

Understanding the sorption behavior of tetra- and hexavalent plutonium on fungus *Rhizopus arrhizus* dead biomass

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Abstract An attempt was made to understand the sorption behaviour of Pu^{4+} and PuO_2^{2+} on *Rhizopus arrhizus* fungus. The sorption data were analyzed using Langmuir, Dubinin–Radushkevich, Freundlich isotherm and Tempkin isotherms, which revealed that the sorption proceeds via chemisorption through mono layer following Langmuir isotherm. The sorption kinetics were analyzed by different models revealing the predominance of pseudo 2nd order kinetics. Oxalic acid and sodium carbonate were used for effective stripping of Pu^{4+} and PuO_2^{2+} , respectively. This biomass was found to be radiolytically stable and finally was applied for processing of SHLW from RR and FBR origins.

Keywords Plutonium · Bio sorption · Isotherm · Sorption kinetics · Radiolytic stability

Introduction

A transuranic radioactive element proven being a promising factor for the success of nuclear programme, Pu as from its fissile nature it describes that it can sustain a nuclear chain reaction which is one the character that qualify Pu as fuel in reactors, it can have other applications too as used as a heat

source in radioisotope thermoelectric generator in aircrafts [1, 2]. The fact that Pu is a man-made element and not found in nature, makes it expensive and as the three stages of nuclear programme in India mainly revolves around the ^{239}Pu in first two most important stages making it more vulnerable, hence judicious and efficient use of the element is one of the prime requisite apart from the environmental risk associated with its radio-toxicity. Therefore preferential separation of plutonium ion is important in front and back end of nuclear fuel cycle. TBP is used extensively for the extraction of plutonium in nuclear industries from spent fuel [3–7]. But due its poor radiolytic stability which resulted in poor efficiency and degraded its selectivity, non-biodegradability, co-extraction of Ru, Rh, generation of large amount of organic liquid waste leads to a need of efficient, selective, radiolytically stable and environmental friendly separation procedure for Pu. Solid phase separation using biomass not only reduces the handling of large amount of organic waste, but also makes the overall separation process cheaper. Many studies have been made and divulge the fact that microbial biomass are very efficient in absorbing metal ions from the aqueous solution [8–14] as they have many potential sites as cell wall, cell envelope, etc. for the uptake of metal ions [8, 15, 16]. It was studied that these microbial biomass could be used to decontaminate waste streams of mining, nuclear fuel cycle, refinery etc., and also could be used to concentrate metals [13, 14, 17, 18]. Biomasses from a bacterial species-*Streptomyces viridochromogenes*, the brewer's yeast-*Saccharomyces cerevisiae*, bacterial species-*Pseudomonas aeruginosa* and *Rhizopus arrhizus* a fungus and many others were studied for uptake of uranyl ion [13, 14, 17, 18]. *R. arrhizus* biomass was the most efficient one of them [14], therefore this biomass in particular draw attention of the researchers. Literatures revealed that *R. arrhizus* secrete small siderophores

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which are mainly chelating compounds of iron. These siderophores are strong iron chelating agents as they form stable hexadentate, octahedral complex preferentially with Fe^{3+} rather with other metal ions. It has been proven that it is also a good chelating agent for plutonium, uranium, aluminium, gallium, chromium, copper, zinc and magnesium [19, 20]. In view of this, the present investigation was based on understanding the sorption behavior of plutonium in tetra and hexa valent oxidation states on *R. arrhizus*. It includes analyzing different sorption isotherms, sorption kinetics, stripping behavior, selectivity and radiolytic stability.

Experimental

Preparation of biomass

The fungus of Mucoraceae family, *R. arrhizus* (wild type) was procured from National chemical laboratory, Pune, India. Then it was cultured in a 150 ml sterilized modified Czepak box [21–23] within a 500 ml erlenmeyer flask at 28 ± 1 °C on a rotary shaker at 150 rpm. Then the biomass acquired from the Rhizopus species was washed with boiling acetone and dried at 110 °C to constant weight. Finally, the dried biomass was ground sieved and the 30–50 mesh size fraction (British standard) was used for the present investigation.

Materials

^{239}Pu stock solution was prepared by dissolving spectra pure PuO_2 in conc. HNO_3 +0.05 M HF followed by fluoride removal by repeated evaporation to dryness. Finally, the aqueous feed acidity was adjusted to 1 M HNO_3 . The oxidation state of plutonium was adjusted using NaNO_2 and AgO for Pu^{4+} and PuO_2^{2+} , respectively. Oxalic acid and Na_2CO_3 used in the present investigation were produced from Thomas Baker Chemical limited and Qualigens fine Chemicals, Mumbai, India respectively. Suprapure HNO_3 (E-Merck, Darmstadt, Germany), CertiPUR[®] solutions of individual elements (E-Merck, Darmstadt, Germany) and quartz double distilled water were used throughout the investigation. All the experiments were carried out with tracer level of ^{239}Pu (μM range).

