ions from wastewater. Its thermal stability could be improved from 40.3% to 99.84% after copper ions adsorption [25].

To the author’s knowledge, the adsorption studies of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) radionuclide onto highly and low-cost adsorbent of dispersed nano copper oxide in polyacrylic/maleic acid have not yet been published. Accordingly, authors decided to study the effective conditions and mechanism of the sorption process.

Over the last few decades, the mechanism of the sorption reaction has been designed using linear regression [26]. Current findings, on the other hand, have revealed an increasing disparity (between predictions and experimental data) and model disability, resulting in model failure [27]. Recently, expanding nonlinear has been identified as a potentially powerful and efficient tool that could lead to further advances in adsorption science [28]. The use of error functions to generate a minimal distribution between experimental equilibrium data and predicted isotherms is common. Depending on how the applied error function is defined, the error distribution between the experimental equilibrium data and the predicted isotherms will be reduced either by minimising the error function or by obtaining maximum error functions. The most popular error function used to acquire the ideal distribution between experimental equilibrium data and isotherms is the coefficient of determination, or R^2 [29]. Recent studies have looked into additional error functions, such as average relative error (ARE), sum of absolute errors (EABS), and corrected Akaike information (AIC_c), to estimate the optimum isotherm [26, 30]. To find the best isotherm fitting, it is advised to use more than one error function.

The purpose of this research was to prepare a novel nano copper oxide composite for the sorption of radionuclides ^{60}Co (II) and $^{152+154}\text{Eu}$ (III). Nano copper oxide biosynthesised with the assistance of the metabolic fungus *Aspergillus terreus*. The monomers of acrylic acid, maleic acid and biosynthesized nano copper oxide were then copolymerized with radiation from a ^{60}Co cell at a dose of 25 kGy. Calcined biosynthesized CuO nanoparticles (Nps) and PAACMA/CuO were characterized. Batch sorption experiments were performed on the radionuclides $^{152+154}\text{Eu}$ (III) and ^{60}Co (II).

To optimise the sorption process, effective sorption factors such as pH, time, temperature, ionic strength, and concentration were investigated. Kinetic and equilibrium isotherms are used for determining the reaction mechanism. Fitting errors were minimised by using linear and nonlinear fitting techniques. Additionally, residual error plots, coefficient of determination (R^2), and corrected Akaike information Criterion (AIC_c) were used to examine the qualitative and quantitative aspects of the fitting results. To show the potential of using PAACMA/CuO nanocomposite as a radioactive waste sorbent, thermodynamic studies and the desorption process of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) were conducted.

Experimental

Materials and Procedure

All precursors used during the study were of analytical grade and used without further purification. Acrylic acid (AA) with purity $\geq 99\%$ got from Elf chem.co, France. Maleic acid (MA) of purity 99% obtained from Loba Chemie India. Copper sulphate ($\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$) 98% purchased from Merck, Egypt. Methylene bis-acrylamide (DAM) was supplied from (Merck, Germany). Extra pure cobalt (II) chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was purchased from BDH (UK). Eu_2O_3 salts got from Merck Co., Germany. The ^{60}Co and $^{152+154}\text{Eu}$ isotopes were produced by neutron irradiation of the corresponding salt in the Second Egyptian Research Reactor (ET-RR-2) at Inshas, Egyptian Atomic Energy Authority with initial activity 100 KBq/L. A 300 mg L^{-1} stock solutions of Co (II) and Eu (III) prepared by dissolving a certain amount of Co (II) and Eu (III) salts in double distilled water then spiked with the ^{60}Co and $^{152+154}\text{Eu}$ radionuclides, respectively. These solutions kept as a stock radioactive solution for all experiments.

Preparation of CuO Nps and PAACMA/CuO Nanocomposite

Aspergillus terreus was cultivated in Czapek-Dox broth medium [23], and CuO Nps was synthesised by hydrolysis of CuSO_4 via the supernatant of the fungus [23]. The CuO Nps collected and washed with distilled water before drying for 24 h at 60 °C and calcined for 2 h at 600 °C (Fig. 1).

The calcined CuO Nps copolymerized with acrylic acid (AA) and maleic acid (MA) in the presence of the cross linker methylene bis-acrylamide (DAM). After mixing 80 mL of deoxygenated water with 18 mL of AA, 2 g MA, 0.5 g DAM, and 0.5–2 g of calcined CuO NPs, the mixture magnetically stirred for 2 h at room temperature. The mixture exposed to gamma radiation at a dose rate of 689.538 Gy/h using a cobalt-60 gamma cell 220. After polymerization, the materials were cut into small pieces and soaked in acetone

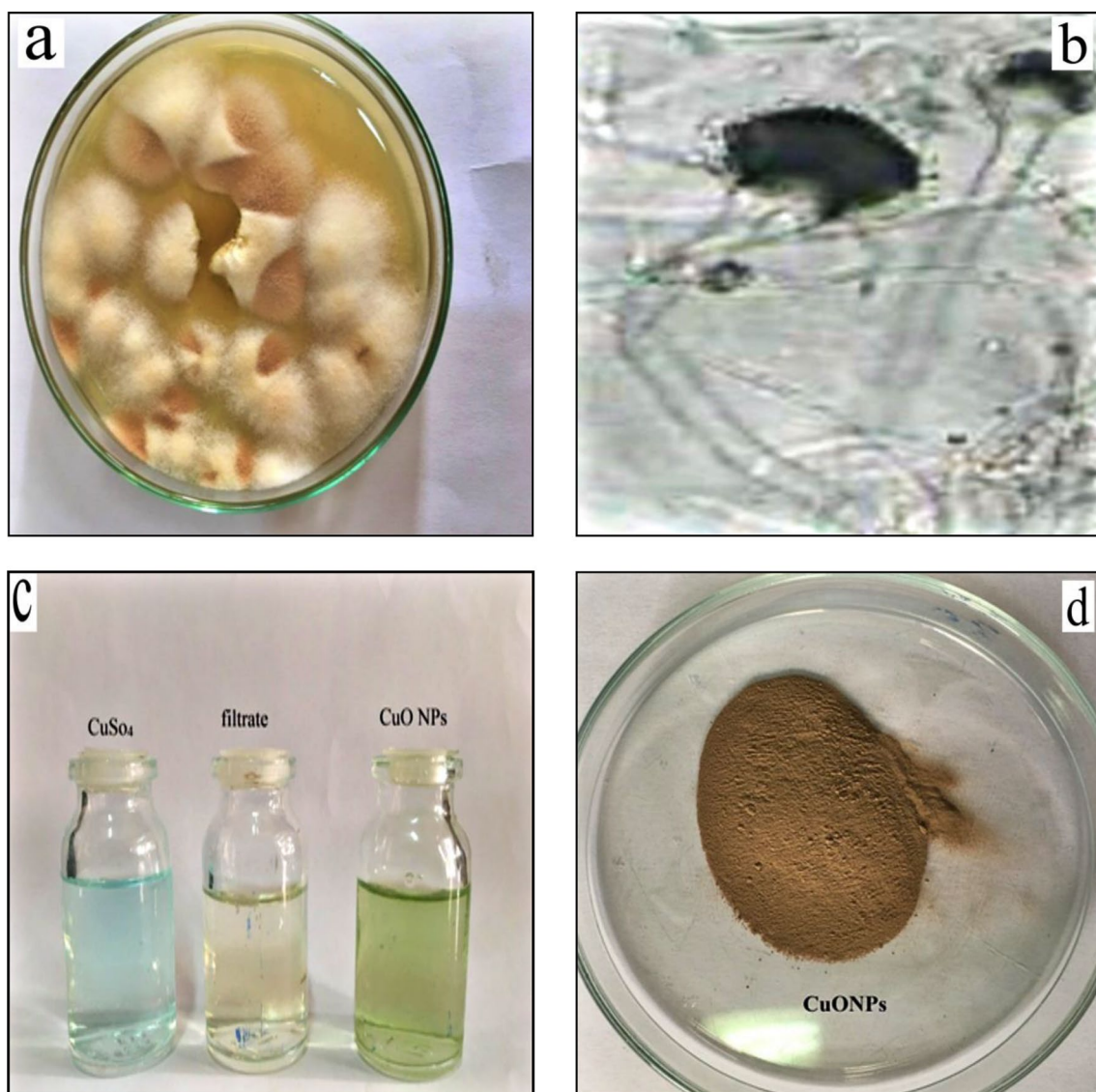


Fig. 1 Macroscopic image of **a** *Aspergillus terreus* **b** *Aspergillus terreus* spores and mycelium under light microscope with magnification power of 10×40 . **c** solutions of CuSO_4 and CuO NPs production by *Aspergillus terreus* **d** dried CuONPs

for 2 h to remove water, unreacted polymer, and impurities before being dried for 24 h in a vacuum oven at 333 K and sieved to size (250 μm). The successful preparation of PAACMA/ CuO nanocomposites with various molar compositions is shown in Table 1. A predicted polymerization mechanism is depicted in Fig. 2.

