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Use of calcium alginate beads and *Saccharomyces cerevisiae* for biosorption of ^{241}Am

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ABSTRACT

Calcium alginate beads, inactivated *Saccharomyces cerevisiae* and inactivated *S. cerevisiae* immobilized in calcium alginate beads (*S. cerevisiae*–calcium alginate beads) are examined as potential biosorption materials as regards their capacity to remove ^{241}Am. In this study, initial experiments were carried out to evaluate the effects of pH (2 and 4) and ^{241}Am initial concentration: 75, 150, and 300 Bq mL^{-1}. The experiments were conducted in a batch reactor. Higher removal capacity was observed at pH 2 with the use of *S. Cerevisiae*, whereas pH 4 performed better for the essays with calcium alginate beads and *S. Cerevisiae*-calcium alginate beads. The pseudo-first-order kinetic model described the kinetics of biosorption. Calcium alginate was the adsorbent of choice to further experiments with synthetic organic liquid waste. A lower removal rate was observed in the organic waste, although calcium alginate beads have also been able to achieve high sorption capacity in less than 4 h. With the organic waste, the highest value of sorption capacity of ^{241}Am was 4.38×10^{-7} mmol g^{-1} with an initial ^{241}Am concentration of 2.31×10^{-8} mmol L^{-1}.

1. Introduction

Americium-241 (^{241}Am; $t_{1/2} = 432.2$ years; Q-value 5637.81 ± 0.12 keV) is the only isotope of americium to have widespread commercial use. It is the radiation source for a number of applications in medicine, research, and industry (Liao et al., 2004). The largest and most common use of this radionuclide is as an indicator component, such as household and industrial smoke detectors (Holcombe, 2015; Still, 2017).

Nevertheless, ^{241}Am toxicity is considered a serious threat because it is a highly radiotoxic isotope and poses a significant risk if ingested or inhaled. According to Keith et al. (2004), this compound can stay in the body for decades and continue to expose the surrounding tissues to both alpha and gamma radiation. This exposure may result in a variety of diseases, such as cancer or birth defects.

Large amounts of radioactive waste containing americium are generated which require adequate treatment methods. Incineration, acid digestion, wet oxidation, electrochemical oxidation, distillation, or absorption (IAEA, 2001; 1992) are examples of methods usually adopted. Although effective, such methods can be costly and unfeasible depending on the quantity or the characteristic of the waste. Recently, new techniques have emerged and some of them propose the use of biosorption (Chen et al., 2020a; Ferreira et al., 2018; Heidari et al., 2017; Lee et al., 2019; Liu et al., 2019; Sivaperumal et al., 2018; Vieira et al., 2019).

Biosorption is considered a low-cost alternative for the treatment of large volumes and low concentrations of metals (1–100 mg L^{-1}) present in liquid radioactive waste. Several types of biosorbents, including yeasts (Chen and Wang, 2016; Wang and Chen, 2006), algae, alginate beads (Yu et al., 2017), and agricultural wastes can be used, isolated or combined. The cell immobilization is a technique that can be used to combine two biosorbents, improving the properties of the final adsorbent. Some properties are chemical stability, higher mechanical

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strength, physical morphology, and anti-degradation ability (Chen et al., 2020a, 2020b; Liao et al., 2004). As a result of these features, immobilized microorganisms are considered more appropriate in industry. Liao et al. (2004) also highlight that immobilized adsorbents present better adsorption-desorption characteristics. To a proper immobilization, suitable carrier materials are crucial. In this work, we employed calcium alginate due to its good cell compatibility, low-cost, and simplicity. In this context, biosorption processes may be interesting approaches for the treatment of liquid organic radioactive waste (LORW), since they combine simplicity and low cost.

LORW is produced from many fields, e.g. production of radioisotopes for medicine, nuclear research institutes, nuclear fuel cycle, etc. Among the radioactive liquid waste generated by these installations, the amount of stored organic waste stands out since the majority of the stored liquid waste comes from extraction processes using organic solvents. An example of organic waste found is the liquid scintillation counting (LSC) cocktail, which is commonly used as a reactant to quantify alpha and beta-emitters.

This paper proposes the use of yeast and a biological origin material to recover ^{241}Am from aqueous solutions and also from a prepared organic solution. In this work, inactivated *S. cerevisiae*, calcium alginate beads, and inactivated *S. cerevisiae* immobilized in calcium alginate beads (*S. cerevisiae*–calcium alginate beads) are the potential biomass for ^{241}Am removal. As far as we know, the use and comparison of these biosorbents have not been previously investigated for the removal of ^{241}Am in aqueous solutions considering kinetic models to accurately evaluate the sorption behavior. Moreover, kinetic and isotherm models are proposed for the use of calcium alginate beads to remove ^{241}Am in an organic solution, considering kinetic and isotherm constants estimated from experimental data.

2. Material and methods

2.1. Biosorption experiments in water

2.1.1. Adsorbent preparation

S. cerevisiae was purchased from Lassaffre, SAF, Argentina. Cellular inactivation was performed by gamma radiation (5 kGy) through the sealed package and confirmed by the addition of methylene blue according to procedures detailed elsewhere (Oyane et al., 2009; Lee et al., 1981).

Calcium alginate beads were prepared, according to a procedure detailed elsewhere (Gok and Aytas, 2009). In sum, 2 g of sodium alginate powder (Sigma, USA) were added into a beaker containing 100 mL of deionized water. In another beaker, a solution of 400 mL of deionized water with 16 g of calcium chloride was prepared. The sodium alginate solution was then slowly dripped into the calcium chloride solution by a peristaltic pump. In the end, the beads were separated from the calcium chloride solution using a Tyler 200 sieve and washed four times with deionized water for the complete removal of the free calcium ions. The moisture content of the calcium alginate beads was about 96%, which was measured by a moisture analyzer (Ohaus, USA), under 100 °C for 120 min. *S. cerevisiae*–calcium alginate beads were prepared in a similar way of that of calcium alginate beads, but with the addition of 2 g of inactivated *S. cerevisiae* with 2 g of sodium alginate (Göksungur et al., 2003).