Method

Determination of K_d at various feed acidity

For the sorption experiment 5 mg of biomass *R. arrhizus* NCIM 997 each, was taken in different tubes and allowed to equilibrate with aqueous phase containing ^{239}Pu (μM level) in various feed acidity (ranging from 0.01–6 M

HNO_3) in a temperature controlled water bath shaker for 2 h. After 2 h of equilibration, it was allowed to settle for 5 min. Then suitable aliquots from the aqueous phase was collected and used for liquid scintillation counting. The K_d values were calculated using the equation below [23].

$$K_d = \frac{(C_0 - C_e) v}{C_e w} \quad (1)$$

where C_0 is the initial plutonium count, C_e is the plutonium count after bio-sorption, v is the volume of the aqueous phase (in mL) and w is weight of the biomass (in gm) taken.

Understanding the sorption isotherm

For understanding the sorption isotherm different amount of biomass (5–25 mg) were taken for the investigation. The bio-sorption experiments were done at 300 K for 2 h.

Kinetics of sorption

For sorption kinetics experiments 20 mg biomass was allowed to equilibrate for different contact time (ranging from 15 to 180 min) at 300 K from an aqueous feed acidity 3 M HNO_3 .

The stripping studies

The stripping of metal ion from *R. arrhizus* is one of the essential requirements for the reusability of the sorbent. The stripping experiments are carried out in as a two step process. In the first step the biomass was allowed to equilibrate with the plutonium in 3 M aqueous feed acidity. In the second step, the loaded biomass was allowed to contact with 1 ml of stripping solution (1 M Na_2CO_3 , 1 M oxalic acid). After second step the aqueous phase was collected to evaluate the % stripping behavior of Pu from loaded biomass.

Processing of simulated high level waste (SHLW)

For checking the selectivity of the *R. arrhizus* biomass towards plutonium ions over other metal ions; biomass was applied to process SHLW of research reactor (RR) and Fast Breeder Reactor (FBR) origin. The raffinate was then directly fed to the plasma for the analysis of the constituents metal ions by Inductive Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with charged coupled device (CCD) as detector. The optimized experimental and instrumental parameters are summarized elsewhere [24]. This is a relative and simultaneously multi elemental method. CertiPUR[®] solutions of individual elements (E-Merck,

Darmstadt, Germany) were used for multi-point calibration (0.05–1000 mg L⁻¹). Though different analytical lines of the analytes were used, the results corresponds to the best performed analytical lines were summarized. Since only μM level of Pu was spiked in SHLW, the spectral interference from Pu was not significant, therefore, Pu separation prior to the ICP-AES analysis was not necessary. The SHLW was prepared in aqueous medium and the individual analyte concentrations were in the range of 100 of mg L⁻¹. It has been demonstrated that these concentrations of concomitant analytes did not show any mutual interference in the specified analytical lines. Therefore, aqueous Merck standards were used for quantification.

The radiolytic stability

For the investigation on the radiolytic stability of the biomass, the biomass was exposed in gamma rays having dose up to 1000 kGy using ⁶⁰Co source in FTD, Bhabha Atomic Research Centre, Mumbai, India. The K_d values for Pu in both the oxidation states were determined using the irradiated biomass following same experimental procedure.

Results and discussions

Variation of K_d values as a function of aqueous feed acidity

Extraction profile for Pu⁴⁺ and PuO₂²⁺ was obtained in Fig. 1 by varying K_d values as a function of aqueous feed acidity. Throughout the feed acidity range the K_d values for Pu⁴⁺ were found to be almost 1.5 times more than that of PuO₂²⁺. The higher sorption efficiency of tetra valent plutonium is attributed to the higher chemical potential

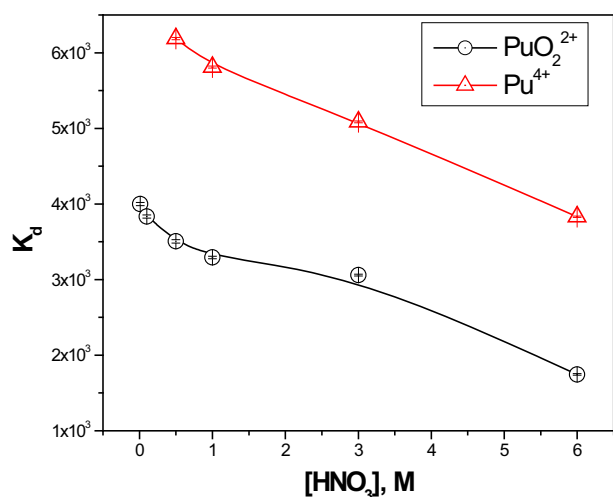


Fig. 1 Extraction profiles for Pu⁴⁺ and PuO₂²⁺ from various aqueous feed acidity using *Rhizopus arrhizus*

compared to hexavalent plutonium [25]. For both the oxidation states the K_d values were found to decrease with increase in aqueous feed acidity. This can be attributed to the fact that at higher feed acidity, the availability of large amount of H⁺ ion competes strongly with the plutonium ion or in other words the ligating sites in the biomass were largely utilized in the protonation [26].

