# Efficient sequestration of plutonium from aqueous medium using nitrogen doped graphene nano walls

V. Sri Datta Chaitanya[1,2] · P. A. Manojkumar[3] · S. Tripurasundari[3] · G. Mangamma[3] · V. K. Madhavan Kutty[2] ·
G. Srinivasa Rao[2] · C. P. Kaushik[1]

## Abstract

Nitrogen doped graphene nanowall(s) deposited on carbon paper is employed in sequestration of trace-level plutonium from aqueous solution using batch adsorption technique. Surface and structural characteristics of the sorbent are studied using SEM and Raman spectroscopy, respectively. Radiometric α-counting of the supernatant solution showed > 90% sorption at pH > 7. Visual Minteq modelling revealed that $Pu(OH)_4$ species is responsible for high sorption. Freundlich model evolved as the best fit, implying multilayer deposition on a heterogeneous surface as the mechanism of sorption. The combination of 10 M $HNO_3$ and EDTA resulted in 75% desorption. The results are promising for the sequestration of trace-level plutonium.

**Keywords** Graphene nano walls · Sorption of plutonium · Nuclear waste management · Speciation of plutonium

## Introduction

Sustaining the nuclear technology to meet the energy requirements of twenty first century has been the important consideration of many developing nations including India. A nation would adopt a nuclear policy which should be continuously evolving with every safety methodology in order to protect man and his environment from any unexpected release of radionuclides into biosphere. Various scientific and technological advancements have surfaced recently for the effective management of the waste streams [1]. The appropriateness of a treatment methodology depends on the type and concentration of constituents in the waste stream under consideration. In addition, it should be fast, efficient and economically viable. Sorption is being proved to be one of such best methodologies to achieve the efficient recovery of the radio elements from the waste streams [2].

For aqueous streams with the metal ion contamination, the sorption technology is applied prodigiously enabling them to innocuous streams to be disposed under recommended procedures. In this context, several conventional sorbents such as activated carbon, activated alumina, silica gels etc. have been used in industrial scale. Despite the wide spread usage, their applicability is hampered by the slow kinetics, low efficiency and reduced scope for regeneration. However, nano sorbents have been considered as a remedy to the above shortcomings. The nano sorbents are efficient, reusable and show improved kinetics in the removal of contaminants. Several metal oxide based sorbents and carbon based sorbents were evaluated for the sorptive removal of contaminants [3]. They can also be functionalized appropriately to tune their functionality for a specific application. Among them, graphene based sorbents are one which showcase excellent chemical and radiation stability, enormous surface area and very good surface site density [4, 5]. Additionally, they can be functionalized by hetero atoms, ions and ligands to enhance the sorption capacity and to improve the selectivity [6–8].

Plutonium is one of the major radionuclide that is given a special attention in waste management due to its long radiological half-life and effective biological half-life. In the Low Level Waste (LLW) and Intermediate Level Waste (ILW) streams from reprocessing plants, the alpha emitting nuclides (e.g. Pu) are present in trace levels. The removal of

✉ V. Sri Datta Chaitanya
   vsdchaitanya@igcar.gov.in

1   Homi Bhabha National Institute, Mumbai 400085, India

2   Integrated Nuclear Recycle Plant, Nuclear Recycle Board, Bhabha Atomic Research Centre Facilities, Kalpakkam, Tamilnadu 603102, India

3   Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamilnadu 603102, India

them will make those liquid streams innocuous and makes it an exempt waste which ultimately leads to zero discharge concept.

Graphene nano walls (GNWs) are an artifact of carbon in which the graphene sheets orient non horizontal to the base surface. The unique surface features of GNWs make it a suitable material for the sorption applications. The high efficacy of graphene based materials for the sorptive removal of plutonium from aqueous solutions have been reported in literature [9, 10]. Spent fuel reprocessing very often encounter acidic environments and hence, some studies were focused on removal of plutonium from acidic media [11–13]. In contrast, there are a few studies on the sorptive removal of Pu from complexing media, as well [14, 15].

Doping of hetero atoms onto the sorbent enhances the properties of a sorbent by changing the chemical environment on its surface [16]. For example, the surface modification by nitrogen leads to the generation of multiple types of groups (e.g. imine, pyridine, pyrrole) on the surface which improves sorption power of the sorbent for the metallic species compared to the pristine sorbent [8, 17]. Recently, for the first time, we have reported the exceptionally high (> 94%) sorption capacity of nitrogen doped graphene nano walls for aqueous Ce (1 ppm) solution at and above neutral pH [Chaitanya et al., communicated 2023]. Cerium, being a surrogate of plutonium, it is natural to extend the study towards plutonium sorption. Since, plutonium shows good affinity towards nitrogen moieties [8, 18–20], it is imperative that the nitrogen modification of the graphene nano sheets make sense in the context of sorption of plutonium. Herein the present study, we focus the sorptive removal of plutonium from aqueous solutions and the study extended to acidic, neutral and basic media. The speciation of plutonium under the experimental conditions was modeled and correlated with the sorption measurements. To investigate the mechanism of sorption, the sorption data was modeled using popular isotherm models. Further, the possibility of recovery of Pu from the sorbent was explored as desorption of sorbed metal, which plays an important role in the context of retrieval of the precious/strategic materials because successful application of a sorption process includes the recovery of the targeted species. Hence the desorption behavior was investigated and the optimized conditions for the recovery of sorbed plutonium were presented.

# Experimental

## Materials and methodology

Nitrogen doped GNWs (N-GNWs) were deposited on carbon paper (CP) using plasma enhanced chemical vapour deposition (PECVD) technique. The samples were characterized

for their morphology using FESEM (Zeiss–Supra 50). Raman studies were conducted in a Renishaw make, 532 nm-Nd-YAG laser spectroscope to extract structural and morphological signatures. Ion exchange purified $Pu(NO_3)_4$ solution was diluted and analyzed by radiometry to get a stock solution of Pu in its tetra valent state [21]. Wherever required oxidation state of Pu was adjusted to $Pu^{4+}$ using appropriate concentration of $NaNO_2$. Experiments on plutonium sorption from aqueous medium were performed on pristine carbon paper, pristine GNWs and N-GNWs using batch adsorption method. The Pu concentration in the solution before and after the sorption was estimated using alpha radiometry using a ZnS(Ag) gross alpha counter. All the experiments were carried out at ambient temperature.