2.1.2. Kinetics of americium adsorption/biosorption

The solution containing ^{241}Am was purchased from the company Amersham, England. The experiments were performed in batch mode, by using known activity concentrations of ^{241}Am in contact with the biosorbents. The concentrations were 75, 150, and 300 Bq mL^{-1} (2.45×10^{-9}, 4.90×10^{-9}, and 9.80×10^{-9} mmol L^{-1}, respectively). The effects of pH and initial concentration of ^{241}Am in rate removal were evaluated. Each biosorbent was placed in polyethylene vials containing 60 mL americium solution. The concentration of biomass applied in the biosorption experiments was selected based on literature (Itoh et al., 1975; Kedari et al., 2001; Volesky et al., 1993), which was 2% mass/-volume of solution. pH was adjusted to 2 or 4 using 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. The flasks were kept under constant stirring at room temperature (around 23 °C) for 30, 60, 120, and 240 min. After the contact times, the solutions were centrifuged for 15 min at 2500 rpm. Fifty milliliters were then collected from the supernatant and placed in 220 mL polyethylene vessels to count the residual radiation by using a scintillator (Tri-carb 2100 TR-Liquid Scintillation Analyzer, Packard-Canberra). The limit of the experimental error of each triplicate was ±5%.

The amount of adsorbed americium was calculated from the difference of the americium concentration in the aqueous solution before and after adsorption. The kinetic study considered the americium uptake by the following equation:

$$q\left(t\right) = \left(\frac{C_i - C(t)}{m}\right)V \tag{1}$$

where q(t) is the uptake of americium in adsorbent at the time t (mmol g^{-1}), C_i is the initial concentration of ^{241}Am in solution (mmol L^{-1}), C_i is the concentration of ^{241}Am in solution (mmol L^{-1}) at the time t, V is the solution volume (L) and m is the sorbent mass (g).

2.1.3. Modeling of adsorption kinetics

The determination of biosorption kinetics is crucial to properly evaluate the removal efficiency of ^{241}Am by using adsorbents (Wang and Guo, 2020a). In this study, pseudo-first-order (PFO) and pseudo-second-order (PSO) are the kinetic models of choice. PFO kinetics is described as a differential equation and is given by (Lagergren et al., 1898):

$$\frac{dq}{dt} = k_1\left(q_{eq} - q\right) \tag{2}$$

where q and q_{eq} are the amounts of adsorbed solute over time and at the equilibrium, respectively; k_1 is the PFO rate constant.

Also, the mathematical equation for PSO kinetics was employed (Ho and McKay, 1999).

$$\frac{dq}{dt} = k_2\left(q_{eq} - q\right)^2 \tag{3}$$

where k_2 is the PSO rate constant, q_{eq} is the amount of adsorbate adsorbed at the equilibrium, and q is the amount of the solute adsorbed in time.

2.2. Experiment with liquid scintillation cocktails (LSC)

2.2.1. Adsorbent and solution preparation

Calcium alginate beads were selected to remove the americium from LSC (Ultima gold AB, PerkinElmer), due to the ease of application and direct and simple comparison with tests performed in water. The organic solvent is a mixture of organic solvents such as toluene, xylene, pseudocumene (1,2,4–trimethylbenzene). It also presents compounds that act as scintillators, which are naphthalene and 2,5–diphenyloxazole, and others (Valdovinos et al., 2016). The reagents used in the experiments were of analytical reagent (AR) grade and were purchased from Sigma, USA.

2.2.2. Americium adsorption in liquid scintillation cocktails

The influence of pH for the adsorption of ^{241}Am in organic scintillation wastes was evaluated to establish the best experimental conditions for the kinetic study. In this case, 6.6 g of calcium beads (0.2 g dry bead) were suspended in 10 mL of the liquid waste and shaken (150 rpm) at room temperature. The contact time was 10 h and the pH varied from 2 to 6. The most suitable pH condition was obtained and then used for the kinetics experiments.

These experiments followed the same method used previously for the removal of americium from water. ^{241}Am initial concentration was about 500 Bq mL^{-1} (1.62 × 10^{-5} mmol L^{-1}) and pH 5. In the study of equilibrium adsorption, the concentration ranged from 4.15 × 10^{-7} to 4.15 × 10^{-6} mmol L^{-1}, diluted with LSC. These experiments were also performed at fixed pH and 10 h of contact time. After the contact time, the residual activity concentration of ^{241}Am in solution was determined using a scintillator (Tri-carb 2100 TR-Liquid Scintillation Analyzer, Packard-Canberra). The experiments were conducted in triplicate. The limit of the experimental error of each triplicate was ±5%.

2.2.3. Modeling of adsorption kinetics and equilibrium

Americium uptake was again calculated by Eq. (1). We employed the distribution constant (K_d) (mL g^{-1}) to assess the pH effect (Eq. (4)) and, once more, PFO (Eq. (2)) and PSO (Eq. (3)) were utilized. Nevertheless, PFO and PSO are now employed to evaluate calcium alginate beads performance in an organic solution and to understand the kinetic mechanisms involved in such an application.

$$K_d = \frac{q}{C_F} \tag{4}$$

where q is the concentration of metal in calcium alginate beads (mol g^{-1}) and C_F is the concentration of metal in the solution (mol L^{-1}).

Isotherms are important tools to analyze the performance of sorbents, which are obtained by performing equilibrium experiments using metal (loid)s ions in batch assays. For the isotherm experiments, contact time and pH were 10 h and 5, respectively. For single solute systems, Langmuir's and Freundlich's isotherms are models widely accepted.

Table 1
Adsorption isotherm equations selected to study ^{241}Am adsorption in calcium alginate beads (Foo and Hameed, 2010; Hinz, 2001; Saadi et al., 2015).