Sorption isotherm

For understanding the sorption mechanism, different sorption isotherm models were taken into consideration. The experimentally obtained data of sorption for Pu⁴⁺ and PuO₂²⁺ were used for fitting in widely four famous sorption isotherm models, Langmuir, Dubinin–Radushkevich (D–R), Freundlich and Temkin isotherms and based on the best linear regression, the operating isotherm model was determined.

Langmuir isotherm

This is most accepted model which assumes the ideal nature of sorbent–sorbate interaction at isothermal condition and presumes certain facts which include that all sites of sorption are equivalent, all the absorbing sites show homogenous nature, sorption is restricted only up to monolayer and there is no interaction between adsorbate molecules on neighboring sites. This isotherm can be explained by the given equation below [27–29].

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \quad (2)$$

where, q_e is the amount of metal ion adsorbed on the fungus biomass at equilibrium condition, C_e is the equilibrium concentration of the Pu⁴⁺ or PuO₂²⁺ ion, q_o is the sorption capacity of biomass for Pu⁴⁺ or PuO₂²⁺ ion in which the sorption capacity of fungus biomass for Pu⁴⁺ was higher than that of PuO₂²⁺ as observed from the experimental data and b is the sorption energy which is also higher for Pu⁴⁺ than PuO₂²⁺ as observed in the present study. The linear regression coefficient of Pu⁴⁺ and PuO₂²⁺ for the Langmuir isotherm were found to be 0.99998 and 0.99982 respectively.

Dubinin–Radushkevich (D–R) isotherm

Dubinin–Radushkevich isotherm model is based on the Polyani potential theory of adsorption. Dubinin–Radushkevich isotherm model can be shown as [30].

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \quad (3)$$

where, X_m is the maximum sorption capacity, ε is the polyani potential, β is the activity constant and q_e is the

amount of adsorbed Pu ion at equilibrium on the *R. arrhizus* biomass. The, ε value could be found out from the given equation below

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (4)$$

in which, R is the universal gas constant i.e. $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, C_e is the Pu ion in equilibrium concentration and T is the absolute temperature. The E energy value can be calculated from the given equation below

$$E = 1/(-2\beta)^{1/2} \quad (5)$$

The E value of Pu^{4+} and PuO_2^{2+} were found to be 537.63 and 719.42 kJ mol^{-1} respectively which suggests that the sorption process is chemi-sorption. The linear regression coefficient of Pu^{4+} and PuO_2^{2+} for the D–R isotherm were found to be 0.97806 and 0.97004 respectively. This high sorption energy for both the metal ion revealed that the sorption process must be through the chemical interaction and it is definitely not physic-sorption.

Temkin isotherm

The main assumption of Temkin isotherm model is that, the heat of adsorption (function of temperature) decreases linearly (not logarithmically) with increasing coverage. This isotherm also neglects the extremely low and high value of concentrations. The model can be quantitatively expressed as [31].

$$q_e = \frac{RT}{b} \ln(A_T C_e) \quad (6)$$

$$q_e = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_e \quad (7)$$

where, A_T is Temkin isotherm equilibrium binding constant (L g^{-1}), b is Temkin isotherm constant, and T is the absolute temperature. In our present investigation it was observed that the b value for PuO_2^{2+} was lower than that of Pu^{4+} whereas overturning result was noted for the A_T values. The linear regression coefficient of Pu^{4+} and PuO_2^{2+} for the Temkin isotherm were found to be 0.99803 and 0.99823, respectively.

Freundlich isotherm

This adsorption isotherm is an experimental relation of the concentration of a solute on the surface of an adsorbent with the concentration of the solute in the liquid. This adsorption model proceeds by assuming certain facts that (i) the adsorbing sites are heterogeneous in nature (ii) adsorption is not restricted only up to monolayer (iii) also the active sites are non-uniform in nature. The following Freundlich isotherm holds good at low pressure and can be showed as [32].

$$\log x/m = \log K_f + 1/n \log C_e \quad (8)$$

where, x/m is the amount of plutonium ions adsorbed per gram of the *R. arrhizus* biomass at equilibrium condition (mg g^{-1}), K_f is Freundlich isotherm constant (mg g^{-1}), C_e is the equilibrium concentration of plutonium (mg L^{-1}), n is sorption intensity and $1/n$ is a function of the strength of adsorption. If ‘ n ’ is unity, then the partition of metal ions between the solid phase and liquid phase are independent of the concentration of metal ion. ‘ n ’ value above unity reveals normal sorption and ‘ n ’ value less than one shows that the sorption process is cooperative [33]. The bio-sorption of Pu^{4+} and PuO_2^{2+} on fungus biomass reveals that the sorption process is cooperative since ‘ n ’ value for Pu^{4+} and PuO_2^{2+} were found below unity i.e., 0.9738 and 0.9315 respectively. The K_f value for Pu^{4+} and PuO_2^{2+} from the observations shows that Pu^{4+} sorption capacity is more than that of PuO_2^{2+} . The linear regression coefficient of Pu^{4+} and PuO_2^{2+} for the Freundlich isotherm were found to be 0.99950 and 0.99988 respectively.