## Graphene nanowalls preparation and characterization

The pristine graphene nano walls (GNWs) were synthesized using RF-plasma enhanced chemical vapour deposition technique (PECVD with methane-argon plasma (1:3 ratio) at $5 \times 10^{-3}$ mbar pressure at 800 °C for 3 h at plasma power of 150 W on Carbon paper of size $20 \times 10$ (mm), the details of system description and synthesis procedure are reported elsewhere [23]. The nitrogen modification of the surface had been achieved by exposing to nitrogen (99.89%) plasma for 30 min at $5 \times 10^{-3}$ mbar pressures. Basic characterization of the pristine and N-doped sorbents was carried out with SEM and Raman spectroscopy. FESEM was used for studying the morphology and plasma induced sputtering. Moreover, the built-in measuring tool in FESEM was used for measuring the average thickness of the film. Raman spectra were collected at ambient conditions with 50 mW laser (532 nm) excitation for an acquisition time of 150 s. The G-peak normalized intensity after background correction was plotted against Raman shift.

## Sorption experiments of Pu with N-GNWs

Batch adsorption technique was used to investigate the sorption of Plutonium by GNWs. In a typical experiment, a strip of nano sorbent (10 mm × 10 mm) was placed in a polypropylene vial containing standard Pu solution (1.0 mg/L) with pre adjusted pH. The vial was set for equilibration on a REMI VM-500 orbital shaker for 3 h. After equilibration, the strip was removed. The supernatant solution was carefully separated and an aliquot of 100 μL of the solution was planchetted on an SS disc. The planchette was counted for gross alpha using a pre calibrated ZnS(Ag) scintillation counter having an efficiency ~ 25% and the concentration of Pu was determined using the count rate and the specific activity of Pu. The sorption percentage, sorption capacity

and distribution coefficient were calculated using the respective formulae

$$\% \text{ Sorption} = \frac{C_0 - C}{C_o} \times 100 \qquad (1)$$

$$\text{Equilibrium sorption capacity} \left(q_e\right) = \left(C_0 - C\right) \times \frac{V}{m} \text{mg g}^{-1} \qquad (2)$$

$$\text{Distribution coefficient} \left(K_d\right) = \frac{C_0 - C}{C} \times \frac{V}{m} \text{mL g}^{-1} \qquad (3)$$

where $C_0$ and $C$ are the concentration of sorbate before and after sorption, respectively, V and m are the volume of the solution and mass of the sorbent used for the sorption reaction, respectively.

To study the effect of pH on the sorption of Pu, stock Pu solution was diluted to 1.0 ppm and the pH was adjusted to the required value using $HClO_4$ and NaOH. In separate vials, Pu solutions at different pH were prepared. The batch adsorption experiment was conducted on 5 ml of the solution as described above and the sorption percentage was calculated in each case. In order to understand the mechanism of adsorption, isotherm studies had been performed. For the isotherm studies, the stock solution was diluted to different concentrations in the range of 0.5–10.0 ppm at a given pH and the sorption experiments were conducted to determine the sorption capacities. The speciation of plutonium was modeled by feeding the various experimental conditions in Visual Minteq 3.1 [22] and the data was represented as Speciation distribution vs pH diagrams.

Recovery of Pu sorbed on the N-GNWs was explored by batch desorption studies. The desorption study was performed on the N-GNWs strips which were sorbed in the pH range 3 to 11. The sorbed N-GNWs strips were dried and transferred to different PVC vials and 5 ml 1 M $HNO_3$ was added and equilibrated for 3 h. The N-GNWs strips were removed from the vials and the supernatant solution was analyzed by α–radiometry to determine the percentage desorption. Since, highest sorption was observed at pH 7 and above (as discussed later), the desorption experiment was conducted on N-GNW strips sorbed at pH 7, by employing 1–10 M $HNO_3$, 10 M $HNO_3$ + 0.1 M oxalic acid, 10 M $HNO_3$ + 0.1 M EDTA as desorbing media.

## Results and discussion

### Characterization of the N-GNWs

The FESEM image shows uniform, fine and corrugated morphology of GNWs deposited on carbon paper (Fig. 1). The SEM image further reveals a very open structure
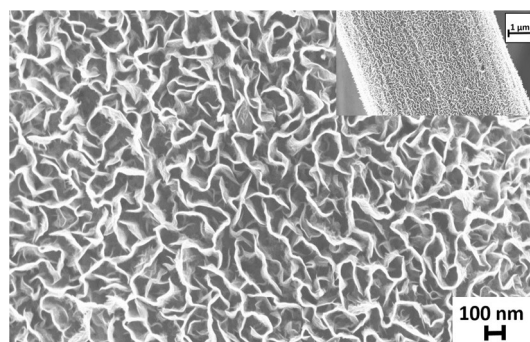


**Fig. 1** FESEM image of N-GNWs showing the corrugated structure of the graphene nano walls on carbon paper substrate and the inset shows the carbon fibre with N-GNWs
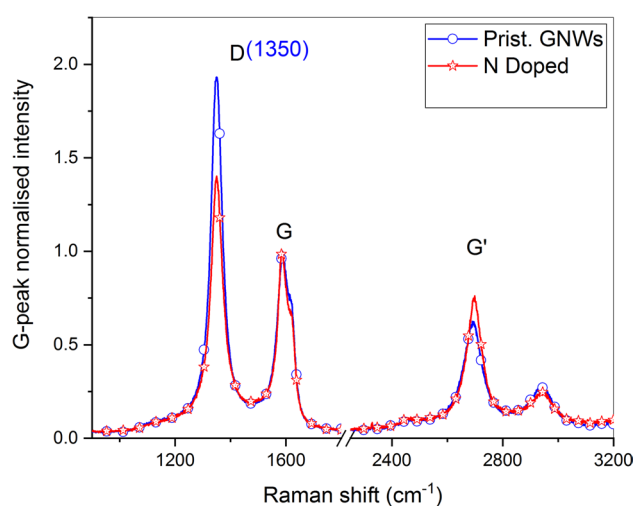