Instruments

The morphology of the particles analysed using a scanning electron microscope (SEM, Philips XL 30 ESEM), which combined with energy-dispersive X-ray spectroscopy and electron backscatter diffraction (25–30 keV accelerating voltage, 1–2 mm beam diameter and 60–120 s counting

time). CuO nanoparticles investigated using a transmission electron microscope (TEM), model JEM2100, manufactured by Jeol.s.b (Japan). Fourier transform infrared (FT-IR) spectra revealed the presence of functional groups (KBr pellet technique on a Perkin Elmer 1600 FTIR Spectrophotometer in wave number range $400\text{--}4000\text{ cm}^{-1}$). The all characterization was performed at $20\text{ }^\circ\text{C}$.

Sorption Studies

The sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) onto CuO Nps and PAACMA/ CuO nanocomposite was studied. Reaction parameters such as pH (1–7), contact time (5 min – 48 h), metal ion concentration ($50\text{--}300\text{ mg L}^{-1}$) and ionic strength

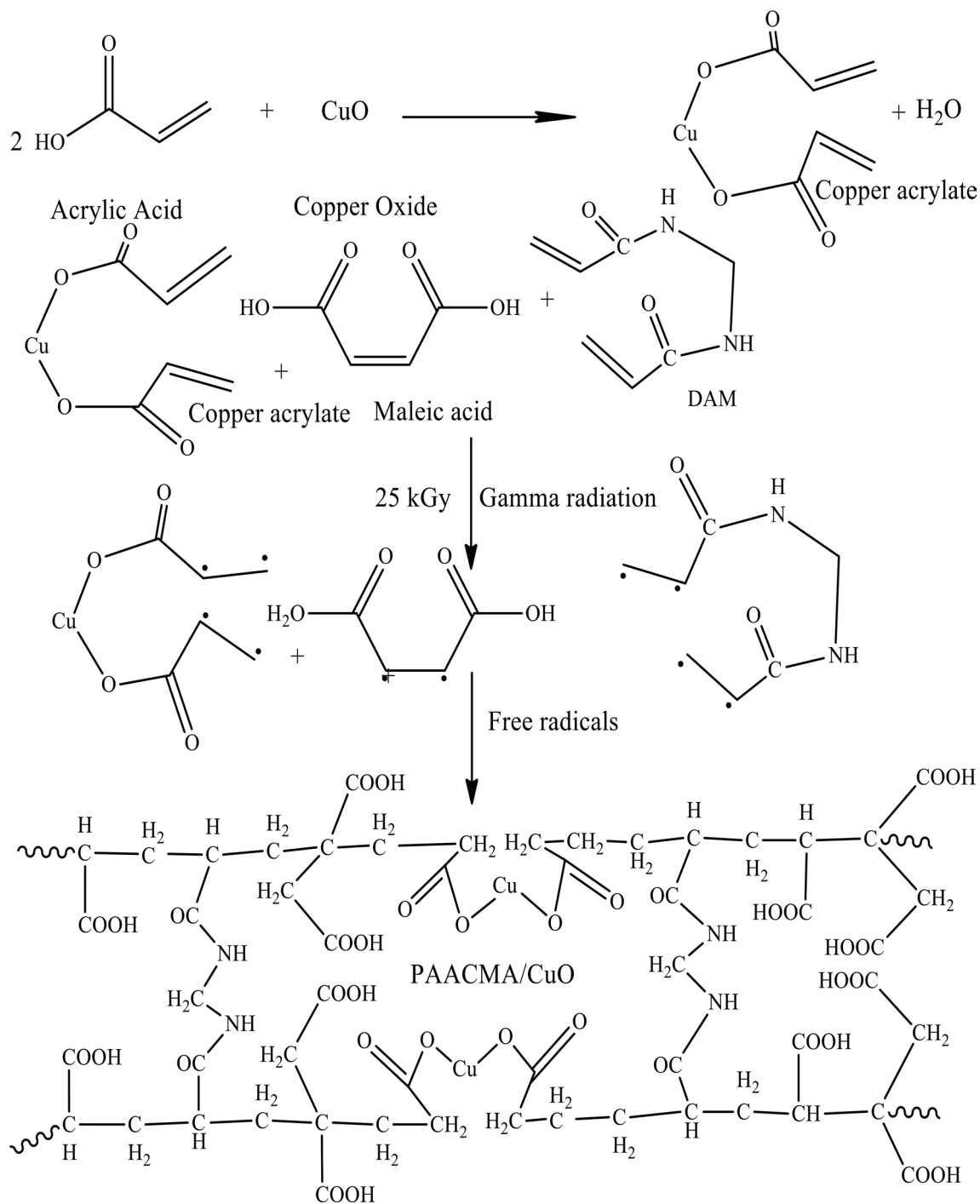


Fig. 2 Predicted mechanism of polymerization of PAACMA/CuO nanocomposite

Table 1 Composition of the co-monomers used to prepare PAACMA/CuO nanocomposites

Sample	AA (Mol %)	MA (Mol %)	CuO (Mol %)	DAM (Mol %)
P ₁ AACMA/CuO	85.71	9.53	2.38	2.38
P ₂ AACMA/CuO	83.72	9.30	4.65	2.33
P ₃ AACMA/CuO	81.81	9.09	6.82	2.28
P ₄ AACMA/CuO	80	8.89	8.88	2.23

were investigated in order to achieve optimal sorption conditions. After contacting 0.1 g of the sorbent with 10 mL of the ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) solutions, samples were filtered and separated from the solution. The sorption efficiency of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) radionuclides was calculated using Eq. (1):

$$\text{Percentage of sorption efficiency} = ((A_o - A_e)/A_o) \cdot 100 \tag{1}$$

The sorbed amount q (mg g⁻¹) was calculated using Eq. (2).

$$q = ((A_o - A_e)/A_o) \cdot C_o \cdot V/m \tag{2}$$

Where A_o and A_e represent the initial and equilibrium concentrations of the radionuclides ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III), m represents the mass of the nanocomposite (g), and V represents the volume of solution (L). Equation (3) was used to calculate the distribution coefficient K_d (mL g⁻¹).

$$K_d = ((A_o - A_e)/A_e) \cdot V/m \tag{3}$$

Kinetic Modelling

The pseudo first order, pseudo second order, and Elovich models were used to propose a mechanism for the sorption

reaction. Table 2 displays the linear and nonlinear equation forms of the selected kinetic modelling.

Where q_e and q_t are the sorbed amounts of radionuclides (mg g⁻¹) at equilibrium time and at any time t, respectively; k₁ (min⁻¹) is the pseudo first rate constant, k₂ (g mg⁻¹ min⁻¹) is the pseudo second order rate constant, α, β are the Elovich constants. α (mg g⁻¹ min⁻¹) represents the rate of chemisorptions at zero coverage, whereas β (g mg⁻¹) represents the extent of surface coverage and chemisorption activation energy.

Adsorption Isotherm Modelling

Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherms were used in this work. Table 3 depicts the linear and non-linear adsorption isotherm modelling forms.

Where q_{max} is the maximum monolayer sorption capacity (mg g⁻¹), b is the sorption free energy constant (b, α, e^{-ΔG/RT}), and C_e is the equilibrium metal ion concentration. The separation factor calculated from the Langmuir constant, R_L, indicates whether the isotherm is linear (R_L = 1), irreversible (R_L = 0), unfavourable (R_L > 1), or favourable (0 < R_L < 1), where K_f denotes Freundlich constants, and n denotes sorption capacity and intensity. q_{mDR} is monolayer capacity for the D-R model, β_{DR} is a constant related to apparent adsorption energy, ε is the polanyi potential, k_T is the maximal binding energy (L mol⁻¹), b_T is the sorption heat, R is

Table 2 Mathematical equations of the applied Kinetic modelling equations

Model	Equation form
Pseudo first order [31, 32]	Linear form $\log(q_e - q_t) = \log q_m - (k_1/2.303)t$ (4)
	Non-linear form $q_t = q_{e(cal)}(1 - e^{-K_1 t})$ (5)
pseudo second order [33, 34]	Linear form $t/q_t = (1/k_2 q_e^2) + (1/q_e) \cdot t$ (6)
	Non-linear form $q_t = ((K_2 q_{e(cal)}^2 t)/(1 + K_2 q_e t))$ (7)
Elovich model [35, 36]	Linear form $q_t = (1/\beta \ln \alpha \beta) + (1/\beta) \ln t$ (8)
	Non-linear form $q_t = 1/\beta \ln(1 + \alpha \beta t)$ (9)

Table 3 Mathematical equations of the applied adsorption Isotherm modelling equations

Model	Equation form
Langmuir [37, 38]	Linear form $1/q_e = 1/q_{max} + 1/bq_{max}(1/C_e)$ (10)
	$R_L = (1/(1 + bC_o))$ (11)
Freundlich [37, 38]	Non-linear form $q_e = (q_m b C_e / 1 + b C_e)$ (12)
	Linear form $\ln q_e = \ln K_f + 1/n \ln C_e$ (13)
Dubinin-Radushkevich [33, 39]	Non-linear form $q_e = K_f C_e^{1/n}$ (14)
	Linear form $\ln q_e = \ln q_{mDR} - \beta \epsilon^2$ (15)
Temkin [39, 40]	$\epsilon = RT \ln(1 + 1/C_e)$ (16)
	Non-linear form $q_{mDR} = e^{-\beta_{DR} \epsilon^2}$ (17)
	Linear form $q_e = RT/b_T \ln A_T + RT/b_T \ln C_e$ (18)
	Non-linear form $q_e = RT/b_T \ln K_T C_e$ (19)

the universal gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), and T is the absolute temperature (K).