Figure 2 represents the linear variations for Langmuir, D–R, Freundlich and Temkin isotherm analyses while Table 1 summarizes different constants and linear regression coefficients for the same.

Sorption kinetics

The kinetics of sorption is one of the important aspects to understand the sorption process. In our present study kinetics data were fitted to three widely accepted models. F , the fractional attainment of equilibrium can be shown in the equation given below.

$$F = C_t/C_{te} \quad (9)$$

in which C_t is the amount of metal sorped on the fungus biomass at time ‘ t ’ and C_{te} is the amount of metal ion sorped on fungus biomass at equilibrium.

Figure 3 shows the plot for $(1-F)$ as a function of equilibration time which shows no appreciable variation in $(1-F)$ for Pu^{4+} and PuO_2^{2+} ions after 120 min that reveals the fact that for attainment of equilibrium 120 min is sufficient. To get into the more insight of the sorption different models are applied as follows.

Lagergren first order rate kinetics

Lagergren pseudo-first order rate equation has been used to describe the kinetic process of liquid–solid phase adsorption in our present study, which can be shown by [34].

$$\log(q_e - q) = \log q_e - \frac{k_{ads}t}{2.303} \quad (10)$$

In which, q_e is the amount of metal ion adsorbed on fungus biomass at equilibrium condition, q is the amount of

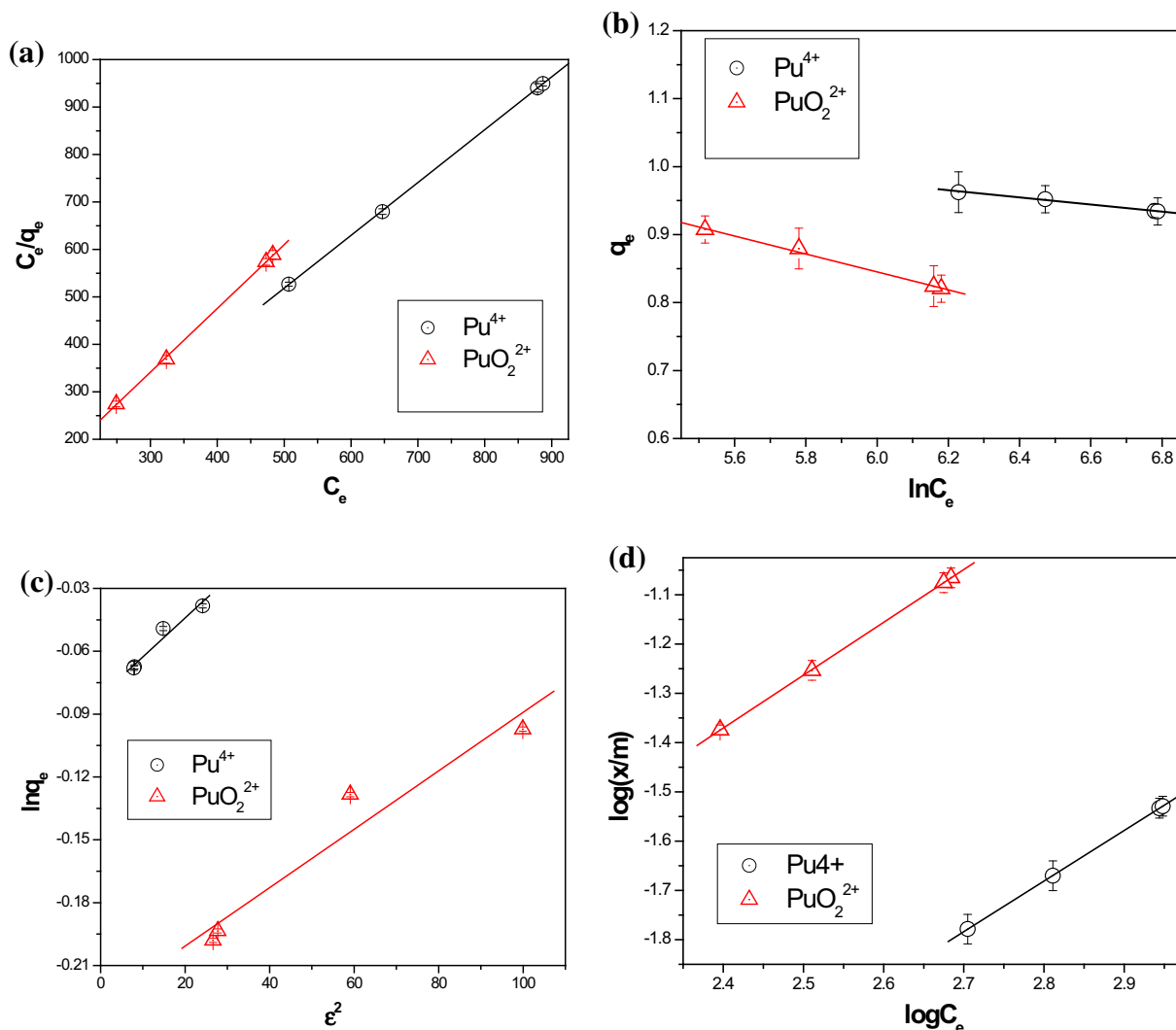


Fig. 2 a Langmuir, b Tempkin, c Dubinin–Radushkevich, d Freundlich isotherm analysis for Pu^{4+} and PuO_2^{2+} on *Rhizopus arrhizus*