Isotherm	Equation (nonlinear form)	nº
Langmuir	$q_{eq} = \frac{Q_0 k_L C_e}{1 + k_L C_e}$	(5)
Freundlich	$q_{eq} = k_f C_e^{\frac{1}{n}}$	(6)
Sips	$q_{eq} = \frac{k_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	(7)
Redlich–Peterson	$q_{eq} = \frac{K_{R_p} C_e}{1 + a_{R_p} C_e^{g}}$	(8)
Two-Site Langmuir	$q_{eq} = \left(\frac{Q_1 b_1 C_e}{1 + b_1 C_e} + \frac{Q_2 b_2 C_e}{1 + b_2 C_e}\right)$	(9)
Radke-Prausnitz	$q_{eq} = \frac{q_{max} K_{RP} C_e}{(1 + K_{RP} C_e)^{\frac{1}{n_{RP}}}}$	(10)

However, other models may better represent the adsorption system. In this context, Langmuir, Freundlich, Sips, Redlich-Peterson, Two-sites Langmuir, and Radke-Prausnitz were evaluated regarding their capacity in explaining the sorption behavior of calcium alginate beads in the removal of ^{241}Am from LSC (Table 1).where: Langmuir model: q_{eq} is the quantity per unit species mass (^{241}Am) removed at equilibrium (mmol g^{-1}), Q_o is the utmost adsorption capability (mmol g^{-1}), k_L is the so-called Langmuir constant and defines the adsorption energy (L mmol^{-1}), and C_e is the concentration of the radionuclide ^{241}Am when the system reaches equilibrium (mmol L^{-1}) (Guo and Wang, 2019). Freundlich model: K_f is a constant that represents the adsorption capacity (L mmol^{-1}), n is a constant that signify the sorption capacity and the active sites' distribution; Note that for $0 < {}^{1}/_{n} \leq 1$, it is recognized as favorable adsorption of the chemical species in the adsorbent and for ${}^{1}/_{n} > 1$, it is treated as unfavorable adsorption. Sips model: k_s is the constant of the adsorption energy (L mmol^{-1}), a_s is the Sips' constant (L mmol^{-1}) and β_s pinpoints the biosorbents' heterogeneity, and in case of $\beta_s = 1$, the model becomes that of Langmuir. Redlich–Peterson model: K_{R_p} and a_{R_p} are constants of the isotherm R–P (mol^{-1} and L mmol^{-1}, respectively), g is an exponent with values between 0 and 1. If $g = 1$, the model becomes that of Langmuir, and if $g = 0$, it becomes the Freundlich isotherm. Two-Site Langmuir model: Q_1 and Q_2 are the adsorption capacities (mmol g^{-1}), the sum of $Q_1 + Q_2$ is the maximum capacity, b_1, and b_2 are coefficients related to the affinity of sites 1 and 2 respectively (L mmol^{-1}). Radke-Prausnitz model: $q_{\max}$ is the upper limit of the adsorption capacity (mmol g^{-1}), K_{RP} is the Radke-Prausnitz constant of the adsorption energy (L mmol^{-1}) and n_{RP} is the exponent of Radke-Prausnitz (dimensionless) (Wang and Guo, 2020b).

The Downhill Simplex optimization method (Nelder and Mead, 1965) was used to predict the parameters of the isotherm models and kinetic constants, by using experimental data. Eq. (11) describes the objective function.

$$F_{obj} = \sum_{j=1}^{n} \left(q_{Am-241}^{EXP} - q_{Am-241}^{MOD}\right)^2 \tag{11}$$

where n is the number of experimental runs, and q_{Am-241}^{EXP} and q_{Am-241}^{MOD} represent, respectively, the experimental and the calculated ^{241}Am concentrations.

The ability of the chosen models in fitting experimental data was compared in terms of the absolute average deviation (AAD, %) (Yao, 2000), given by:

$$AAD\ \% = \frac{|q_{cal} - q_{exp}|}{N} \tag{12}$$

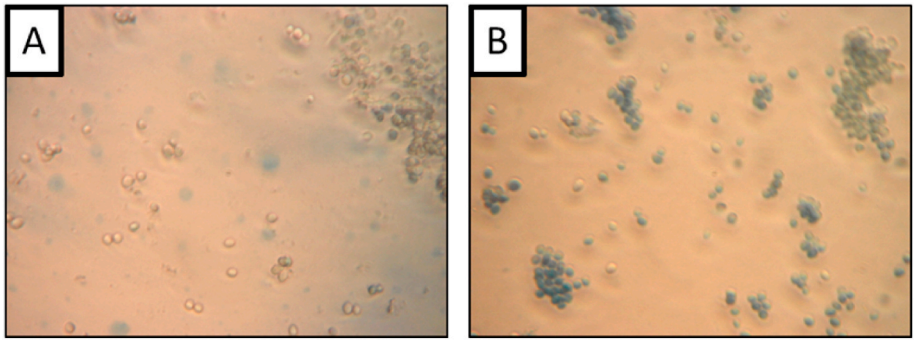


Fig. 1. *Saccharomyces cerevisiae* (A) Alive; (B) Inactivated by radiation.

3. Results and discussion

3.1. Biosorption

3.1.1. Biosorption of ^{241}Am by Saccharomyces cerevisiae inactivated by radiation (SC)

Death of *S. cerevisiae* by gamma radiation (5 kGy) was confirmed by the bluish coloration inside its cells after the addition of methylene blue dye (Fig. 1).

Fig. 2 depicts the uptake amount (q) of ^{241}Am ions by *S. cerevisiae* as a function of time. It is noted that the amount of the radionuclide uptake by *S. cerevisiae* increases in function of time until it reached the equilibrium. The first half-hour of kinetic essay ($Q_{0.5h}$ – see Fig. 2) is fundamental for the adsorption of americium, which revealed that the highest uptake capacity of this biosorbent is achieved with pH 2 and an americium concentration of 300 Bq mL^{-1} ($Q_{0.5h,\ SC} = 3.93 \times 10^{-10}$ mmol g^{-1}). The pH value of 2 indicated higher ^{241}Am uptake for the middle (150 Bq mL^{-1}) and upper (300 Bq mL^{-1}) activity concentrations, but did not indicate any substantial difference for the lowermost (75 Bq mL^{-1}) activity concentration. The removal percentage achieved by *S. cerevisiae* reached 97.2% using 1.2 g of the adsorbent.