Thermodynamic Parameters

The thermodynamic parameters such as standard Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were used to determine the spontaneity, nature, and adsorbent suitability of the adsorption process [41]. Equations (20, 21, 22) were used to calculate thermodynamic parameters using temperature-dependent adsorption isotherms.

$$K_d = q_e/C_e \quad (20)$$

$$\Delta G^0 = -RT \ln K_d \quad (21)$$

$$\ln K_d = -\Delta H^0/RT + \Delta S^0/R \quad (22)$$

where K_d is the distribution coefficient, mL g^{-1} ; R represents the general gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (K). ΔH^0 and ΔS^0 are obtained from the slope and intercept of the $\ln K_d$ against $1/T$ graph, respectively.

Desorption Studies

The ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) solutions were replaced with 10 mL of 0.1 M desorbing agents, including FeCl_3 , AlCl_3 , EDTA, HCl, and NaOH, following the sorption experiments. The concentrations of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) were then determined as previously mentioned, and the desorption efficiency was calculated using Eq. (23). This was followed by 24 h of shaking.

$$\text{Desorption}\% = (C_{aq}/C_s) * 100 \quad (23)$$

Error Functions

The suitability of a model equation for experimental results was typically evaluated using an error function. The difference between theoretically predicted and actual experimental data values was computed by error functions. It is possible to examine error functions using quantitative or qualitative criteria [42]. It is frequently preferable to use both qualitative and quantitative criteria. The coefficient of determination (R^2) [29] and corrected Information about Akaike (AIC_c) [30] error functions were used for quantitative criteria, while residual error plots were used for qualitative evaluation of the kinetic and adsorption isotherm modelling.

$$R^2 = 1 - \frac{\sum_{i=1}^n (q_{\text{calc.}} - q_{\text{exp.}})^2}{\sum_{i=1}^n (q_{\text{calc.}} - q_{\text{mean}})^2} \quad (24)$$

$$\text{AIC}_c = (n \ln(\text{SER}/n)) + (2(p+1)) + (2(p+1)(p+2)/n - p - 2) \quad (25)$$

Where q_{exp} (mg g^{-1}) is the number of sorbed radionuclides obtained from Eq. (2), q_{calc} (mg g^{-1}) is the number of sorbed radionuclides obtained from the model, n is the number of experimental data points, and p is the number of modelling parameters. The model with the highest R^2 and the lowest value of AIC_c was the best fit.

Results and Discussions

Characterization of the Composite

Zero Point Charge

The pH of the zero point charge (pH_{ZPC}) used as a base point for determining the type of sorbent because the surface charge is zero at a certain pH level. The sorbent surface charge is positive before the pH_{ZPC} , indicating that it works as an anionic exchanger, and negative after pH_{ZPC} , indicating that it works as a cationic exchanger. The efficiency of the sorbents was determined by the value pH_{ZPC} over a wide pH range. The zero point charge was determined by mixing 0.1 g of $\text{P}_4\text{AACMA/CuO}$ nanocomposite at 20°C with 10 mL of 0.1 M NaCl and shaking the solution for 24 h at 20°C in pH intervals ranging from 1 to 11. Finally, after shaking, the pH was measured, and the zero point charge was calculated by graphing the initial pH against the pH difference ($\text{pH}_f - \text{pH}_i$). The plot intersected the x-axis (pH_i) at the zero point charge [43]. According to Fig. 3, the pH_{ZPC} was 2.9, implying that the $\text{P}_4\text{AACMA/CuO}$ nanocomposite can be

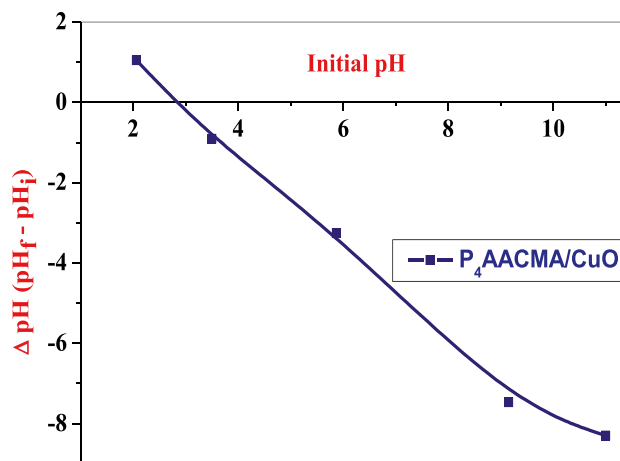


Fig. 3 Zero point charge of $\text{P}_4\text{AACMA/CuO}$ nanocomposite

used effectively for ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) at pH levels higher than this value ($\text{pH} > 2.9$).

FT-IR Analysis

FT-IR spectrum of biosynthesized nano CuO are represented in Fig. 4. A small broad peak was observed at 3480 cm^{-1} assigned to the O–H group stretching vibration for hydrogen bonding of physically adsorbed water or moisture content [44]. Furthermore, the band was observed at 1630 cm^{-1} assigned to the bending vibration of O–H group combined with copper atoms [45]. In the lower wavenumber region ($< 600\text{ cm}^{-1}$), two peaks are shown in spectrum. These are the characteristics peaks of Cu–O bond vibrations, confirming the synthesis of CuO nanoparticles [46]. The spectrum of the $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite at $20\text{ }^\circ\text{C}$ had a broad band at 3421 cm^{-1} , which corresponds to OH stretching for the COOH group. The band at 2927 cm^{-1} represented C–H asymmetric vibration, while the band at 1736 cm^{-1} represented the C=O group. The 1457 cm^{-1} band represented the deformation of C–H bending vibration [47]. The C–O group is represented by the band at 1249 cm^{-1} . The presence of

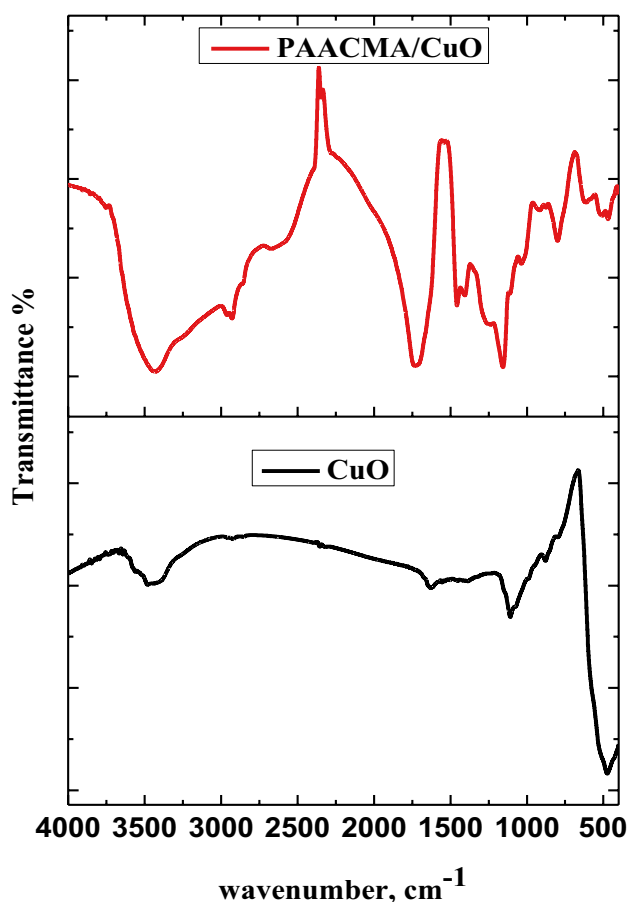


Fig. 4 FTIR of the Nano CuO and $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite

CuO in the polymeric matrix was confirmed by the bands at $1106, 876, 507, \text{ and } 469\text{ cm}^{-1}$ [46].

Morphological Analysis

Figure 5 shows the TEM micrographs of CuO NPs to investigate the nano character of CuO particles. The crystalline nanoparticles were well dispersed and had a size of less than 50 nm with spherical and porous structure. The SEM micrograph of CuO NPs clearly showed rough agglomeration of nanostructural homogeneities with spherical morphologies of CuO nanoparticles. The SEM micrograph of $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite show variation in morphological features and appeared rough and entangled structure and agglomeration with intergranular micropores and spherical morphologies of CuO nanoparticles are distributed randomly between the polymeric matrix. Incorporation of CuO Nps into the polymeric matrix caused cavities and roughness of the $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite resulting in a heterogeneous framework of the synthesised nanocomposite [23].