metal ion adsorbed on fungus biomass at time ‘ t ’ and k_{ads} is the rate constant which can be calculated from the plot of $\log(q_e - q)$ versus ‘ t ’ (Fig. 3). From the observation of our study it was revealed that the k_{ads} value for PuO_2^{2+} was found higher than that of Pu^{4+} . The linear regression coefficients of both Pu^{4+} and PuO_2^{2+} for Lagergren model were 0.97030 and 0.98483 respectively. The poor linear regression coefficients also revealed that probably Lagergren first order rate kinetics is not operative for the present case.

Intra particle diffusion model

Intra particular diffusion model is one of the widely accepted models in analyzing sorption kinetics [30, 35, 36] can be expressed by the given equation below [35, 36].

$$q = k_p t^{0.5} + C \tag{11}$$

in which k_p stands for the intra-particle diffusion rate constant and C is the intra-particle diffusion constant. From the above equation a plot for q , amount of sorbate adsorbed as a function of the square root of the time can be drawn (Fig. 3), where the slope (k_p), is the rate constant and c , intercept of the plot and is directly proportional to the boundary layer thickness. Both the intra-particle diffusion rate constant and the intra-particle diffusion constant values for Pu^{4+} is higher than that of PuO_2^{2+} . The linear regression coefficients of both Pu^{4+} and PuO_2^{2+} for Intra particle diffusion model were 0.85716 and 0.8817, respectively. The linear regression coefficients for the present model were found even poorer than the former model suggesting the actual sorption kinetics is far from the intra particle diffusion model.

Table 1 Sorption isotherm for Pu⁴⁺ and PuO₂²⁺ on *Rhizopus arrhizus*

Metal ion	q_0 (mg g ⁻¹)	b (L mol ⁻¹)	χ^2
Langmuir isotherm			
Pu ⁴⁺	89.87	3.40	0.99998
PuO ₂ ²⁺	74.37	4.63	0.99982
Metal ion	K_f (mg g ⁻¹)	N	χ^2
Freundlich isotherm			
Pu ⁴⁺	108.2	0.9738	0.99950
PuO ₂ ²⁺	44.9	0.9315	0.99978
Metal ion	X_m (mg g ⁻¹)	E (kJ mol ⁻¹)	χ^2
Dubinin–Radushkevich isotherm			
Pu ⁴⁺	92.19	53.76	0.97806
PuO ₂ ²⁺	79.56	71.94	0.97004
Metal ion	A_t (L mg ⁻¹)	B	χ^2
Tempkin isotherm			
Pu ⁴⁺	80.72	47.22	0.99803
PuO ₂ ²⁺	41.26	18.75	0.99823

Pseudo-second-order kinetics

Pseudo second order kinetics is expressed in the equation given below as [37].

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

where K_2 is the pseudo second order rate constant (unit: g mg⁻¹ min⁻¹). The plots of t/q as the function of t , gave the straight lines (Fig. 3). From the slope value q_e was evaluated and substitute to the intercept value to obtain K_2 . The linear regression coefficients of both Pu⁴⁺ and PuO₂²⁺ for pseudo-second-order kinetics model were 0.9999 and 0.9997 respectively. The closeness of regression coefficients towards unity revealed the sorption proceeding via pseudo-second-order kinetics (Table 2).

As retrieving the adsorbed metal ions from the biomass is essential aspect for understanding its reusability. A series of stripping agents have been employed for the effective back extraction of Pu⁴⁺ and PuO₂²⁺ from the loaded biomass but only 1 M sodium carbonate or 1 M oxalic acid were found to be effective. Figure 4 showed the % stripping behavior of plutonium in different oxidation states from the biomass. It was observed that 1 M oxalic acid can strip 90 and 78% of tetra and hexa valent plutonium,

respectively while the % stripping using sodium carbonate was found to be 84 and 85% respectively. This study revealed that for tetra valent plutonium oxalic acid is successful whereas for hexa valent plutonium sodium carbonate serves the purpose.

Radiolytic stability of *Rhizopus arrhizus* biomass

Radiation stability of biomass is an important factor for using it for extraction of metal ions from the radioactive waste as it would be going through high amount radiation and there is risk of being degraded to and forming degradation products. The sorbent to be used for the processing of radio-toxic metal ions must have very high radiolytic stability. In view of these the biomass was allowed to exposed up to gamma dose of 1000 kGy and with the irradiated biomass the K_d values for tetra and hexavalent plutonium were evaluated. It was observed that after 500 kGy gamma exposure the K_d value for Pu⁴⁺ became ~94% of its original value while that for PuO₂²⁺ becomes ~95%. After a gamma exposure of 1000 kGy the K_d values for Pu⁴⁺ becomes ~86% and for PuO₂²⁺ it becomes ~78% (Fig. 5). The overall study revealed that this biomass is radiolytically stable to process radioactive waste solution.