Adsorbates–adsorbent interactions reached equilibrium within 0.5 h for $[^{241}Am]_0 = 75$ Bq mL^{-1} (pH 2 and 4) and $[^{241}Am]_0 = 150$ Bq mL^{-1} (pH 2). Under pH 4, the $[^{241}Am]_0 = 150$ Bq mL^{-1} took more time to achieve equilibrium (2 h). For the uppermost ^{241}Am concentration (300 Bq mL^{-1}), equilibrium was not achieved during the time observed of 4 h, presenting the highest values of q regardless of pH.

The results corroborate those described in the literature by Liu et al.

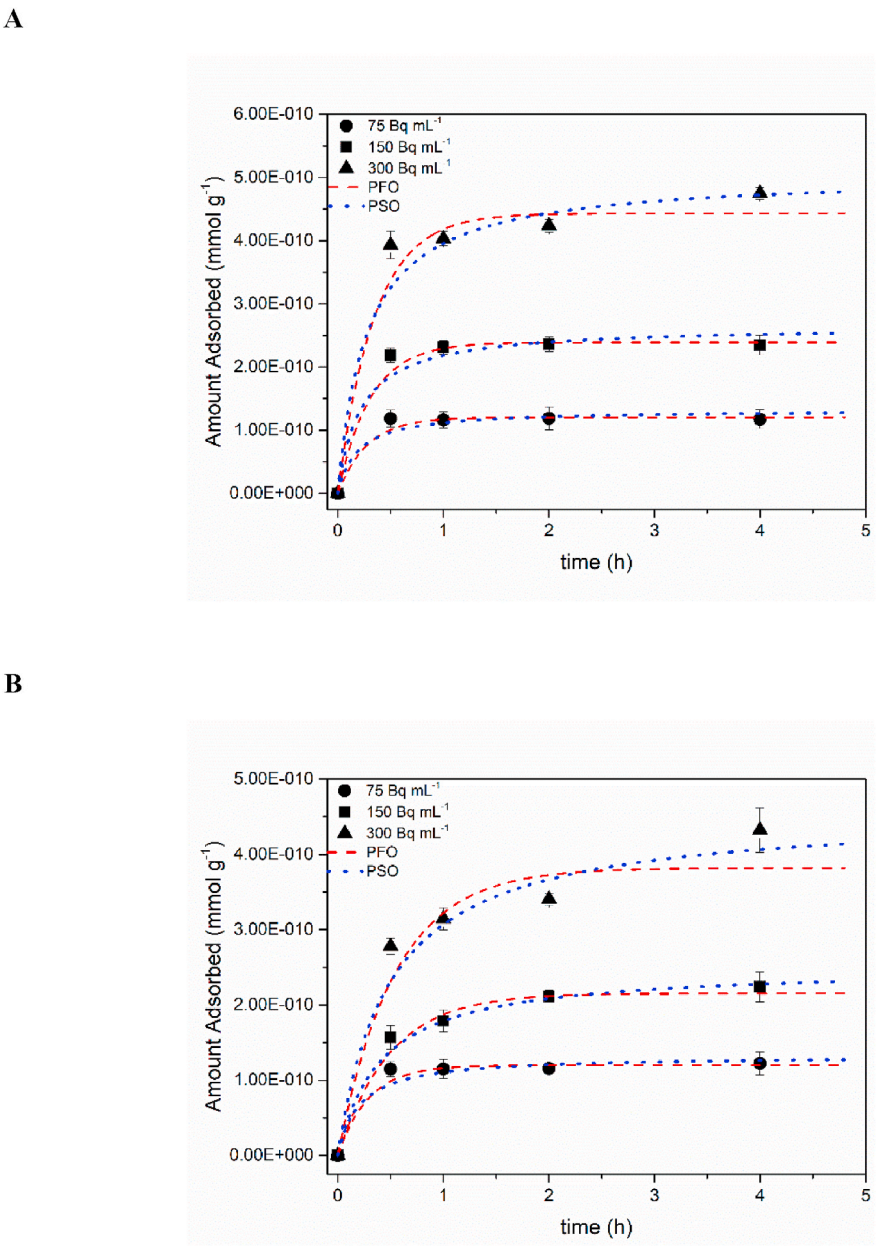


Fig. 2. Biosorption of americium by inactivated *S. cerevisiae*. (A) pH 2; (B) pH 4. $[^{241}Am]_0$ of 75, 150, and 300 Bq mL^{-1}.

(2002) who used inactivated *S. cerevisiae* for ^{241}Am biosorption in aqueous solution with initial activity concentrations from 2.22 kBq mL^{-1} to 555.00 kBq mL^{-1}. The authors studied the effects of pH, contact time, and temperature. *S. cerevisiae* removed 99% of americium after 60 min of reaction with a pH between 1 and 3 and temperatures between 10 and 45 °C. According to Liu et al. (2002), the reason for the optimum pH found (1–3) in the biosorption of ^{241}Am by *S. cerevisiae* is that, under increasing pH, americium may be present as hydroxide colloid, which reduces the adsorption rate. Liu et al. (2002) took longer to achieve equilibrium (16 h) using inactivated *S. cerevisiae* for the biosorption of ^{241}Am. However, they employed a much higher americium initial concentration (1.08×10^3 Bq mL^{-1}) compared to the present work (max: 300 Bq mL^{-1}).

According to Chojnacka (2010), the reaction order is linked to the mechanism of adsorption. Usually, these mechanisms are ion-exchange or surface precipitation in their hydroxide, sulfide, or carbonate forms. Table 2 highlights that PFO best represents most of the experiments conducted with *S. cerevisiae*, with higher values of R^2. The only case that PSO better represented the system was for pH 4 and [^{241}Am] = 300 Bq mL^{-1}.

3.1.2. Biosorption of ^{241}Am by calcium alginate beads

The uptake amount (q) of ^{241}Am ions by the calcium alginate beads as a function of time is depicted in Fig. 3. Calcium alginate beads exhibited the same behavior as *S. cerevisiae*, which means that the increase in concentrations also yielded an increase in adsorption capacities. Equilibrium was achieved when the initial americium concentration was 75 or 150 Bq mL^{-1}. On the other hand, equilibrium was not clearly achieved for the highest initial concentration of americium (300 Bq mL^{-1}). 2 h was the time that most of the experimental conditions reached equilibrium.