**Fig. 2** Raman spectra of the pristine and n-doped graphene nano walls Nitrogen doping has reduced the $I_D/I_G$ ratio. The increase in the FWHM of D, G and G' peaks is due to generation of different types of defects

indicating availability of large surface area which may be available for sorption. The height of the nanowalls is measured to be approximately 200 nm. Nitrogen doped GNWs and pristine GNWs appear identical in its surface morphology.

Raman spectra of pristine GNWs and nitrogen doped GNWs are shown in Fig. 2. The increase in FWHM of *D*-peak and G-peak of N-GNWs, indicate addition of more defects due to nitrogen doping while the FWHM of G' peak is reduced with plasma exposure, which indicates increased monolayer like character compared to pristine GNWs. An increase in background intensity observed in between *D* and *G* peaks is attributed to generation of structural defects upon nitrogen doping [17, 23]. The Raman study further reveals molecular level modification of vibrational spectra due to addition of heavier and more electronegative nitrogen.

## Sorption studies of plutonium

Initial experiments were conducted to explore the sorption of plutonium in acidic medium. Experiments conducted between 0.5–10 M of $HNO_3$ didn't give encouraging results (Table 1). Reduced sorption of nitrate species of plutonium may be attributed to the attachment of protons to the sorbent surface and consequent non availability of active sites. In the acidic range of 10–0.5 M of $HNO_3$, the surface is fully protonated and the cationic plutonium species e.g. $[Pu(NO_3)_2]^{2+}$ prefer to be in solution due to electrostatic repulsion leading to decrease in sorption percentage. Our results compare with a similar experimental observation reported with increasing concentration of the $HNO_3$ with carbonated coffee powder and GO, respectively [11, 12]. Hence, further sorption experiments were and conducted in aqueous medium in the range—pH 3 to pH 11.

Perchloric acid was chosen as the medium suitable for improved plutonium sorption experiments as it approximates the behavior of free aqua plutonium ions as $ClO_4^-$ is least complexing [15]. Initially, sorption experiments were carried out in 0.1 M $HClO_4$ for CP, GNWs and N-GNWs. For CP, the sorption observed was meagre, whereas the GNWs yielded sorption efficiency of 65%. The N-GNWs resulted in more than 90% sorption under identical experimental conditions. Hence, further experiments were focused on N-GNWs in perchloric acid medium. The sorption efficiency of N-GNWs against pH for 0.1 M and 1.0 M of perchloric acid are plotted in Fig. 3a, c, respectively. It is found that the sorption is low and shows a gradual increase till the sorption edge is reached (pH ~ 5 & pH ~ 7 for 0.1 M and 1.0 M $HClO_4$, respectively). Thereafter, the sorption is greater than 92% and maintained around this range even at higher pH (Fig. 3a, c). This variation is a typical characteristic of the sorption of actinides onto various metal oxide based and carbon based sorbents [24, 25]. There are several reports in literature citing similar trend for the sorption of Pu by various graphene based sorbents [26, 27].

In the region below the sorption edge (Fig. 3a, c), the sorbent encounters excess $H^+$ ions in its vicinity. As a result, the competitive sorption of $H^+$ ion supersedes the positive Pu ions. Hence, the sorption of Pu ions is initially low at low pH and gradually increases with decreasing the $H^+$ ion concentration or increasing pH. Above the sorption edge, the sorption occurs due to the de-protonation of the surface functional groups by which the surface becomes highly available for the sorption of plutonium species.

The variation in the sorption efficiency with pH can be further explained using the sorbate speciation, as it has a profound influence on the sorption efficiency. The speciation of the Pu(IV) with reference to Fig. 3a, c are calculated using Visual Minteq 3.1 and their distributions are shown in Fig. 3b, d. It is evident from the figures that, the major species are $[Pu(OH)_2]^{2+}$, $[Pu(OH)_3]^+$ and $[Pu(OH)_4]$ and are responsible for the sorption in the pH range from pH 1 to pH 11 and is in line with literature [28, 29]. Therefore, both pH of the solution and speciation of the sorbate play a prominent and synergistic role in the sorption of plutonium.

## Role of pH and ionic strength in the sorption

The effect of strength of perchlorate ion on the sorption efficiency of Pu species is shown in Fig. 3a, c (0.1 M and 1.0 M of $ClO_4^-$ respectively) and there is no much difference as the speciation of Pu(IV) is almost same in both cases. A low but finite decrease is observed with increase of perchlorate concentration in the region below the sorption edge and is attributed to the subtle change in the speciation (Fig. 3b, d) leading to different relative distributions of $[Pu(OH)_2]^{2+}$ and $[Pu(OH)_3]^+$ in the range ~ pH = 2 − 3, and process can be understood as the sorption follows outer sphere complexation/ion exchange mechanism. After the sorption edge where quantitative sorption of Pu occurs, there is no change in the sorption efficiency with the increase in strength of $ClO_4^-$ which shows the inner sphere complexation of Pu species onto the surface.

Solution pH is an important variable in the sorption process of aqueous metallic species. It plays a major role in establishing the equilibrium among different species. As a result, the change in pH of the solution as a consequence of sorption, gives important information about the mechanistic aspects of sorption. During the synthesis of N-GNWs, the nitrogen incorporation broadly generates three types of regions with respect to nitrogen viz. electron rich (n-type), electron deficient(p-type) and polar [17]. The O-containing groups such as –OH are also present on the surface. The pH of the solution shifts to higher side which shows the absorption of protons by various n-type nitrogen moieties and oxygen moieties present on the sorbent. But in case of basic pH, the protonated functional groups release $H^+$ ions into the solution which lowers the pH value of the solution.