Processing of the simulated high level waste solutions originating from research reactor and fast breeder reactor origin using *Rhizopus arrhizus* biomass

The development of the new biomass material will be successful when it can selectively separate the targeted metal ions from complex waste matrix. In view of this the selectivity of *R. arrhizus* was investigated by processing SHLW solution originating from Research reactor and Fast breeder reactor origin. After processing the raffinate was fed directly to plasma for the analysis by ICP-AES. The analytical results were summarized in Table 3. The study revealed that Cr, Fe, Mn, Ni, Sr, Ce, La and Pr were co-extracted along with plutonium while the other metal ions are either not extracted or only partially extracted. Pu (in μ M range) was spiked into the SHLW solutions and they were processed by the sorbent. The K_d values for pure Pu solution (tracer level) was determined without adjusting the oxidation states and compared that in SHLW conditions.

In SHLW conditions, the K_d values for Pu were found to decrease moderately due to the co-extraction of other metal ion on the sorbent. This will lead to decrease in the availability of the coordinating sites on sorbent.

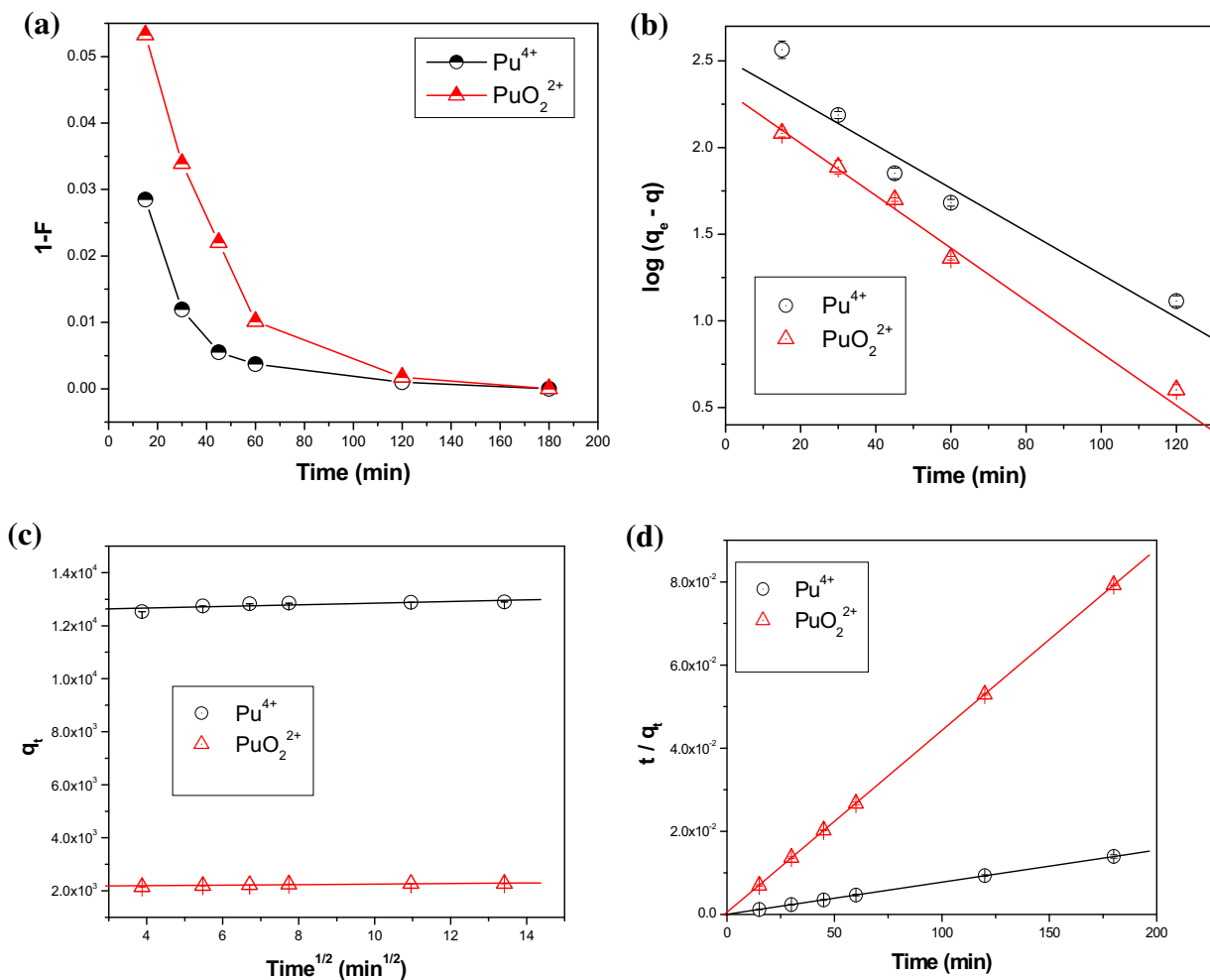


Fig. 3 Analysis of sorption kinetics for Pu^{4+} and PuO_2^{2+} on *Rhizopus arrhizus* using various models; **a** $1-F$ versus time, **b** Lagergren pseudo-first order, **c** Intra particular diffusion model, **d** Pseudo second order kinetics