However, for the calcium alginate beads as the adsorbing material, pH 4 presented better results in terms of q for all ^{241}Am concentrations evaluated. These results are supported by Singhal et al. (2011), who found that pH 4 is the best for adsorption of ^{241}Am by calcium alginate beads. According to the authors, this occurs because of the ionization of the COOH group of the alginate biopolymers. Under pH 4, maximum ionization is accomplished as a result of the availability of the ionizing site for binding with Am^{3+}. The first half-hour of kinect essay displayed that the highest uptake capacity of calcium alginate beads is achieved with pH 4 and $[Am]_0 = 300$ Bq mL^{-1} ($Q_{0.5h,\ \text{calcium alginate beads}} = 2.78 \times 10^{-10}$ mmol g^{-1}). This value was lower than that obtained for *S. cerevisiae* ($Q_{0.5h,\ S.\ cerevisiae} = 3.93 \times 10^{-10}$ mmol g^{-1}). These results demonstrated that this biopolymer has a high removal capacity of ^{241}Am, reaching a maximum of 4.59×10^{-10} mmol g^{-1} ($[^{241}Am]_0 = 300$ Bq mL^{-1}/2.45×10^{-12} mol L^{-1}, pH = 4, time: 4 h).

This result corroborates to that obtained by Mimura et al. (2001), who obtained 90% removal of ^{241}Am, for an initial americium concentration of 2.10×10^{-9} mol L^{-1} in 24 h of contact. In 2002, Mimura et al. (2002) found that only calcium alginate removed simultaneously about 90% of various radionuclides (Cs, Y, Co, Eu, and Am) in solution with a concentration of 10 μg mL^{-1}. Equilibrium was achieved in 24 h in the latter work. PFO better fitted all the experiments conducted with calcium alginate beads with higher values of R^2 (Table 2).

3.1.3. Biosorption of ^{241}Am by S. cerevisiae–calcium alginate beads

Adsorption of ^{241}Am ions as a function of time was evaluated by means of the parameter q with both *S. cerevisiae* and calcium alginate beads materials, namely *S. cerevisiae*–calcium alginate beads (see Fig. 4). ^{241}Am ions were better adsorbed in pH 4, which is similar to that observed when only calcium alginate beads were employed. Conversely, for some experimental conditions, equilibrium was achieved faster ($[^{241}Am]_0 = 150$ Bq mL^{-1}, pH 2 and 4). As seen for only *S. cerevisiae* or calcium alginate beads, no clear equilibrium was observed for the uppermost activity concentration used. For the other experimental conditions, 1 h was the time that met equilibrium.

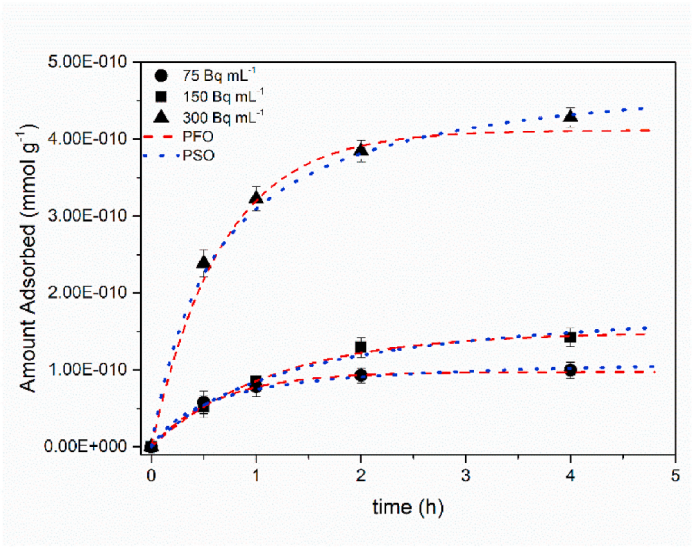
PFO better fitted all the experiments conducted with *S. cerevisiae*–calcium alginate beads with higher values of R^2 (Table 2). The results so far demonstrated that the biosorption of ^{241}Am by inactivated *S. cerevisiae*, calcium alginate beads, and *S. cerevisiae*–calcium alginate beads highlighted similar sorption capabilities, depending on pH, and could be applied as a promising material for radioactive waste management i.e. efficient adsorbent for removal of ^{241}Am from aqueous solution. PFO also better fitted the experiments conducted with *S. cerevisiae*–calcium alginate beads with higher values of R^2 (Table 2). The better fit for the PFO model in all variations of the biosorbents here

Table 2
Kinetic parameters of pseudo-first-order and pseudo-second-order models[a] for the adsorption of ^{241}Am onto calcium alginate beads, inactivated *S. cerevisiae*, inactivated *S. cerevisiae*–calcium alginate beads.

				PFO			PSO		
Adsorbent	pH	C_0 (Bq mL^{-1})	$q_{eq}\cdot10^{10}$ (mmol g^{-1})	k_1 (h^{-1})	$q_{eq}\cdot10^{10}$ (mmol g^{-1})	R^2	$k_2\cdot10^{-2}$ (g mmol^{-1} h^{-1})	$q_{eq}\cdot10^{10}$ (mmol g^{-1})	R^2
Inactivated *S. cerevisiae*	2	75	1.18	3.62	1.20	0.962	4.06	1.33	0.913
	2	150	2.35	3.22	2.39	0.973	1.73	2.66	0.931
	2	300	4.75	2.87	4.43	0.969	0.72	5.05	0.952
	4	75	1.22	3.46	1.20	0.964	3.74	1.33	0.924
	4	150	2.24	2.02	2.16	0.985	0.98	2.51	0.983
	4	300	4.33	1.85	3.82	0.956	0.45	4.56	0.967
Calcium alginate beads	2	75	1.00	1.59	0.97	0.995	1.52	1.17	0.990
	2	150	1.42	0.86	1.49	0.997	0.38	1.98	0.991
	2	300	4.28	1.50	4.12	0.993	0.33	4.97	0.992
	4	75	1.11	2.03	1.09	0.992	1.93	1.27	0.977
	4	150	1.92	1.45	1.92	0.998	0.67	2.33	0.988
	4	300	4.59	1.80	4.54	0.993	0.39	5.37	0.976
S. cerevisiae– Calcium alginate beads	2	75	0.99	1.45	0.99	0.993	1.28	1.20	0.978
	2	150	1.48	1.74	1.43	0.991	1.16	1.70	0.979
	2	300	3.98	1.32	3.99	0.998	0.28	4.91	0.988
	4	75	1.10	1.82	1.09	0.995	1.65	1.28	0.983
	4	150	1.96	1.75	1.93	0.993	0.87	2.29	0.977
	4	300	4.44	1.62	4.28	0.994	0.35	5.12	0.988

[a] k_1 and k_2 are the rate constants of the first and second-order models, respectively.