Sorption Studies

Table 4 showed the sorption efficiencies of nano-CuO and $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposites with varying CuO concentrations toward ^{60}Co (II) and $^{152+154}\text{Eu}$ (III). CuO Nps, on the other hand, had low sorption efficiencies towards both radionuclides studied. The sorption efficiencies of $\text{P}_4\text{AACMA}/\text{CuO}$ composites enhanced as the mol percentage of nano CuO increased. This was caused by ionic polymer adsorption on the surface of the nano CuO oxide particle, which led to a high surface charge density and an increase in the electrostatic attraction between the nanopolymer and the adsorbed ^{60}Co (II) ions or $^{152+154}\text{Eu}$ (III) [48]. When compared to the other $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposites compositions, $\text{P}_4\text{AACMA}/\text{CuO}$ with composition (80% AA, 8.89% MA, 8.88% CuO and 2.23% DAM) exhibited the highest sorption efficiency toward ^{60}Co (II) ions and $^{152+154}\text{Eu}$ (III) ions, made it the optimum composition of choice for the sorption study.

Optimization of the Sorption Parameters

Effect of pH

Figure 6a showed the results of an investigation into how pH affects the sorption efficiencies of the $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite towards the ^{60}Co (II) and $^{152+154}\text{Eu}$ (III). The nanocomposite at pH 3 only adsorbed 33.47% of ^{60}Co (II) and 67.04% of $^{152+154}\text{Eu}$ (III) despite an initial metal ion concentration of 100 mg L^{-1} . ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) sorption increased to 38.52 and 89.86%, respectively, when the pH was raised to 4. At pH 6, ^{60}Co (II) was eliminated in 96%

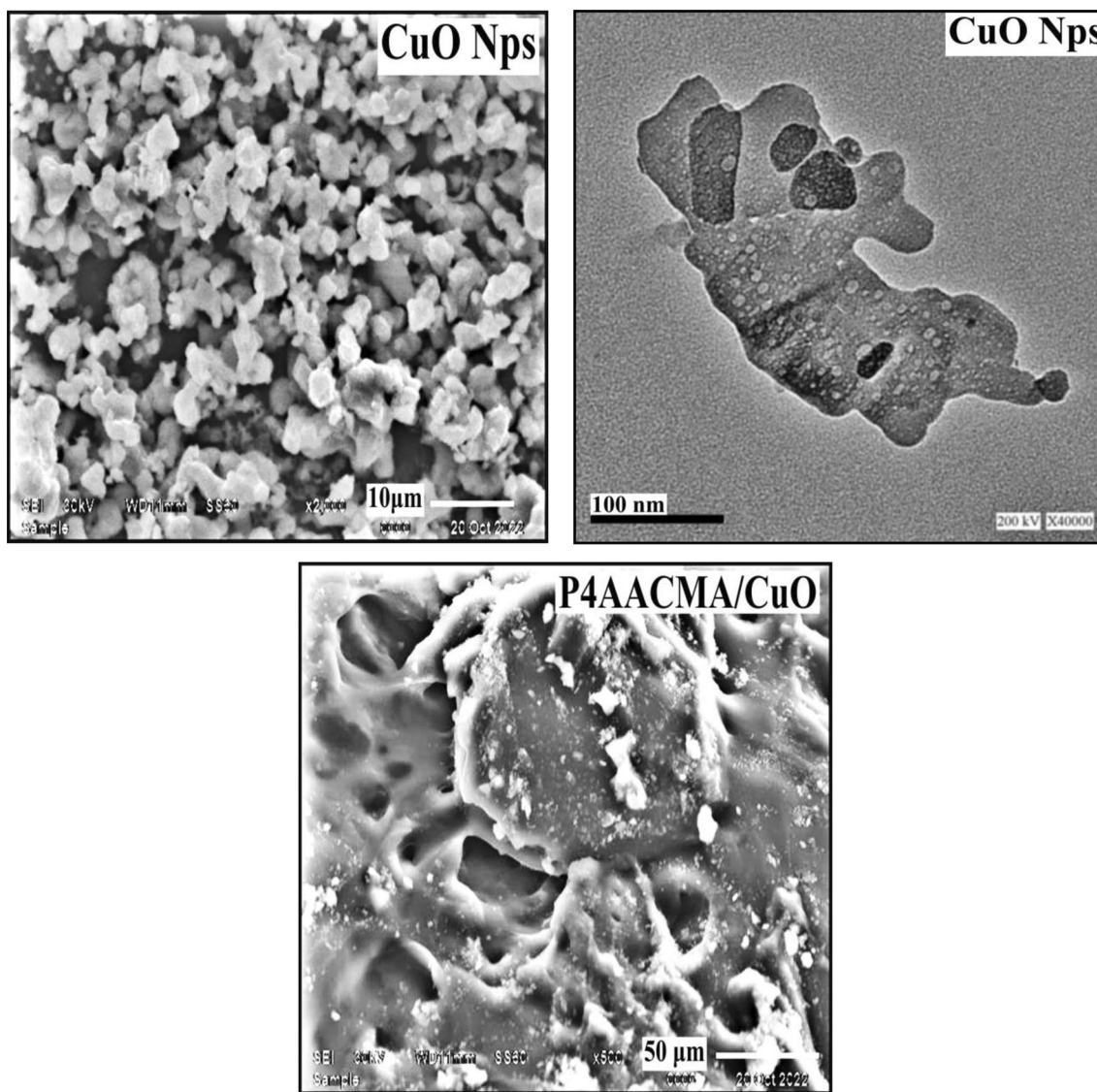


Fig. 5 SEM and TEM of nano CuO , SEM of P₄AACMA/CuO nanocomposite

Table 4 Sorption efficiencies of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) radionuclides onto PAACMA/CuO nanocomposites

Sample	Sorption efficiencies (%)	
	⁶⁰ Co(II)	¹⁵²⁺¹⁵⁴ Eu (III)
CuO	12.53	20.82
P ₁ AACMA/CuO	46.290	76.875
P ₂ AACMA/CuO	46.640	77.468
P ₃ AACMA/CuO	48.860	81.146
P ₄ AACMA/CuO	51.505	85.536

of instances while ¹⁵²⁺¹⁵⁴Eu (III) was eliminated in 91.82% of instances. The main function group of the P₄AACMA/CuO nanocomposite was COOH that may have higher pH

deprotonation. Additionally, because the surface charge of P₄AACMA/CuO nanocomposite changed to be negative in accordance with p*H*_{ZPC} (pH 2.9), positively charged metal ions and its surface functional groups tend to attract each other electrostatically.

The precipitation curves of Co (II) and Eu (III) in the absence of the prepared nanocomposite that served as a blank, shown in Fig. 6b, showed that a significant precipitated quantity of Co (II) began to appear after pH 4.5 and of Eu (III) after pH 4. Figure 6c and d depicted the speciation diagrams of Co (II) and Eu (III) at various pH values as determined by the Hydra/Medusa chemical equilibrium software [49]. Co (II) is the most dominant species in the charts up to pH 4.5, then Co (OH)₂ species appears after pH 4.5 and becomes dominant at pH 6. The trivalent species

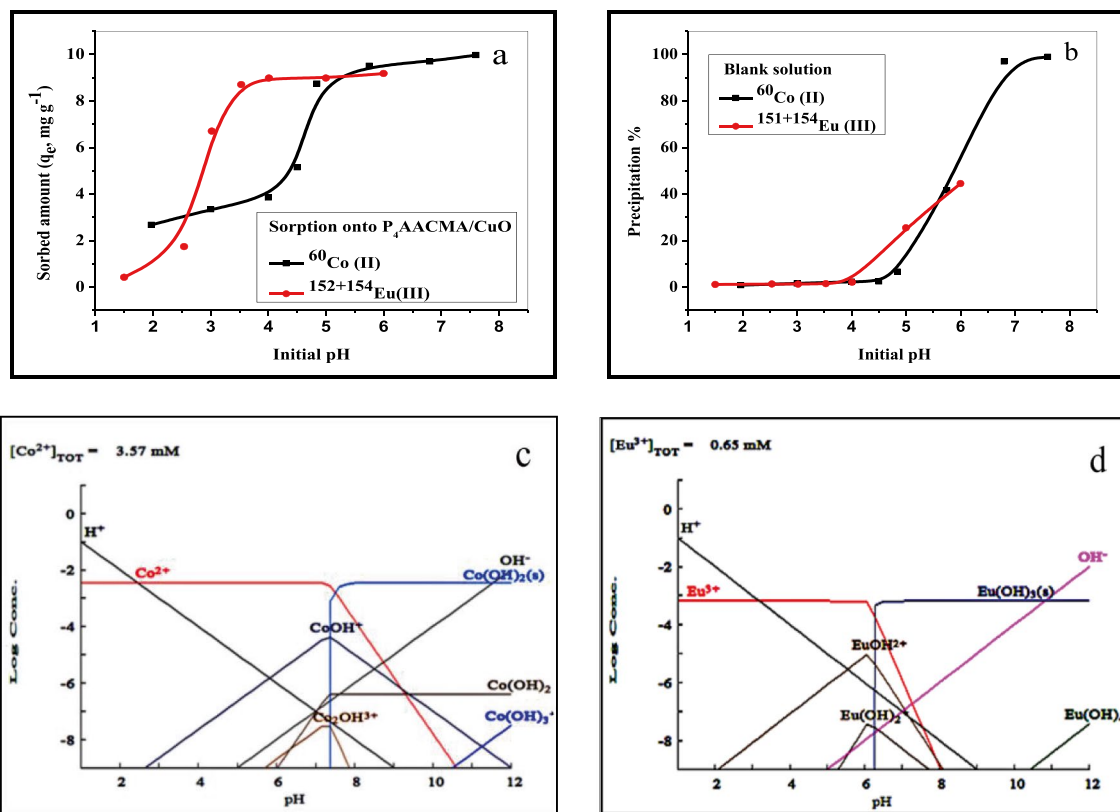


Fig. 6 **a** pH Impact on sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite **b** precipitation curve [$C_i = 100 \text{ mg L}^{-1}$, Time = 24 hours, $V/m = 0.1 \text{ L g}^{-1}$, Temperature = 20°C] **c**, **d** speciation of Co (II) and Eu (III) at different pH and 25°C