Table 2 Sorption kinetics of plutonium on *Rhizopus arrhizus*

Metal ion	q_e	k_{ads}	χ^2
Lagergren first order kinetics			
Pu^{4+}	324.85	0.028	0.97030
PuO_2^{2+}	212.75	0.034	0.98483
Metal ion	k_p ($\text{mg g}^{-1} \text{min}^{-1}$)	C	χ^2
Intra particle diffusion model			
Pu^{4+}	30.51	12,544.32	0.85716
PuO_2^{2+}	10.41	2151.92	0.88170
Metal ion	q_e (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	χ^2
Pseudo second order			
Pu^{4+}	1.29E+04	1.56E-04	0.9999
PuO_2^{2+}	2.29E+03	3.55E-04	0.9997

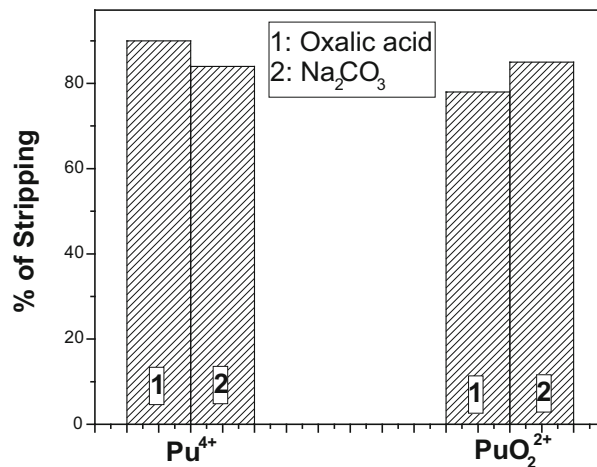


Fig. 4 Stripping behaviour of Pu^{4+} and PuO_2^{2+} from loaded *Rhizopus arrhizus*

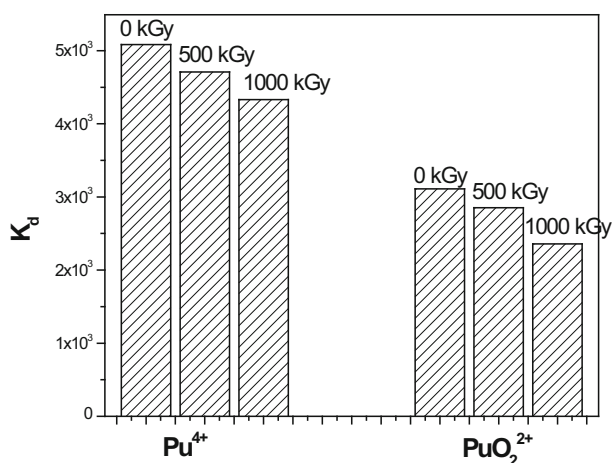


Fig. 5 Radiation stability of *Rhizopus arrhizus* towards various gamma dose

A comparative study on the efficacy of different biomass in metal ion sorption

In the long stretch of time different biomass like *Pseudomonas*, Chitosan, Arca shell, some fungus, some algae are being tested as sorption materials for radio nuclides in the front and back end of the nuclear fuel cycle [38]. Table 4 summarized a comparison of total evaluation of the bio mass presently under investigation with that reported in the literatures. Dhami et al. reported the high efficiency of different biomass originating from *Rhizopus* family only at 0.01 M HNO_3 feed solution [39]. Though the extraction efficiency was found to be encouraging, the feed acidity is far from HLW solution (3 M HNO_3). Moreover the literature only reports the K_d values without throwing any light on the sorption mechanism, kinetics,

Table 3 Analytical results obtained after processing the SHLW of RR and FBR origin using *Rhizopus arrhizus*