Keeping the track of pH throughout the sorption process renders important information regarding the mechanism of sorption. From Table 2, it can be seen that for initial pH 5, more protons are absorbed from 0.1 M $HClO_4$ than 1.0 M $HClO_4$ by the sorbent shifts the final pH to 6.33 and 5.48

**Table 1** Sorption of Pu (1 ppm) from Nitric acid by N-GNWs. The sorption percentage is found to be small (~ 3% max.)

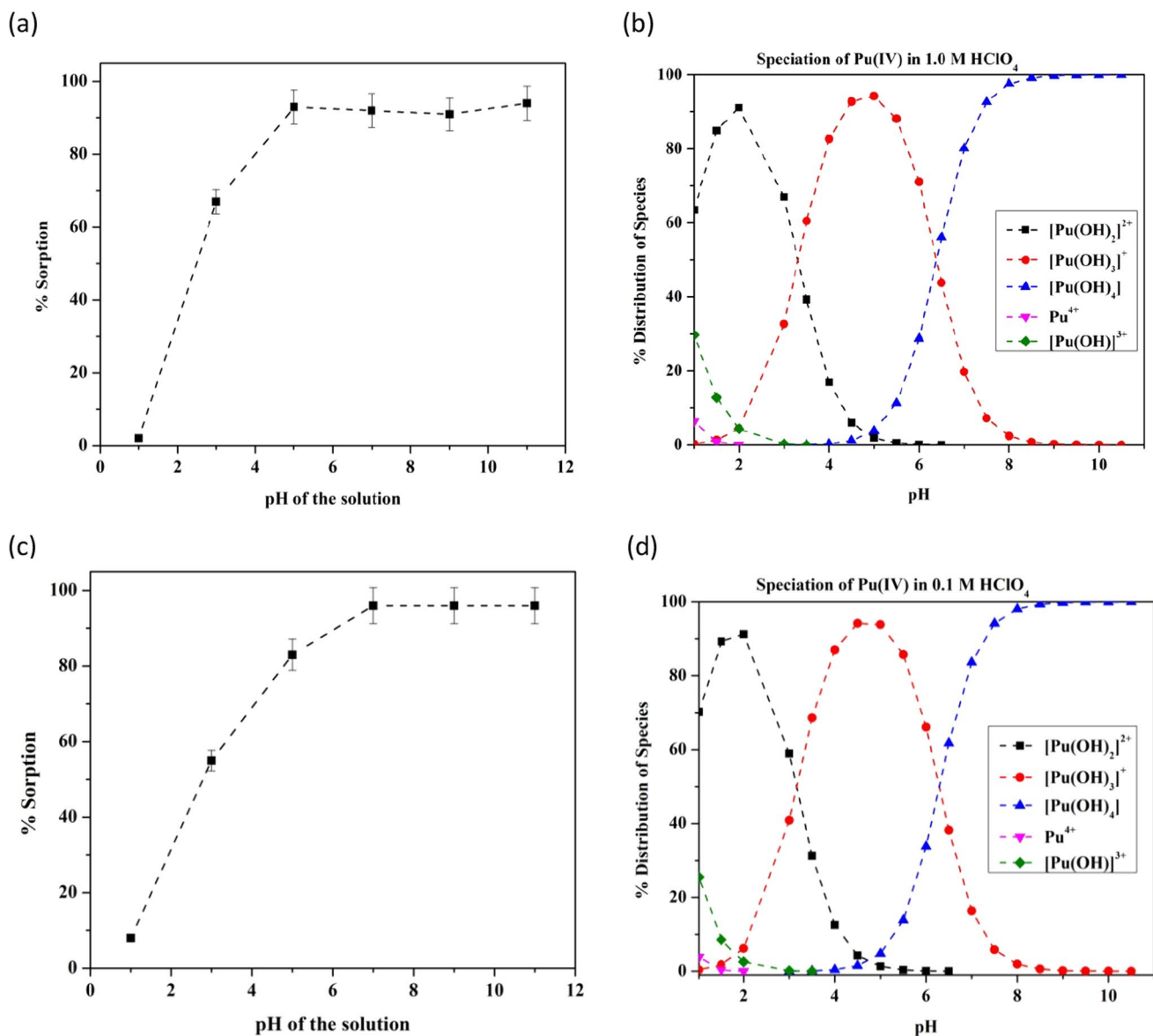| [HNO$_3$], M | Percentage sorption (%) |
| --- | --- |
| 0.5 | 3 |
| 1.0 | < 1 |
| 4.0 | 3 |
| 8.0 | 3 |
| 10.0 | < 1 |

(a)



(b)



(c)



(d)



**Fig. 3** **a** and **c**—Variation of sorption efficiency with pH of the solution from 0.1 M and 1.0 M of perchloric acid respectively. **b** and **d**—Speciation of Plutonium at 0.1 M and 1.0 M perchloric acid respectively. Maximum sorption is observed for $Pu(OH)_4$

**Table 2** Change in solution pH due to sorption

| pH before sorption | pH after sorption from | |
| --- | --- | --- |
| | 1 M $HClO_4$ | 0.1 M $HClO_4$ |
| 3.0 | 2.74 | 2.88 |
| 5.0 | 5.48 | 6.33 |
| 7.0 | 6.78 | 7.10 |
| 9.0 | 7.58 | 7.86 |
| 11.0 | 8.58 | 10.70 |

The increase/decrease in pH is due to protonation & deprotonation of various functional groups on the sorbent

respectively and correspondingly the sorption is higher in former case. Hence the change in solution pH corresponds to the sorption of plutonium species. Lastly, it should be kept in mind that various O-containing and N-containing functional groups on the surface of N-GNWs have different $pK_a$ values and the final pH after sorption is the resultant of all of these changes.