A



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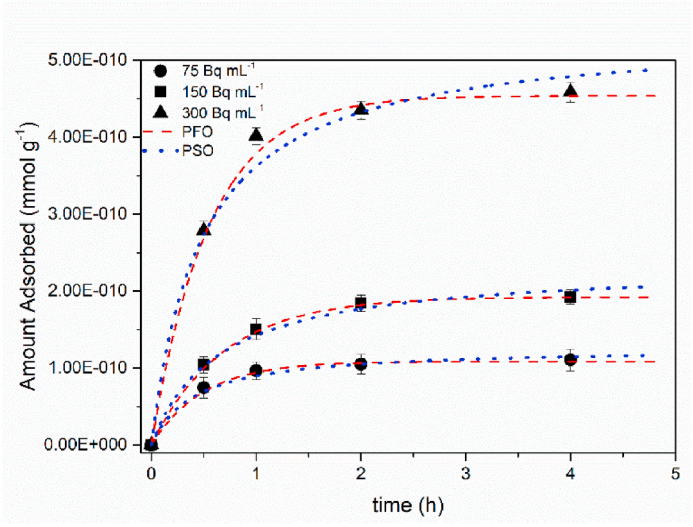
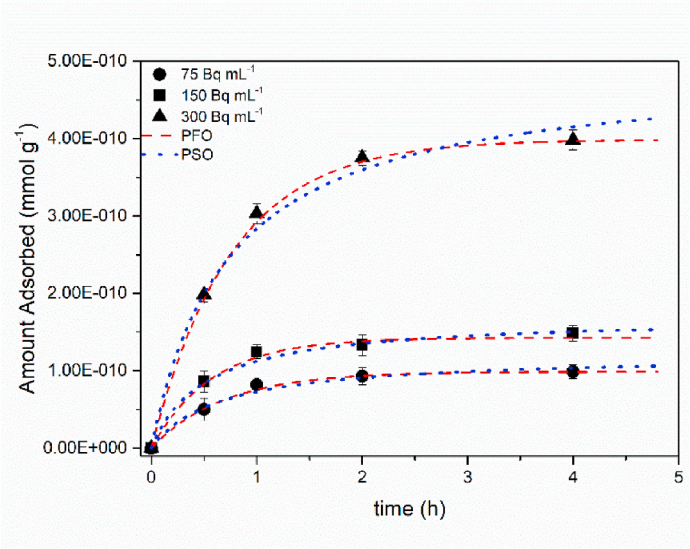


Fig. 3. Biosorption of americium by calcium alginate beads. (A) pH 2; (B) pH 4. $[^{241}Am]_0$ of 75, 150, and 300 Bq mL^{-1}.

A



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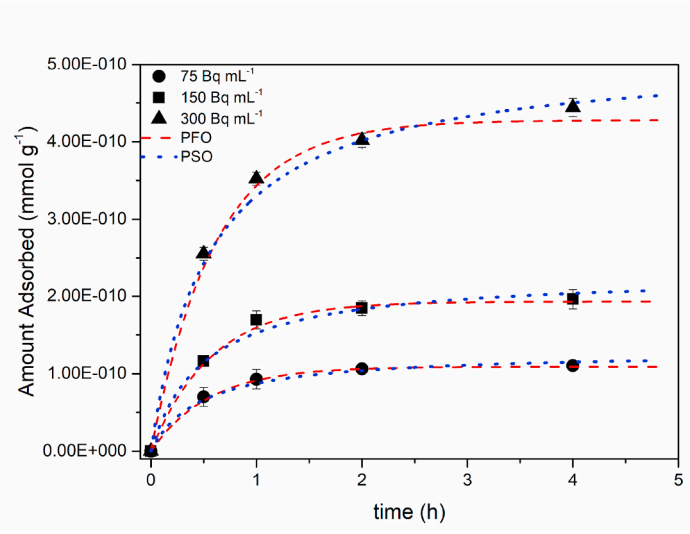

Fig. 4. Biosorption of americium by *S. cerevisiae*–calcium alginate beads. (A) pH 2; (B) pH 4. $[^{241}Am]_0$ of 75, 150, and 300 Bq mL^{-1}.

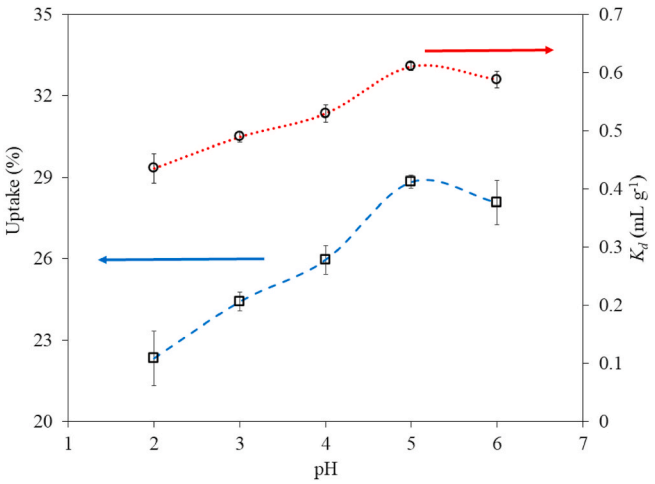

Fig. 5. The effect of pH on the adsorption of ^{241}Am in scintillation cocktails onto calcium alginate beads (^{241}Am: 3.90 × 10^{-3} mg L^{-1}, t = 10 h, T = 25 °C). (□, blue dashed line) Uptake of ^{241}Am (%). (○, red dotted line) K_d (mL g^{-1}). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

proposed is an indication that the removal of ^{241}Am predominantly occurred by physisorption.