Eu (III) predominates up to pH 6, with the positive species EuOH^{2+} and $\text{Eu}(\text{OH})^{2+}$ appearing at pH ranges 3–5. At pH values above 6, $\text{Eu}(\text{OH})_3$ predominated, with precipitation accounting for the vast majority of Eu (III) removal. To avoid precipitation, the sorption experiments were carried out at pH 4.5 for Co (II) and pH 3.53 for Eu (III). The sorbed amounts of Co (II) at pH 4.5 were 5.150 mg L^{-1} . In addition, the amount of Eu (III) sorbed increased from 0.415 mg L^{-1} at pH 1.5 to 8.705 mg L^{-1} at pH 3.53. Finally, the results revealed that Eu (III) had higher sorption efficiency onto $\text{P}_4\text{AACMA}/\text{CuO}$ than Co (II). This could be due to the higher electrostatic interaction of Eu (III) as trivalent ions compared to Co (II) as divalent ions [50].

Time

Figure 7 depicted the effect of contact time on the sorption of Co (II) and Eu (III) onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite from 5 min to 48 h. The equilibrium state was appointed after contacting time 24 h, as the results indicated no further change in the sorbed amounts for both elements. The sorbed amounts of the two studied elements increased substantially because the number of available active sites on the surface of $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite was initially large enough

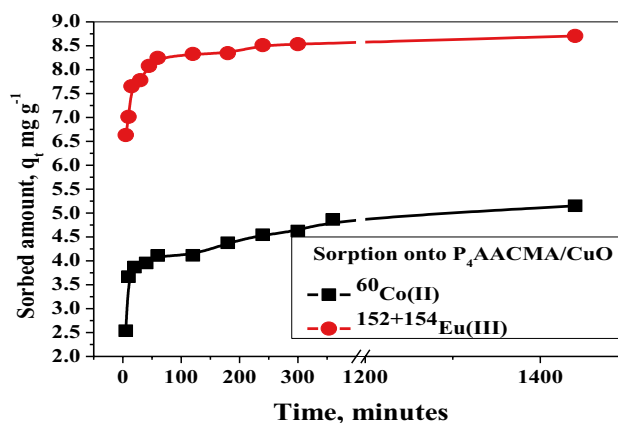


Fig. 7 Time impact on sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite [$C_i = 100 \text{ mg L}^{-1}$, pH 4.5 for ^{60}Co (II) and pH 3.53 for $^{152+154}\text{Eu}$ (III), Temperature = 20°C , $V/m = 0.1 \text{ L g}^{-1}$]

to overcome the resistance to transfer of Co (II) and Eu (III) from aqueous phase to $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite surface [50]. The increase in sorbed amount slowed gradually from 30 min to the saturation state at 24 h as an equilibrium time. This is due to a decrease in the number of active

sites of the caused by metal ion occupancy, so there were no more available active sites on the P₄AACMA/CuO nanocomposite surface after the equilibrium time. At the equilibrium state, the sorbed amounts of Co (II) and Eu (III) onto P₄AACMA/CuO nanocomposite were 5.1505 and 8.705 mg g⁻¹, respectively.

Effect Co (II) and Eu (III) Concentrations

Figure 8 depicted the amount of metal ion sorbed as a function of initial concentration, which ranges from 50 to 300 mg L⁻¹ and labelled with the appropriate radioactivity of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III). There is a relationship between metal ion concentration and sorbed amount on composite, which means that increasing the concentration of Co (II) and Eu (III) in the solution increased the sorbed amount of metal ions. The driving force of Co (II) and Eu (III) at the surface interface has increased as the number of effective interactions or collisions between initial metal ions and active sites on the surface of the P₄AACMA/CuO nanocomposite has increased. Because Eu (III) has a higher charge density than Co (II), Eu (III) had higher sorption efficiency than Co (II). The sorbed amount of Co (II) increased from 4.176 to 11.939 mg g⁻¹ at 300 mg L⁻¹, while it increased from 4.55 to 18.16 mg g⁻¹ over the same initial metal ion concentration range for Eu (III).

Ionic Strength

The impact of ionic strength on the sorption reaction was studied by incorporating 0.1 g of the nanocomposite with 10 mL of the sorbents at pH 4.5 for ⁶⁰Co (II) and 3.53 for ¹⁵²⁺¹⁵⁴Eu (III) and ranging the concentration of NaCl from 0.02 to 0.2 mol L⁻¹. Ionic strength had a significant effect

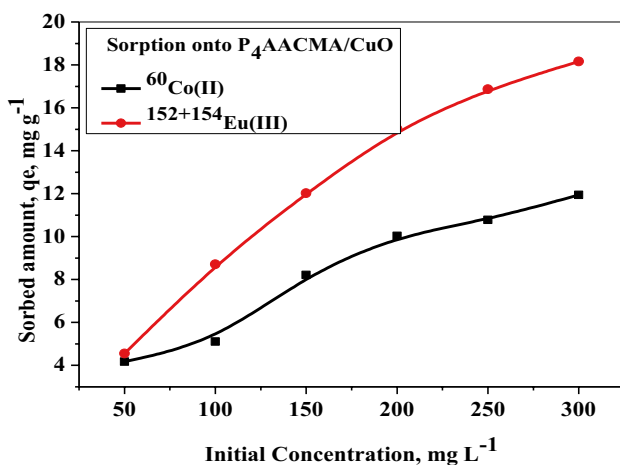


Fig. 8 Concentration impact on sorption of ⁶⁰Co(II) and ¹⁵²⁺¹⁵⁴Eu (III) onto P₄AACMA/CuO nanocomposite [Equilibrium time = 24 hours, pH 4.5 for ⁶⁰Co (II) and pH 3.53 for ¹⁵²⁺¹⁵⁴Eu (III), Temperature = 20 °C, V/m = 0.1 L g⁻¹]

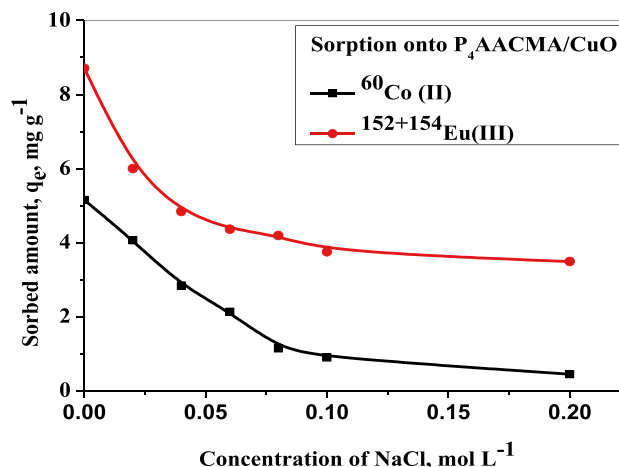


Fig. 9 Effect of ionic strength of NaCl on sorption of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu(III) radionuclides onto P₄AACMA/CuO nanocomposite [C_i = 100 mg L⁻¹, Equilibrium time = 24 hours, pH 4.5 for ⁶⁰Co(II) and pH 3.53 for ¹⁵²⁺¹⁵⁴Eu (III), Temperature = 20 °C, V/m = 0.1 L g⁻¹]

on the sorption reaction of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) ions onto P₄AACMA/CuO nanocomposite, as shown in Fig. 9. The sorbed amounts of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) ions decreased from 5.1505 to 8.704 mg g⁻¹ to 4.06 and 5.99 mg g⁻¹, respectively, in the presence of 0.02 mol L⁻¹ NaCl. The sorbed amounts of the radionuclides ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) decreased to 0.442 mg g⁻¹ and 3.485 mg g⁻¹, respectively, at the concentration of 0.2 mol L⁻¹ NaCl. The competition between Na (I) and ⁶⁰Co (II) or ¹⁵²⁺¹⁵⁴Eu (III) ions in the solution, as well as the electrostatic stability of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) in the solution by Cl⁻ anions, could be contributed to this trend. These aspects reduced the rate at which these radionuclides diffuse onto the surface of the nanocomposite. This implies that the predicted physical adsorption or ion exchange chemisorption occurred, as well as an outer-sphere interaction between the radionuclides ⁶⁰Co (II) or ¹⁵²⁺¹⁵⁴Eu (III) and the P₄AACMA/CuO nanocomposite surface [51, 52] existed.