## Effect of initial concentration of Pu on the sorption

The effect of initial concentration of Pu on the sorption efficiency is also explored by conducting sorption experiments by varying the Pu concentration in the range 0.5–10.0 mg/L

and the results are shown in Table 3. It is seen that the sorption efficiency of Pu increases with its initial concentration but it's not saturated. Hence, it is important to know the mechanism operating in the sorption process. Additionally, the distribution coefficient for Pu sorption is found to be in the range of $6.7 \times 10^7$ (calculated empirically) which is exceptionally high. Considering these two aspects, the mechanism operating behind the sorption process is deduced from isotherm analysis for the prediction of a suitable model.

The study of isotherms provides insights in to the nature of sorption process (chemisorption or physisorption, monolayered or multilayered sorption) and yields important parameters which are characteristic of the sorbent (e.g. porosity) and the sorption process involved (e.g. maximum sorption capacity, sorption energy). It also indicates the strength of adsorbate-adsorbent interactions. In the present study, the sorption data have been fitted to the popularly used Freundlich, Dubinin-Radushkevich (D-R) and Temkin adsorption models.

## Freundlich isotherm model

The Freundlich isotherm model assumes the surface to be heterogeneous and the sorption as multilayered. The governing relationship in linear form is expressed as

$$\ln q_e = \ln K_f + (1/n) \ln C_e \tag{4}$$

where $K_f$ is Freundlich isotherm constant (mg/g) and n is adsorption intensity. Ce and $q_e$ denote the concentration (mg/L) and sorption capacity (mg/g) respectively at equilibrium. In Eq. (4), the value of n which is encompassed in the slope, gives the strength of sorption while the intercept gives the magnitude of $K_f$ which indicates the maximum sorption capacity. In particular, if n = 1, the partition of the metal ion between the solid and liquid phases is independent of the concentration of the metal ion. Values larger than or smaller than 1 indicate normal sorption and cooperative adsorption, respectively.

Figure 4a shows the plot of $\ln q_e$ versus $\ln C_e$ which shows a linear behavior and when linearly fitted, yields a Regression coefficient $(R^2) \sim 0.9997$. The linear behavior confirms the chemical heterogeneity of the sorbent

surface. In addition, the sorption capacity was calculated to be 89,757 mg/g which is exceptionally high in comparison with a recently reported study (carbonate treated coffee powder: $K_d = 30.9$ mg/g) [12] The value of n is 0.755 which indicates the mechanism as cooperative sorption.

## Dubinin-Radushkevich (D-R) isotherm model

Unlike the Freundlich isotherm model, the Dubinin–Radushkevich isotherm model is an empirical one conceived for the sorption on heterogeneous surface with a Gaussian energy distribution. The D-R isotherm is expressed in linear form as follow

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{5}$$

where $q_e$, $q_m$ are the equilibrium sorption capacity(mg/g) and maximum sorption capacity (mg/g) respectively, $\beta$ is activity coefficient and $\varepsilon$ is Polanyi potential (kJ/mol)

$$\varepsilon = RT \ln \left(1 + 1/C_e\right) \tag{6}$$

where R is gas constant, T is absolute temperature and $C_e$ is equilibrium concentration of sorbate.

In this model, $\ln q_e$ plotted against $\varepsilon^2$ yields a straight line whose intercept $q_m$ gives the maximum sorption capacity and sorption energy calculated from the slope $\beta$ using the relation

$$E = 1 \Big/ (2\beta)^{1/2} \tag{7}$$

Figure 4b shows a linear plot of $\ln q_e$ against $\varepsilon^2$ with a regression coefficient $\sim 0.9679$. The $q_m$ was calculated to be 40,945 mg/g and the sorption energy was found to be 3.162 J/mol which suggests the nature of sorption process indeed pertains to physisorption.

**Temkin isotherm model:** The Temkin isotherm model considers the adsorbent-adsorbate interactions and assumes a linear relationship between the heat of adsorption and the surface coverage of the form

$$q_e = (RT/b) \ln A + (RT/b) \ln C_e \tag{8}$$

where b (kJ/mol) and A (L/mg) are Temkin isotherm parameters which signify heat of adsorption and equilibrium binding constant, respectively.