3.2. Biosorption of ^{241}Am from an organic aqueous solution

3.2.1. Effect of initial pH

The effect of the initial pH on the biosorption of americium in scintillation cocktails was studied as calcium alginate beads as the selected adsorbent. The experimental conditions were: [^{241}Am]$_0$ = 3.90 × 10^{-3} mg L^{-1} (1.62 × 10^{-5} mmol L^{-1}), 25 °C, and pH 2, 3, 4, 5, and 6. Consequently, the pH values of the solutions were adjusted to these pH values prior to the experiments. Fig. 5 shows the effect of pH on the adsorption of ^{241}Am in scintillation cocktails onto calcium alginate beads.

Higher removal rates were obtained at pH 5 (average adsorption: 29%) and pH 6 (average adsorption: 28%) and also for the distribution constant (K_d) (mL g^{-1}). Predictions of chemical equilibrium made by Hydra-Medusa software (data not shown, [^{241}Am]$_0$ = 3.90 × 10^{-3} mg L^{-1}) highlight that up to pH 5 the only present species are Am^{3+} and H^+. At pH 5, OH^- is initially formed, and subsequently above pH 6, $AmOH^{2+}$, $AmOH_2^+$, and $AmOH_3$(s) (pH > 8.5) are produced. In the presence of these compounds, particularly $AmOH_3$(s), ^{241}Am adsorption could be negatively affected.

Wu et al. (2007) stressed pH 5 as the most appropriate value for the adsorption of americium. Their conclusion was based on their results of speciation distribution, which showed that hydrated Am^{3+} is the dominant species at this pH. Nonetheless, optimum pH can alter significantly depending on the evaluated sorption process. Lee et al. (2011) studied pH in the sorption of Am^{3+} onto kaolinite. They demonstrated higher sorption of americium ions by increasing pH, which highlighted 98% of sorption under a concentration of 10^{-5} mol L^{-1} of Am^{3+}.

Bhagyashree et al. (2014) carried out americium sorption experiments using nanocrystalline MnO_2. Sorption percentages were higher than 90% for all evaluated pH (1–8.5). No significant differences were found regarding pH. Kumar et al. (2013) demonstrated americium sorption on smectite-rich natural clay. They found that higher pH values provided higher Am^{+3} sorption. On the other hand, maximum Am^{+3} sorption was obtained in pH 8. Luo et al. (2003) found 2 as the optimum pH value in the sorption of americium by *Candida* sp.

Singhal et al. (2011) and Gok and Aytas (2009) observed an optimum pH on the adsorption of ^{241}Am in water onto calcium alginate, which was 4. Our tests with water also revealed pH 4 as the most appropriate for the biosorption of ^{241}Am by calcium alginate beads. Nevertheless, under the presence of organics, pH 5 demonstrated better results of americium uptake. Fuks et al. (2018) employed magnetic calcium alginate and found high removal rates of ^{241}Am from aqueous solution regardless of pH (1.5–7). The presence of organics may have interfered in americium-calcium alginate beads interplay, impairing the sorption process and consequently affecting pH. Since pH 5 presented the best results regarding ^{241}Am sorption in LSC, this pH was kept constant for the biosorption kinetics and equilibrium studies.

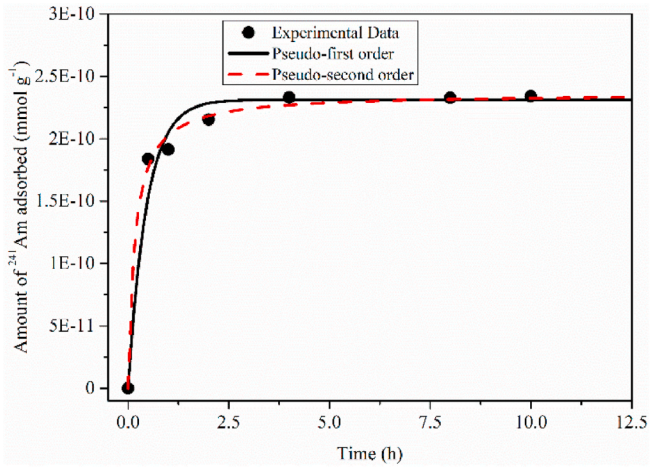

Fig. 6. Experimental kinetics of the removal of ^{241}Am from scintillation cocktails onto calcium alginate beads.

Table 3
Parameters of kinetics estimated for^{241}Am sorption by calcium alginate beads.

Model	Parameters	Values
Pseudo-first order	q_{eq} (mmol g^{-1})	2.314 × 10^{-10}
	k_1 (h^{-1})	0.036
	AAD (%)	5.460
Pseudo-second order	q_{eq} (mmol g^{-1})	2.364 × 10^{-10}
	k_2 × 10^{-2} (g mmol^{-1} h^{-1})	0.042
	AAD (%)	2.500

3.2.2. Biosorption assays with liquid scintillation cocktails

The results of the biosorption experiments show that the americium concentration in calcium alginate beads increased as a function of time until the equilibrium was reached (Fig. 6).

The equilibrium time was 3.75 h. This value is significantly higher than that obtained for the removal of ^{241}Am in water (2 h). Note that 4 h reached the maximum ^{241}Am removal, which was 2.32 × 10^{-10} mmol g^{-1}. This value is about half of that obtained when water was used (4.59 × 10^{-10} mmol g^{-1}). This is an indication that the presence of organics in the aqueous media decreased the biosorption of ^{241}Am into the calcium alginate beads. On the other hand, these values are in the same order of magnitude. It shows that the application of other treatments to remove the organics before biosorption could not be necessary depending on the criteria to dispose of such waste.

Chetty et al. (2006) also worked with an organic liquid scintillator solution but employed ion exchange resins as the adsorbent. These adsorbents are widely known and the theory well consolidated, which provides a better understanding of the process and parameters optimization. The costs must be also taken into consideration for scale-up. In this context, biosorbents are more attractive than ion exchange resins.