Temperature

Figure 10 depicted the study of the effect of temperature on the sorption reaction over a temperature range of 20 to 50 °C. The sorption of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) radionuclides were affected by temperature, suggesting a chemical mechanism for the reaction [45]. The findings demonstrated that increasing temperature accelerated the rate of the sorption reaction due to an increase in radionuclide kinetic energy, which led to an increase in radionuclide diffusion at the surface of the nanocomposite, thereby enhanced the sorption process. Increased sorption on the surface of the nanocomposite and promoted deprotonation

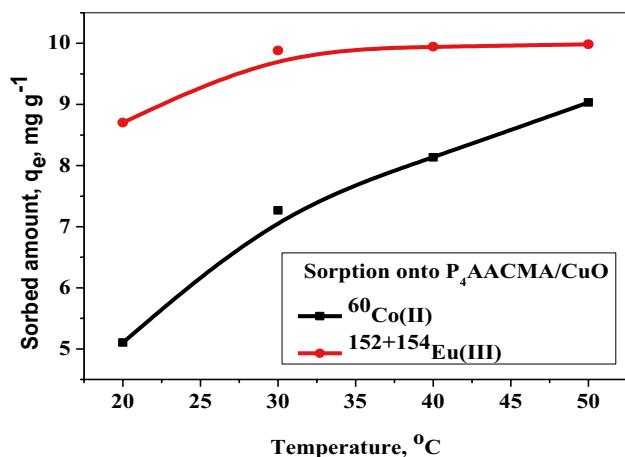


Fig. 10 Effect of Temperature on sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) radionuclides onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite. [$C_i=100\text{ mg L}^{-1}$, Equilibrium time = 24 hours, pH 4.5 for ^{60}Co (II) and pH 3.53 for $^{152+154}\text{Eu}$ (III), $V/m = 0.1\text{ L g}^{-1}$]

of the active group were additional effects of increased temperature [53].

Kinetic Modelling

The rate and pathways of radionuclide adsorption on the nanocomposite were determined using kinetic modelling. Three kinetic models were used to determine the correct mechanism for the sorption reaction: pseudo first order, pseudo second order, and the Elvoich model. Figure 11 depicted a linear plot examination. In addition to the coefficients of determination (R^2) and AIC_c values, the more fitted model can be identified by comparing the calculated q_t to the experimental q_t . The Elvoich model's coefficients and can be used to distinguish between physisorption and chemisorption reactions by comparing their coefficients α and β .

The results in Table 5 showed that the pseudo second order model had good fitting results, such as higher coefficients of determination, lower AIC_c values, and consistency with the equilibrium sorbed amount (q_{exp}). The residual error plots were examined, and the pseudo second order employed the lowest residual error possible, as shown in Fig. 11e, f. This refers to the chemisorption nature of the reaction, which occurs via electrostatic attraction of the ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) radionuclides and negatively charged surface of the $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite, which was

consistent with the pH_{ZPC} results. Furthermore, the Elvoich model expressed the initial adsorption rate and the desorption constant. The highest and lowest parameter values for ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) confirmed the sorption reaction's chemisorption nature.

Isotherm Modelling

The isotherm model was used to determine the interaction of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) with the surface of $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite. Figure 12 depicted the residual error plots of the investigated models with linear and non-linear regression plots of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm modelling. The linear and non-linear regression results were listed in Table 6. For both linear and nonlinear regression, the residual error plots had the lowest D-R values. The highest R^2 , in linear regression revealed that the sorption mechanism was regulated by the Langmuir isotherm and D-R model regulated the sorption reaction in non-linear regression. Thus, linear regression indicated that monolayer coverage of Co (II) and Eu (III) causes sorption onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposites. Chemisorption was responsible for the sorption of Co (II) and Eu (III) ions onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposites, as E values were greater than 8 kJ mol^{-1} in non-linear regression [54]. The D-R mechanism outperformed the Langmuir isotherm because it did not consider a homogeneous surface or constant adsorption potential. The sorption mechanism was controlled by the D-R mechanism in terms of AIC_c for both linear and nonlinear regression because D-R fitting had the lowest AIC_c values. Non-linear regression was found to be more accurate in determining the best isotherm [55].

Thermodynamic Studies

The plot of $\ln K_d$ versus $1/T$ for the sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite shown in Fig. 13. Table 7 showed the results of ΔG° , ΔH° and ΔS° . The free energy change ΔG° obtained during the sorption reaction at 293, 303, 313, and 323 K was all negative, indicating that the sorption process was spontaneous and favourable. Furthermore, an increase in negative ΔG° values by increase in temperature indicated a greater driving force for metal ion binding. The presence of a positive value for ΔH° indicated that the sorption process was endothermic. The increased randomness at the ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) molecules onto the $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite

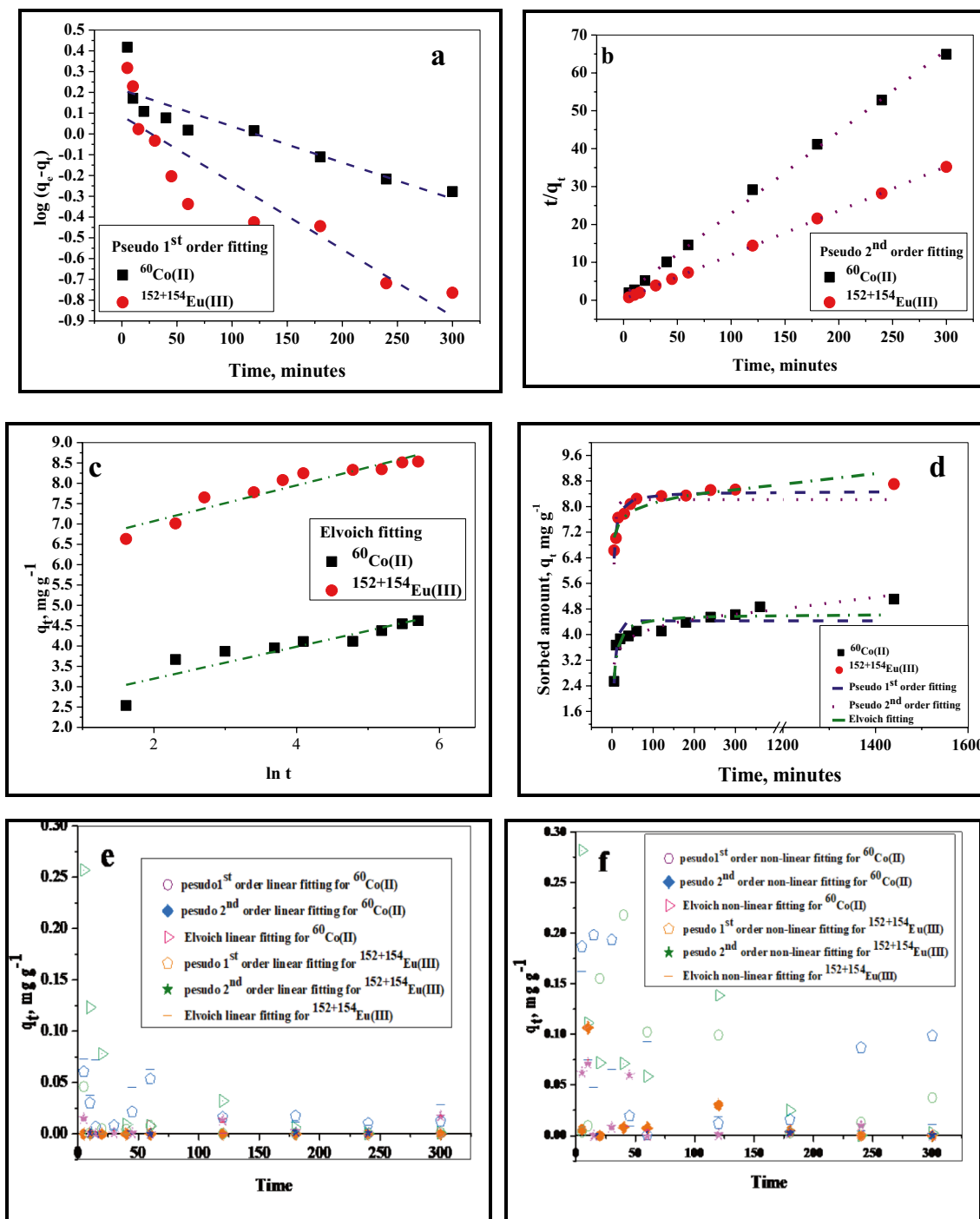


Fig. 11 Kinetic model plots for the sorption of $^{60}\text{Co(II)}$ and $^{152+154}\text{Eu(III)}$ onto $\text{P}_4\text{AACMA/CuO}$ nanocomposite **a–c** linear fitting **d** non linear fitting **e** residual error for linear regression **f** residual error for non- linear regression

interface during the sorption process was indicated by a positive value of ΔS° .