Figure 4c shows a plot of $q_e$ versus $\ln C_e$ and fitted to linear form with a regression coefficient of $\sim 0.9291$ From the figure, the slope and intercept A (equilibrium binding constant) are found to be 0.2107 J/mol and 22.9932 L/mg, respectively. From the value of b, the heat of adsorption (RT/b) is calculated as 11.76 kJ/mol, which indicates the nature of sorption is physisorption. However, the
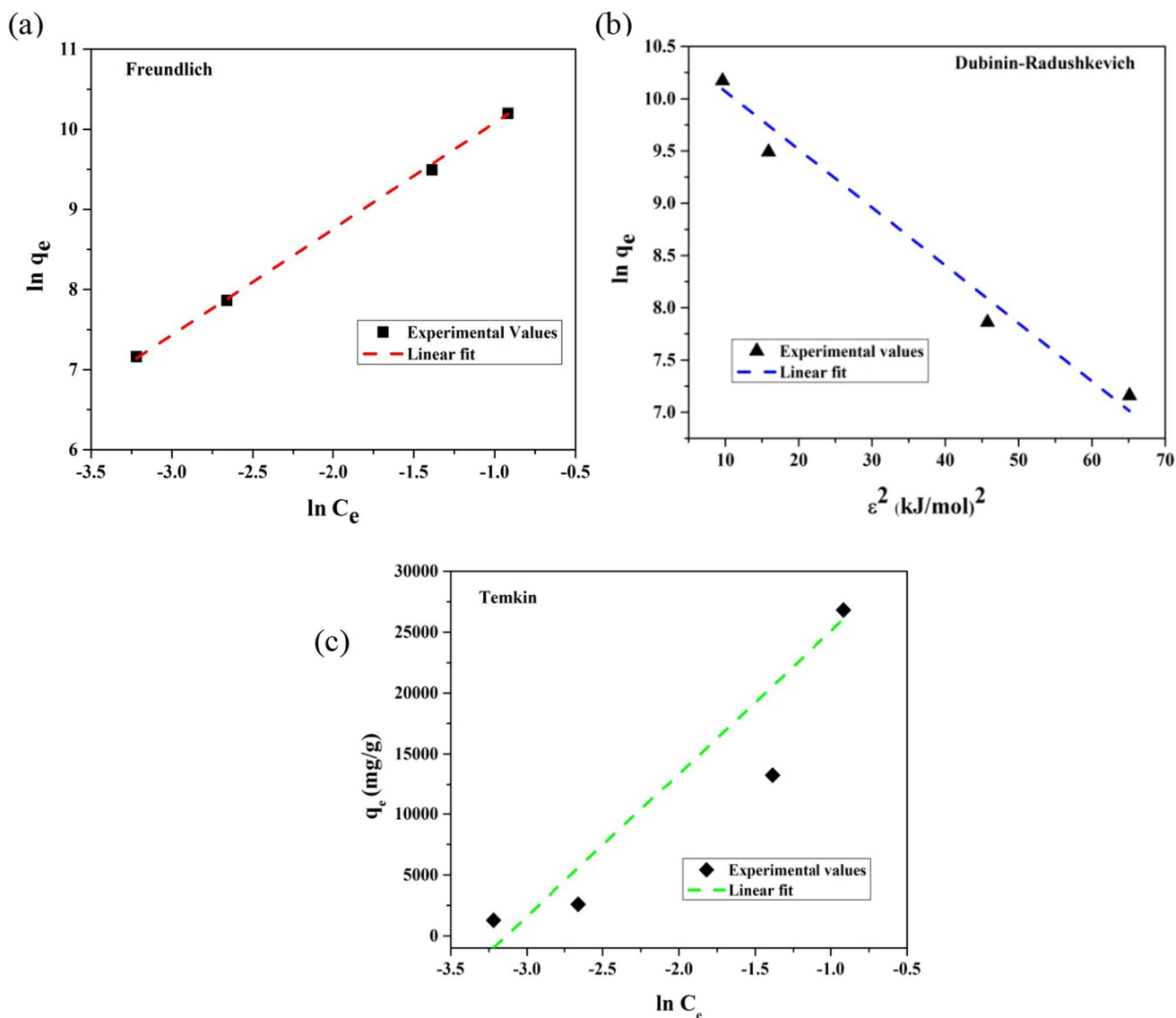
**Table 3** Effect of initial concentration of Pu on sorption. The sorption is more than 90% over the studied concentration range

| Conc. of Pu (mg/L) | Sorption efficiency (%) |
|---|---|
| 0.5 | 92 |
| 1.0 | 93 |
| 5.0 | 95 |
| 10.0 | 96 |

**Fig. 4** Isotherm curves for the sorption of Pu on N-GNWs at pH = 5 from 0.1 M HClO$_4$ (**a**) Freundlich Isotherm (**b**) Dubinin-Radushkevich isotherm (**c**) Temkin isotherm

**Table 4** Calculated isotherm constants for the sorption of Pu(IV) by N-GNWs

| Isotherm model | Constants | | | Inference |
|---|---|---|---|---|
| Freundlich | K$_F$(mg/g) | n | R$^2$ | Cooperative sorption, surface is heterogenous and the sorption is multilayered |
| | 89,757 | 0.7552 | 0.9997 | |
| Dubinin-Radushkevich | q$_m$ (mg/g) | ε(J/mol) | R$^2$ | Sorption energy = 3.162 kJ/mol, nature of sorption is physisorption |
| | 40,945 | 3.1620 | 0.9679 | |
| Temkin | b (J/mol) | A(L/mg) | R$^2$ | Heat of Sorption = 11.76 kJ/mol, |
| | 0.2107 | 22.9932 | 0.9291 | Nature of sorption is physisorption. Equilibrium binding const = 22.9932 L/mg |

experimental data doesn't fit to a straight line as assumed in the Temkin's model.

The isotherm parameters obtained from various isotherm models are tabulated (Table 4). From the $R^2$ value, it can be concluded that the Freundlich isotherm model fits well for the experimental data of sorption of Pu by N-GNWs than the other isotherm models. From the Freundlich isotherm fitting parameters, it can be concluded that the sorption capacity is 89,757 mg/g which is huge and highly promising for the separation of plutonium over a wide concentration range. As the sorption seems to follow Freundlich's model, it can also be said that the surface of N-GNWs is heterogenous with large number of binding sites for sorption enhanced by nitrogen doping on GNWs.

From the data of sorption and isotherm analysis, it can be said that Pu binds effectively with N-GNWs during sorption. Earlier, there were several reports which emphasize the strong affinity of Pu to the nitrogen containing groups. The surface of N-GNWs contains different types of nitrogen moieties along with oxygen containing groups. The hard-hard interactions of these N-moieties and O-containing groups with Pu species lead to the effective sorption of Pu onto N-GNWs surface. However it can be reiterated that since Pu shows stronger affinity towards N-centres than O-centres [8] The N-doping effectively increases the potential of graphene nano walls for the sorption of plutonium. Hence an exploratory study to give a roadmap for recovery of plutonium was carried out.

## Desorption studies of Pu from N-GNWs

For the successful deployment of a sorbent for intended applications, the recovery of the targeted species is important. However, in the context of nuclear species, the immobilization of the species gives a special advantage despite its recovery. This option is not preferable for the alpha radionuclides because of their long radiological half-life. Therefore, the recovery of sorbed plutonium from the sorbent surface plays an important role.