Element	Analytical line (nm)	FBR			RR		
		Initial (mg L^{-1})	Final (mg L^{-1})	K_d	Initial (mg L^{-1})	Final (mg L^{-1})	K_d
Al	309.271	–	–	–	250	238.35	9.78E+00
Ag	328.068	5	13.64	1.27E+02	–	–	–
Ba	230.424	70	16.97	6.25E+02	100	9.23	1.97E+03
Ca	396.847	–	–	–	400	393.51	3.3E+00
Cd	361.051	5	4.99	4.01E–01	300	115.03	3.22E+02
Cr	205.618	–	–	–	400	47.09	1.50E+03
Fe	259.941	–	–	–	1500	140.61	1.93E+03
Mg	280.27	–	–	–	300	292.80	4.92E+00
Mn	257.611	–	–	–	500	76.44	1.11E+03
Na	588.995	–	–	–	500	486.00	5.76E+00
Ni	221.648	–	–	–	300	24.39	2.26E+03
Sr	407.771	30	4.51	1.13E+03	50	7.33	1.16E+03
Ce	393.373	200	22.17	1.60E+03	100	12.50	1.40E+03
La	333.749	75	11.79	1.07E+03	100	7.06	2.63E+03
Pr	414.311	50	2.38	4.00E+03	–	–	–
Nd	401.225	30	29.12	5.99E+00	–	–	–
Sm	359.26	50	9.31	8.73E+02	–	–	–
Zr	339.198	15	6.71	2.47E+02	–	–	–
Ru	240.272	10	2.86	4.98E+02	7.5	8.61	2.58E+01
Mo	202.095	1.5	1.45	6.90E+00	30	29.50	3.39E+00
Pd	340.458	5	4.94	2.35E+00	–	–	–
Gd	342.247	5	1.17	6.50E+02	–	–	–
Dy	364.54	5	4.73	1.11E+01	–	–	–
Eu	381.967	5	1.54	4.48E+02	–	–	–
Pu	–	–	–	2.55E+03 (4.82E+03)	–	–	1.86E+03 (4.26E+03)

Data inside the parenthesis are for Pu without adjusting the oxidation state, spiking as tracer (in μM range) in SHLW solutions

Table 4 A comparative study between different biomass as sorbent materials and their efficiency in the sorption of radio nuclides

Metal ion	Biomass	K_d	Remark	Reference
Pu ⁴⁺	<i>Rhizopus arrhizus</i> (wild type)	5085.88 (3 M HNO ₃)		Present investigation
PuO ₂ ²⁺	<i>Rhizopus arrhizus</i> (wild type)	3059.39 (3 M HNO ₃)		Present investigation
Am ³⁺	<i>Rhizopus arrhizus</i> (NCIM 877)	2742.95 (pH-2)	High K_d values only at lower acidity, sorption mechanism, kinetics, radiolytic stability, selectivity have not been investigated	[40]
Am ³⁺	<i>Rhizopus arrhizus</i> (NCIM 878)	1529.94 (pH-2)		[40]
Am ³⁺	<i>Rhizopus arrhizus</i> (NCIM 997)	14888.0 (pH-2)		[40]
Am ³⁺	<i>Rhizopus Nevius</i> (NCIM 958)	2884.44 (pH-2)		[40]
Tc ⁴⁺	Chitosan	54	Low K_d values	[41]
I ⁺	Chitosan	88		[41]
Cs ⁺	Chitosan	134		[41]
UO ₂ ²⁺	Crosslinked Chitosan	125 (pH-6)	K_d values are not so high, sorption mechanism, radiolytic stability, stripping have not been investigated	[39]
Th ⁴⁺	Crosslinked Chitosan	44.7 (pH-6)		[39]
Cs ⁺	Crosslinked Chitosan	24.3 (pH-6)		[39]
Eu ³⁺	Crosslinked Chitosan	1.54 (pH-6)		[39]
Am ³⁺	Crosslinked Chitosan	3.37 (pH-6)		[39]
Sr ²⁺	Crosslinked Chitosan	1.38 (pH-6)		[39]

stripping, radiolytic stability and selectivity. Similarly, Dutta et al. reported the sorption of UO₂²⁺, Th⁴⁺, Cs⁺, Eu³⁺, Am³⁺, Sr²⁺ ions on cross linked chitosan biomass from pH 6 [40, 41]. But in this investigation the reported K_d values were not that high to be considered as a good sorption. Additionally, this biomass has not been evaluated for different aspects of sorption as specified earlier. In our present investigation not only the higher K_d values for Pu⁴⁺ and PuO₂²⁺ were reported even from 3 M HNO₃ feed acidity but also a total evaluation of the material was carried out including efficiency, mechanism, selectivity, stability against radiation, kinetics and stripping behavior.

Conclusions

In the present investigation, *R. arrhizus* was demonstrated as highly efficient and selective bio-sorption material for tetra and hexavalent plutonium ion. The sorption capacities for Pu⁴⁺ and PuO₂²⁺ were found to be 89.87 and 74.37 mg g⁻¹, respectively. The very high sorption energy obtained from Dubinin–Radushkevich (D–R) isotherm (for Pu⁴⁺ and PuO₂²⁺ 537.63 and 719.42 kJ mol⁻¹, respectively) revealed the sorption process is chemi-sorption. The analysis of the sorption kinetics revealed that it followed pseudo second order kinetics. This *R. arrhizus* biomass was found to be radiolytically stable with ~20% reduction of K_d values for Pu⁴⁺ and PuO₂²⁺ on 1000 kGy gamma exposure. Oxalic acid was found to be efficient of desorption of Pu⁴⁺ while sodium carbonate was useful for PuO₂²⁺. During processing of SHLW from RR and FBR origin, the biomass was found to co-extract Cr, Fe, Mn, Ni, Sr, Ce, La and Pr along with plutonium.

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