A good agreement was obtained for both pseudo-first and pseudo-second-order and the experimental data (Table 3). However, according to the calculated AAD (%), pseudo-second-order best fitted the experimental conditions (AAD_{PSO} = 2.50%, AAD_{PFO} = 5.46%).

As expected, rate constant values (k) for the biosorption of ^{241}Am

Table 4
Parameters predicted by the adsorption isotherm models for ^{241}Am from scintillation cocktails biosorption onto calcium alginate beads and the absolute average deviation values obtained for each model.

Model	Parameters				AAD (%)
Langmuir	Q (mmol g^{-1})	K_L (L $mmol^{-1}$)			4.934
	8.768×10^{-4}	3.22×10^{4}			
Freundlich	K_f (L $mmol^{-1}$)	1/n			1.661
	0.925	0.828			
Sips	K_s (L $mmol^{-1}$)	a_s (L $mmol^{-1}$)	β_s		1.562
	1.634	1.869×10^{5}	0.857		
Redlich Peterson	K_{RP} (mol^{-1})	a_{RP} (L $mmol^{-1}$)	β		1.400
	2.958×10^{1}	1.269×10^{4}	0.572		
Two-Site Langmuir	Q_1 (mmol g^{-1})	Q_2 (mmol g^{-1})	b_1 (L $mmol^{-1}$)	b_2 (L $mmol^{-1}$)	4.936
	1.987×10^{-6}	1.581×10^{-4}	1.590×10^{3}	1.268×10^{5}	
Radke-Prausnitz	q_{max} (mmol g^{-1})	K_{RP} (L $mmol^{-1}$)	n_{RP}		1.062
	9.901×10^{-4}	2.487×10^{4}	4.513×10^{2}		

were much lower when the scintillation cocktail was the liquid solution. The maximum adjusted value for k under scintillation cocktails was 0.042 g $mmol^{-1}$ h^{-1}. On the other hand, the minimum k value obtained for the biosorption of ^{241}Am in water was 0.33 g $mmol^{-1}$ h^{-1} (PSO, pH 2, $[^{241}Am]_0 = 300$ Bq mL^{-1}). The rate of reaction was 7–56 times higher in water than in the synthetic organic solution, depending on the experimental conditions.

The highest value of sorption capacity of ^{241}Am was 4.38×10^{-7} mmol g^{-1} with an initial ^{241}Am concentration of 2.31×10^{-8} mmol L^{-1}. The parameters of the isotherms were obtained using calcium alginate beads (Table 4), and the experimental versus the calculated data is depicted in Fig. 7.

According to the AAD (%), the Radke-Prausnitz isotherm model best represented our experimental data. The Radke-Prausnitz isotherm model is widely adopted in most adsorption systems at low adsorbate concentrations (Subramanyam and Ashutosh, 2012). This isotherm is reduced to a linear isotherm when the adsorbate concentration is low. In the case of high adsorbate concentration, it becomes the Freundlich isotherm or the Langmuir isotherm, depending on the Radke-Prausnitz model exponent (Ayawei et al., 2017). Bhagyashree et al. (2014) compared Langmuir and Freundlich isotherm models and the results were similar to ours. It should be noted that there is not a single model that best describes equilibrium data, but this will depend on each system studied.

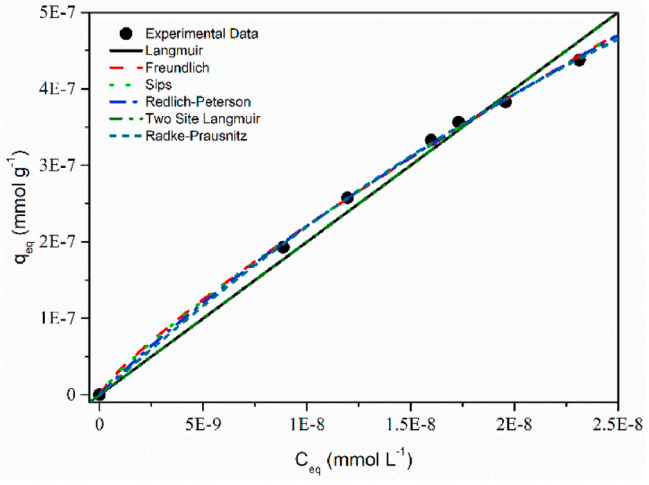

Fig. 7. Experimental data and model prediction of the biosorption kinetics of ^{241}Am in scintillation cocktails into calcium alginate beads.

4. Conclusions

For all experimental conditions, the use of the highest americium concentration used (300 Bq mL^{-1}) promoted the maximum uptake capacity of the biomaterials. However, the best pH varied depending on the material. pH 2 was the best for *S. cerevisiae* ($q_{max} = 4.75 \times 10^{-10}$ mmol L^{-1}, equilibrium in 0.5 h). For calcium alginate beads and *S. cerevisiae*–calcium alginate beads, pH 4 presented better results. For the former, $q_{max} = 4.59 \times 10^{-10}$ mmol L^{-1} and equilibrium achieved in 2 h. For the latter, $q_{max} = 4.44 \times 10^{-10}$ mmol L^{-1} with the equilibrium being reached in 1 h.

PFO better fitted most of the essays conducted with these biosorbents with higher values of R^2. This is an indication that the removal of ^{241}Am predominantly occurred by physisorption.

When calcium alginate beads were put into contact with liquid scintillation cocktails contaminated with americium, pH 5 showed the best results in terms of removal (%) and distribution constant (K_d) (mL g^{-1}). The complex nature of the scintillation solutions interfered in the sorption process negatively. Optimum contact time for americium removal was experimentally determined as 3.75 h. The Radke-Prausnitz isotherm model was the model that best fitted the experimental data.

The findings of this study indicate that these materials are easy to handle, stable, and have the potential to be applied in the treatment of americium-contaminated solutions, especially calcium alginate beads to treat organic radioactive waste. Finally, further work is required to evaluate these biomaterials in the presence of more complex matrices, which may present multi-metals compositions that can interfere significantly in the sorption process.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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