In the present study, an attempt was made to recover sorbed Plutonium by chemical desorption technique, in which the desorption medium could be one which dissolves the sorbed plutonium and inert to the sorbent. Such a recovery could be manifested with the aid of complexant [12, 26, 30]. For the sorbents with nitrogen containing functional groups, complete desorption of radionuclides is extremely hard due to the strong affinity of sorbate species with the N-containing groups[8]. Hence, there is a requirement to find a suitable desorbing environment such as acids that are aided by complexants.

In the desorption study three sets of experiments had been conducted on the Pu sorbed N-GNWs strips with, viz. nitric acid, nitric acid and oxalate and nitric acid and
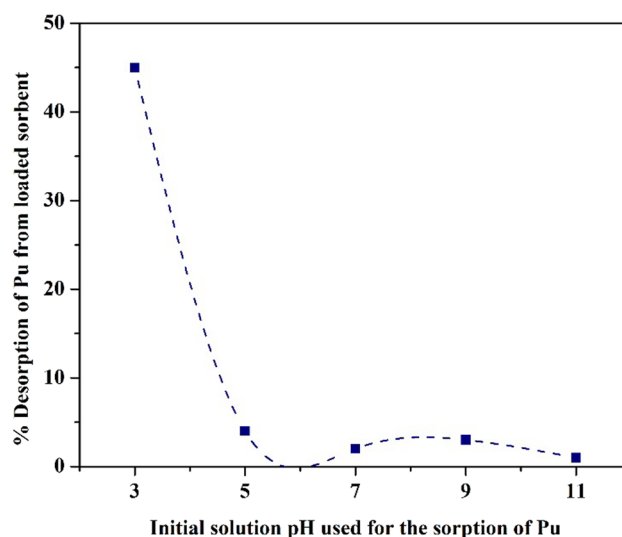


**Fig. 5** Desorption percentage of Plutonium from the N-GNWs sorbent plotted against the sorption pH (Desorbing medium: 1 M $HNO_3$)

EDTA. In the first experiment, the desorption by 1 M $HNO_3$ for the sorbent strips which are equilibrated with Pu solution of pH 3 to pH 11 are analysed. Figure 5 shows the desorption percentage is maximum for the sorbent strips exposed to pH 3 Pu solution. It is inferred from Fig. 5 that the desorption percentage is low for N-GNWs strips sorbed at higher pH. This may be attributed to the strong binding of $Pu(OH)_4$ species to the nitrogen and oxygen containing functional groups on the sorbent surface. Similar observations were reported in the literature [8, 31].

It should be noted that, for the sorption experiment as described in the previous section, highest sorption was achieved at pH 7 and above. Hence, the requirement is for a suitable desorption condition for the sorbent strips exposed to pH 7 and above. Therefore, the extent of desorption is tested for the N-GNWs strips sorbed at pH 7 Pu solution for nitric acid of concentration 3 M, 6 M, 8 M and 10 M. However, the desorption percentage only marginally increased from 3 to 6%. Nevertheless, 10 M $HNO_3$ was fixed as the benchmark concentration to provide the best feasible acidic environment for further experiments. Under this condition, when (potassium) oxalate (0.1 M) is used as the complexing agent, the desorption percentage is ~50% and when EDTA (0.1 M) is used, desorption percentage is ~75%. The higher efficiency of EDTA over oxalate may be attributed to its superior complexation ability ($K_{oxalate} = 10^{16}$; $K_{EDTA} = 10^{24}$) which may effectively overcome the binding forces between sorbed Pu species and the surface. Hence, it is inferred that both high acidity (10 M $HNO_3$) and aid of (0.1 M EDTA) complexing agent are very efficient in desorption of plutonium.

The sorption of Pu on N-GNWs is highest at pH above 6 and the predominant species that exist in this range is $Pu(OH)_4$. The Pu sorbed under the above conditions may be desorbed efficiently using 10 M $HNO_3$ and 0.1 M EDTA. The study provides a road map for the sequestration of trace level of Pu form aqueous waste streams.

## Conclusions

The present study shows the efficacy of nitrogen doped graphene nano walls for the sequestration of plutonium (> 93%) from aqueous solutions containing trace levels. The speciation studies revealed that maximum sorption shall be achieved at pH 7 from a solution having $Pu(OH)_4$ as the major species. The mechanistic aspects of sorption were explored using the batch adsorption studies and found that the sorption follows inner sphere complexation mechanism at highest sorption efficiency. From the isotherm analysis, it was deduced that the sorption follows Freundlich mechanism suggestive of the heterogeneity of the sorbent surface which is attributed to the various O and N containing functional groups. The nanosorbent showed an enormous sorption capacity of 89,757 mg/g, demonstrating N-GNWs on carbon paper a promising sorbent material. An exploratory study on desorption studies showed that the combination of 10 M $HNO_3$ + 0.1 M EDTA could recover 75% of the sorbed plutonium. The study provides a viable roadmap for recovery of Pu from trace levels in aqueous medium.

## Declarations

## References

1. Kadadou D, Said EA, Ajaj R, Hasan SW (2023) Research advances in nuclear wastewater treatment using conventional and hybrid technologies: Towards sustainable wastewater reuse and recovery. J Water Process Eng 52:103604

2. Rout DR, Jena HM, Baigenzhenov O, Hosseini-Bandegharaei A (2023) Graphene-based materials for effective adsorption of organic and inorganic pollutants: A critical and comprehensive review. Sci Total Environ 863:160871

3. Ansari AA, Shamim MA, Khan AM, Anwar K, Wani AA (2023) Nanomaterials as a cutting edge in the removal of toxic contaminants from water. Mater Chem Phys 295:127092

4. Karthik V, Selvakumar P, Senthil Kumar P, Vo D-VN, Gokulakrishnan M, Keerthana P, Tamil Elakkiya V, Rajeswari R (2021) Graphene-based materials for environmental applications: a review. Environ Chem Lett 19:3631–3644