Desorption Studies

Figure 14 depicted the results of desorption of $^{60}\text{Co(II)}$ and $^{152+154}\text{Eu(III)}$ using a different desorbing reagents.

Table 5 The calculated kinetic parameters for the sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) onto $\text{P}_4\text{AACMA/CuO}$ nanocomposites

Model Parameter	$\text{P}_4\text{AACMA/CuO}$			
	^{60}Co (II)		$^{152+154}\text{Eu}$ (III)	
	Linear	Non linear	Linear	Non linear
Pseudo-first order				
q_t (mg/g) (calculated)	1.627	4.429	1.222	8.218
K_1 (min^{-1})	4.030×10^{-3}	0.164	7.392×10^{-3}	0.281
R^2	0.790	0.702	0.819	0.604
AIC_c	-54.321	-40.004	-52.212	-38.485
Pseudo-second order				
q_t (mg/g) (calculated)	4.642	4.630	8.572	8.472
K_2 (g/mg.min)	0.0332	0.0561	0.0465	0.072
R^2	0.998	0.870	0.999	0.925
AIC_c	-239.564	-49.931	-55.273	-56.877
q_t (mg/g) (experiment)	5.1505		8.704	
Elovich kinetic model				
α (mg/g. min)	182.836	227.643	5.6×10^5	1.6894×10^7
β (g/mg)	2.546	2.606	2,272	2.738
R^2	0.811	0.832	0.895	0.840
AIC_c	-35.684	-30.213	-46.459	-48.492

The highest R^2 and the lowest AIC_c are in bold

The results indicated that 55.53% and 95.04% of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III), respectively were quantitatively desorbed from the loaded $\text{P}_4\text{AACMA/CuO}$ nanocomposite with 0.1 mol L^{-1} EDTA solution. 0.1 mol L^{-1} NaOH had poor desorbing percentage due to the deprotonation of the surface [56]. Hence, ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) find it was difficult to be detached from the adsorbent. However, HCl had the ability to cover loaded $\text{P}_4\text{AACMA/CuO}$ nanocomposite surface with $[\text{H}^+]$ and hence, ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) detached easily [44]. However, EDTA had higher desorption efficiency than HCl due to the strong complexation of EDTA. For AlCl_3 and FeCl_3 used as desorbing agents by ion exchange but the difference in ionic size among $[\text{H}^+]$, Al(III) and Fe(III) caused the difference in desorption efficiencies. The order of desorbing efficiencies was $\text{EDTA} > \text{HCl} > \text{AlCl}_3 > \text{FeCl}_3 > \text{NaOH}$.

Comparative Studies

Table 8 summarized the adsorbent materials [33, 38, 44, 57–62] to that of the $\text{P}_4\text{AACMA/CuO}$ nanocomposite for the adsorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) radionuclides. As a result, $\text{P}_4\text{AACMA/CuO}$ nanocomposite can be considered as a prospective low-cost adsorbent for ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) radionuclides from radioactive waste solution.

Conclusion

A nanocomposite of polyacrylic acid/maleic acid with nano copper oxide (PAACMA/CuO) was successfully prepared and well characterized. The prepared PAACMA/CuO nanocomposite was used for sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) radionuclides from aqueous solutions. CuO was synthesised in nano-size less than 50 nm by hydrolysis of its salt in the presence of the fungus *Aspergillus terreus* and then cross linked with acrylic acid and maleic acid via free radical polymerization. $\text{P}_4\text{AACMA/CuO}$ nanocomposite with acrylic acid (80%), maleic acid (8.89%), CuO (8.88%), and 2.23% cross linker (DAM) was chosen for batch testing. The best sorption conditions (pH 4.5 for ^{60}Co and pH 3.53 for $^{152+154}\text{Eu}$, 24 hours equilibrium time at 20°C) were used. The reaction kinetic was controlled by pseudo second order based on residual plots, (R^2), and (AIC_c). Due to R^2 , the sorption reaction mechanism was regulated with D-R model for non-linear regression, and with Langmuir model for linear regression. While the D-R model was used to control the sorption reaction mechanism based on residual error plots and AIC_c results for linear and non-linear regression. The $\text{P}_4\text{AACMA/CuO}$ nanocomposite had a monolayer adsorption capacity of 11.04 mg g^{-1} for Co (II) and 21.54 mg g^{-1}

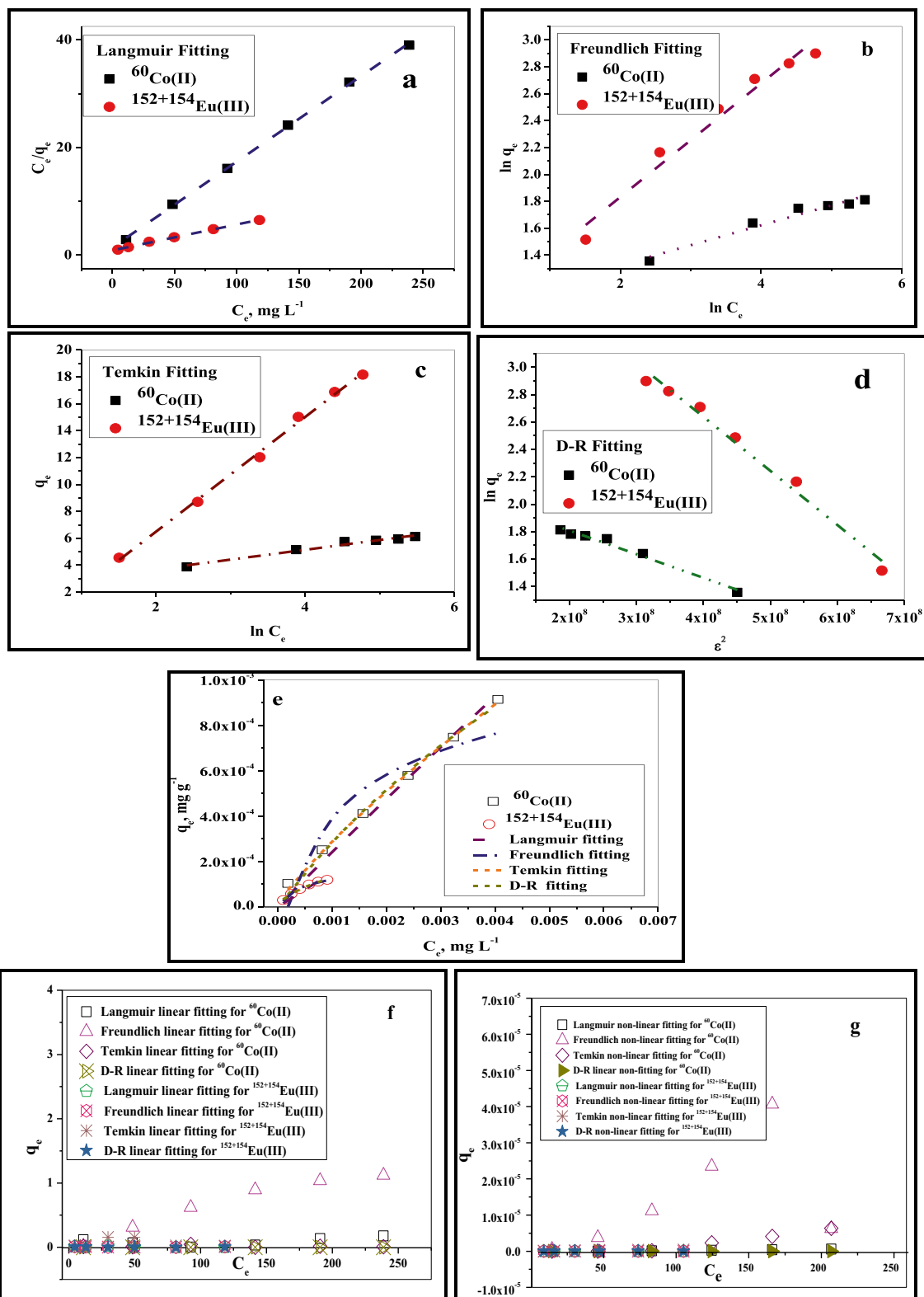


Fig. 12 Isotherm modeling plots for the sorption of $^{60}\text{Co(II)}$ and $^{152+154}\text{Eu(III)}$ onto $\text{P}_4\text{AACMA/CuO}$ nanocomposite—**d** linear fitting **e** non-linear fitting **f** residual error for linear regression **g** residual error for non-linear regression

Table 6 The calculated Isotherm parameters for the sorption of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposites

	$\text{P}_4\text{AACMA}/\text{CuO}$			
	$^{60}\text{Co}(\text{II})$		$^{152+154}\text{Eu}(\text{III})$	
	Linear	Non linear	Linear	Non linear
Langmuir isotherm				
q_{mL}	6.2869 mg L^{-1}	1.873×10^{-4} (mmol g^{-1}) ~ 11.04 mg g^{-1}	20.829 mg L^{-1}	1.42×10^{-4} (mmol g^{-1}) ~ 21.57 mg g^{-1}
K_L	0.11011 L mg^{-1}	13.0376 (L mmol^{-1})	0.0536 L mg^{-1}	0.6217 (L mmol^{-1})
R_L	0.591	0.8037	0.4932	0.999
R^2	0.999	0.977	0.999	0.715
AIC_c	-7.287	-84.287	-22.441	-126.112
Freundlich isotherm				
n	6.757	1.2385	2.367	1.687
K_f ($\text{mmol n}^{-1} \text{g}^{-1} \cdot \text{L}^{-n}$)	2.802 ($\text{mg n}^{-1} \text{g}^{-1} \cdot \text{L}^{-n}$)	0.077 ($\text{mmol n}^{-1} \text{g}^{-1} \cdot \text{L}^{-n}$)	2.681 ($\text{mg n}^{-1} \text{g}^{-1} \cdot \text{L}^{-n}$)	0.00784 ($\text{mmol n}^{-1} \text{g}^{-1} \cdot \text{L}^{-n}$)
R^2	0.949	0.986	0.962	0.987
AIC_c	4.183	-84.284	-22.5397	-144.733
D-R isotherm				
q_{mDR} (mol g^{-1})	0.14598	0.00645	0.3578	7.925×10^{-4}
β_{DR} ($\text{mol}^2 \text{kJ}^{-2}$)	0.172×10^{-8}	0.065×10^{-7}	0.394×10^{-8}	0.038×10^{-7}
E (kJ mol^{-1})	17.049	8.770	11.265	11.470
R^2	0.974	0.989	0.98	0.993
AIC_c	-38.216	-119.63	-26.797	-149.244
Temkin isotherm				
K_T	1.386×10^3 (L g^{-1})	5.277×10^3 (L mol^{-1})	0.125×10^3 (L g^{-1})	$1.759.64 \times 10^4$ (L mol^{-1})
b_T	3.344×10^3 (kJ g^{-1})	9.73×10^6 (kJ mol^{-1})	5.71×10^2 (kJ g^{-1})	5.77×10^7 (kJ mol^{-1})
R^2	0.967	0.827	0.996	0.983
AIC_c	-17.873	-84.529	-8.85	-84.529

The highest R^2 and the lowest AIC_c are in bold

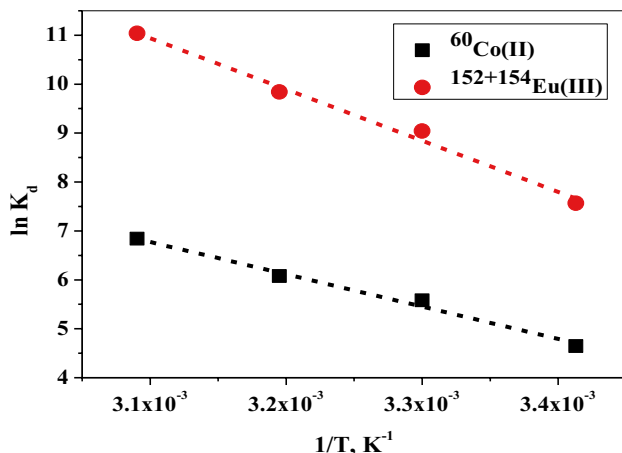


Fig. 13 Thermodynamic plots for the sorption of $^{60}\text{Co}(\text{II})$ and $^{152+154}\text{Eu}$ (III) onto $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite

for Eu (III). According to desorption studies, EDTA at 0.1 mol L^{-1} concentration could recover 55.46% and 95.044% of the sorbed radionuclides ^{60}Co (II) and $^{152+154}\text{Eu}$ (III), respectively. Thermodynamically, the sorption process was endothermic in nature and took place spontaneously. Finally, the results indicate that the $\text{P}_4\text{AACMA}/\text{CuO}$ nanocomposite has great potential to be used as an economic and effective sorbent for preconcentration and recovery of ^{60}Co (II) and $^{152+154}\text{Eu}$ (III) from aqueous solutions. It was recommended to use more than one error function as a deciding factor when selecting the best isotherm. For superior advancements in the field of adsorption science, non-linear regression was preferred over linear regression.

Table 7 Thermodynamic parameters for the sorption of ⁶⁰Co (II) and ¹⁵²⁺¹⁵⁴Eu (III) onto P₄AACMA/CuO nanocomposite

Radionuclide	$\Delta H \text{ kJ mol}^{-1}$	$\Delta S \text{ J mol}^{-1} \text{ K}^{-1}$	Temperature (K)			
			293	303	313	323
			$\Delta G \text{ kJ mol}^{-1}$			
⁶⁰ Co(II)	54.929	226.606	- 11.466	- 13.732	- 15.998	- 18.264
¹⁵²⁺¹⁵⁴ Eu(III)	87.063	360.843	- 18.663	- 22.272	- 25.880	- 29.489

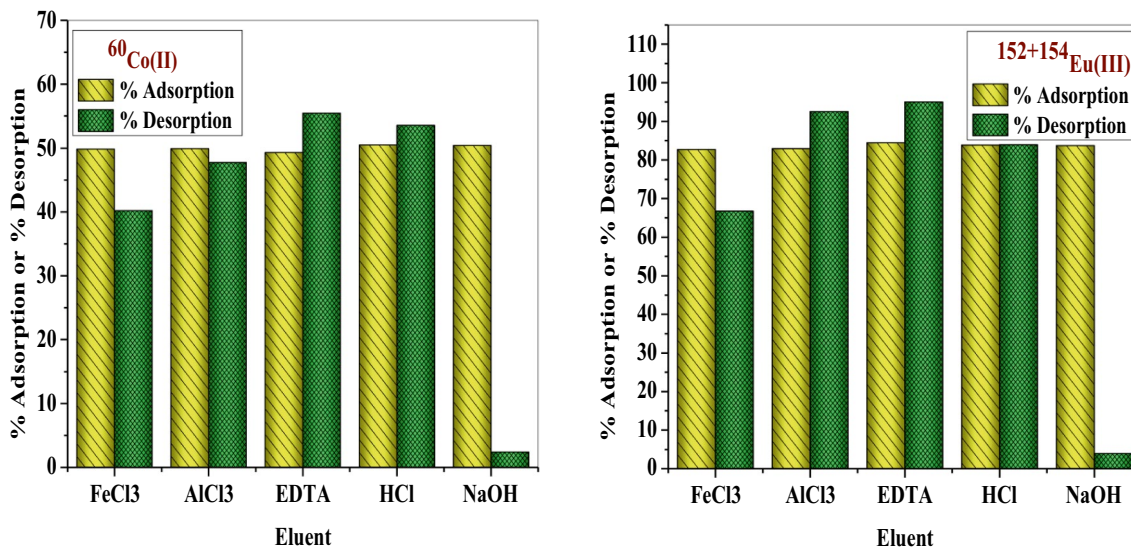


Fig. 14 Desorption efficiencies of ⁶⁰Co(II) and ¹⁵²⁺¹⁵⁴Eu (III) from loaded P₄AACMA/CuO nanocomposite with different desorbing agents

Table 8 Comparison of monolayer adsorption capacity of adsorbents reported in literature for ⁶⁰Co(II) and ¹⁵²⁺¹⁵⁴Eu(III) adsorption

Adsorbent	pH	Temp	$q_{max}, \text{mg g}^{-1}$		References
			Metal ions		
			Eu(III)	Co(II)	
Mesoporous KZnFC	4.5	25 °C	–	10.5	[57]
sepiolite	3.9	25 °C			[58]
	4.5				
Zirconium tungstate ion exchanger	6	25 °C	–	4.06	[59]
TiO _{2(0.5)} /SiO _{2(0.5)}	5.5	25 °C	–	2.892	[33]
Aluminum silicate	6	25 °C	–	59.31	[38]
Non-living Chlorella vulgaris biomass			–	91.99	
Aluminum silicate/Chlorella vulgaris composites			–	99.24	
MnO ₂ @PPy			54.74	–	[60]
GO-MnO ₂	3.01	25 °C	103.43	–	[44]
Cellulose functionalized with thiourea	NR	25 °C	27	–	[61]
Si-AL800-chitosan			–	160	[62]
P ₄ AACMA/CuO	3.5	20 °C	–	21.57	This study
	4.5		11.04	–	

NR not found

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Data Availability All the data used for this work are publicly available.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Research Involving Human and Animals Rights Not applicable.

Ethical Approval The authors confirm that the manuscript has been read and approved by all authors. The authors declare that this manuscript has not been published and not under consideration for publication elsewhere.

Consent to Participate All of the authors consented to participate in the drafting of this manuscript.

Consent for Publication All of the authors consent to publish this manuscript.

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