5. Yu S, Wang X, Tan X, Wang X (2015) Sorption of radionuclides from aqueous systems onto graphene oxide-based materials: a review. Inorg Chem Front 2:593–612

6. Hu R, Shao D, Wang X (2014) Graphene oxide/polypyrrole composites for highly selective enrichment of U(VI) from aqueous solutions. Polym Chem 5:6207–6215

7. Verma S, Kim KH (2022) Graphene-based materials for the adsorptive removal of uranium in aqueous solutions. Environ Int 158:106944

8. Sun Y, Shao D, Chen C, Yang S, Wang X (2013) Highly efficient enrichment of radionuclides on graphene oxide-supported polyaniline. Environ Sci Technol 47:9904–9910

9. Lujaniene G et al (2016) Sorption of radionuclides and metals to graphene oxide and magnetic graphene oxide. J Radioanal Nucl Chem 307:2267–22758

10. Wu QY, Lan JH, Wang CZ, Zhao YL, Chai ZF, Shi WQ (2014) Understanding the interactions of neptunium and plutonium ions with graphene oxide: scalar-relativistic DFT investigations. J Phys Chem A 118:10273–10280

11. Ali I, Zakharchenko EA, Myasoedova GV, Molochnikova NP, Rodionova AA, Baulin VE, Burakov AE, Burakova IV, Babkin AV, Neskoromnaya EA (2021) Preparation and characterization of oxidized graphene for actinides and rare earth elements removal in nitric acid solutions from nuclear wastes. J Mol Liq 335:116260

12. Patil P, Sarathbabu M, Pathak S, Sengupta A (2023) Carbonate treated coffee powder (CTCP) for selective sorption of $Pu^{4+}$ over $Am^{3+}$, $Np^{4+}$, $NpO_2^{2+}$, and $PuO_2^{2+}$ from aqueous acidic solution: Investigation on mechanism, kinetics, thermodynamics, stripping and radiolytic stability. Appl Radiat Isot 194:110695

13. Kumar P, Sengupta A, Deb AKS, Dasgupta K, Ali SM (2016) Sorption behaviour of $Pu^{4+}$ and $PuO_2^{2+}$ on amido amine-functionalized carbon nanotubes: experimental and computational study. RSC Adv 6:107011–107020

14. Chaitanya VSD, Madhavan Kutty VK, Jawahar NR, Kaushik CP (2022) Sorption of plutonium from aqueous medium containing oxalate using zero-valent iron nano particles. J Radioanal Nucl Chem 331:2515–2522

15. Vats BG, Pius IC, Noronha DM, Kannan S (2018) A novel approach for extraction of plutonium and americium from aqueous complexing media. J Radioanal Nucl Chem 317:227–234

16. Chen F, Guo L, Zhang X, Leong ZY, Yang S, Yang HY (2017) Nitrogen-doped graphene oxide for effectively removing boron ions from seawater. Nanoscale 9:326–333

17. Manojkumar PA, Krishna NG, Mangamma G, Albert SK (2019) Understanding the structural and chemical changes in vertical graphene nanowalls upon plasma nitrogen ion implantation. Phys Chem Chem Phys 21:10773–10783

18. Jarvis NV, Hancock RD (1994) The affinity of plutonium (IV) for nitrogen donor ligands. Radiochim Acta 64:15–22
19. Hancock RD, Bartolotti LJ (2013) A DFT study of the affinity of lanthanide and actinide ions for sulfur-donor and nitrogen-donor ligands in aqueous solution. Inorg Chim Acta 396:101–107
20. Andreev GB, Budantseva NA, Fedoseeva AM.(2007) In: Krivovichev SV, Burns PC, Tananaev IG (Eds.) Structural Chemistry of Inorganic Actinide Compounds. Elsevier, pp. 363–407
21. Bagawde SV, Ramakrishna VV, Patil SK (1976) Oxalate complexing of tetravalent actinides. J Inorg Nucl Chem 38:1669–1672
22. Gustafsson JP (2013) Visual MINTEQ version 3.1 Sweden. Downloaded from: https://vminteq.lwr.kth.se/ (Accessed on 03/09/2019)
23. Manojkumar PA, Mangamma G, Amirthapandian S, Pandian R, Sairam TN, Albert SK (2019) Role of process gas ratio on the structural and plasmonic properties of graphene nanowalls. Diam Relat Mater 97:107452
24. Gupta NK, Choudhary BC, Gupta A, Achary SN, Sengupta A (2019) Graphene-based adsorbents for the separation of f-metals from waste solutions: a review. J Mol Liq 289:111121
25. Bhagyashree K, Mishra RK, Shukla R, Kasar S, Kar A, Kumar S, Kumar S, Kaushik CP, Tyagi AK, Tomar BS (2013) Sorption of plutonium from low level liquid waste using nano $MnO_2$. J Radioanal Nucl Chem 295:1561–1566
26. Romanchuk AY, Slesarev AS, Kalmykov SN, Kosynkin DV, Tour JM (2013) Graphene oxide for effective radionuclide removal. Phys Chem Chem Phys 15:2321–2327
27. Sengupta A, Gupta NK (2017) MWCNTs based sorbents for nuclear waste management: A review. J Environ Chem Eng 5:5099–5114
28. Knopp R, Neck V, Kim JI (1999) Solubility, Hydrolysis and Colloid Formation of Plutonium(IV). Radiochim Acta 86:101–108
29. Choppin GR (2006) Actinide speciation in aquatic systems. Mar Chem 99:83–92
30. Crane RA, Dickinson M, Scott TB (2015) Nanoscale zero-valent iron particles for the remediation of plutonium and uranium contaminated solutions. Chem Eng J 262:319–325
31. Wang X, Yu S, Jin J, Wang H, Alharbi NS, Alsaedi A, Hayat T, Wang X (2016) Application of graphene oxides and graphene oxide-based nanomaterials in radionuclide removal from aqueous solutions. Sci Bull 61:1583–1593