



Full Length Article

Sustainable recovery of rare earth elements from aqueous media using fruit pomaces: adsorption performance, thermodynamics, and environmental assessment



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ABSTRACT

The valorization of waste biomasses for recovering Critical Raw Materials (CRMs), particularly Rare Earth Elements (REEs), is a promising approach to enhance sustainability and resource efficiency. This study investigates the adsorption performance of bergamot, grape, and olive pomaces toward Nd^{3+} and Dy^{3+} ions under varying pH conditions, both in the absence of an ionic medium and in $0.10 \text{ mol/dm}^3 \text{ NaNO}_3(\text{aq})$, following different biomass pretreatment protocols. Comparative tests with La^{3+} enabled evaluation of light (Nd^{3+} , La^{3+}) vs. heavy (Dy^{3+}) lanthanide ion behavior. Biomass characterization was performed using Attenuated Total Reflectance Fourier Transform Infrared (ATR FT-IR) spectroscopy and Scanning Electron Microscopy – Energy-Dispersive X-ray (SEM-EDX) analysis to assess changes in surface chemistry and morphology after adsorption. Kinetic and isotherm analyses showed pseudo-second-order kinetics and Langmuir behavior, respectively. The highest capacity was observed for water-pretreated bergamot pomace at $30 \text{ }^\circ\text{C}$, pH 5.0, without ionic medium, and measured adsorption efficiency followed the trend: Dy^{3+} (0.45 mmol/g) > Nd^{3+} (0.38 mmol/g) > La^{3+} (0.35 mmol/g). The materials exhibited good reusability across adsorption/desorption cycles, supporting their potential as sustainable biosorbents. For the first time, direct isothermal titration calorimetry (ITC) was used to determine adsorption thermodynamics. Life Cycle Assessment (LCA) and Techno-Economic Assessment (TEA) further evaluated the environmental and economic feasibility of bergamot pomace under different processing scenarios.

Introduction

In recent years, the search for sustainable resource management has

grown driven by the depletion of conventional mineral resources and the increasing demand for high-tech applications based on CRMs (Critical Raw Materials), such as REEs (Rare Earth Elements) [1]. These elements

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are crucial for a variety of advanced technologies, including electronics (light-emitting diodes, lasers, electronic video displays, magnets), renewable energy systems and catalysts, highlighting the strategic importance of ensuring a stable supply. Traditional mining of REEs is often associated with environmental degradation and geopolitical uncertainties, thus requiring the exploration of alternative sources and sustainable extraction methods [2]. China, United States of America and Australia are the leading producers of rare earth elements, with China holding 90 % of the global production [3,4]. In the specific cases of neodymium (Nd) and dysprosium (Dy), their main applications include magnets (43.2 %), catalysts (17 %), polishing powders (11.2 %), metallurgy (7.1 %), glass (6.4 %), battery alloys (3.6 %), ceramics (3 %), phosphors (0.5 %), pigments (0.3 %), and other uses (7.6 %) [5]. Since the applications mentioned above are increasingly significant, and with the demand for REEs expected to grow in the future, it is essential to develop protocols aimed at their recovery and reuse. This will help reduce dependence on natural resources and lessen environmental impact. One of the primary strategies already being utilized is the so-called “green mining”, which involves recovering resources from urban waste through the valorization of WEEEs (Waste of Electrical and Electronic Equipment), but currently only 1 % is being recycled [6]. This aligns with the key objectives of the European Green Deal and Energy Transition [7]. Unfortunately, the separation of REEs from WEEEs is a hard task. At present, the most used methods are based on mechanical and/or metallurgical treatments. Mechanical recycling works by separating various components based on size, density, and magnetic properties. Yet, this method is quite rough and is mainly applicable to WEEEs with a high REEs content, making it unsuitable for all types of e-waste. As for metallurgical processes, two primary methods are used: pyrometallurgy and hydrometallurgy. Pyrometallurgy involves heating WEEEs to high temperatures in the presence of a reducing agent, to obtain target metals in their elemental form. While effective, this process is highly energy consuming. Hydrometallurgy, on the other hand, involves two steps: first, leaching the e-waste with aqua regia, followed by LLE (Liquid-Liquid Extraction) and precipitation. This method allows the recovery of target metals from the solution in their oxidized form. Again, though highly efficient, it requires the employment of toxic and corrosive chemicals [3,8–10]. As a result, finding alternative strategies to overcome the main limitations of established methods (such as the use of toxic solvents in LLE and high energy costs) is of great importance and has become a hot topic in environmental chemistry research [11]. Literature indicates that one of the most explored strategies for recovering REEs from complex matrices is improving LLE. In this sense, emerging techniques include dispersive liquid-liquid extraction [12], solidified floating organic drop extraction [13] and extraction using ionic liquids [14]. Alternatively, the adsorption of REEs on various materials has been extensively studied. Examples include ionic exchange resins [15], task-specific polymers [16], and green adsorbents [17]. Additionally, various bio-based materials, both in their natural form and functionalized, have been investigated for this purpose [18–20]. Adsorption is considered one of the most promising technologies to separate metals and REEs from aqueous solutions [21]. Its appeal lies in its simplicity and the feasibility of using a wide range of adsorbents, resulting in cost-effective and sustainable processes. Moreover, adsorption offers advantages over LLE, including reduced waste and lower consumption of organic solvents. As a result, waste biomasses derived from agricultural and industrial processes have emerged as attractive candidates for sorption applications. These materials are abundant, underutilized (e.g., for biofuel, pellet production, soil amendments, etc.), and inexpensive, with a high potential for effective removal of metal ions from aqueous solutions, offering the double benefit of waste reduction and resource extraction [22]. Basing on the above, this study investigates the adsorption capabilities of three distinct biomasses – BP (Bergamot Pomace), GP (Grape Pomace) and OP (Olive Pomace) – for the removal of Nd^{3+} and Dy^{3+} ions, two key REEs, from aqueous solutions. These biomasses were selected due to their local availability,

composition, and surface chemistry properties. The pomaces underwent various pre-treatment methods to enhance their adsorption efficiency. Specifically, water pre-treatments were used to remove water-soluble molecules, whilst nitric acid pre-treatments were performed to eliminate alkaline (Na^+ , K^+) and alkaline-earth (Ca^{2+}) metal cations [23]. ATR FT-IR (Attenuated Total Reflectance Fourier Transform Infrared) spectroscopy and SEM-EDX (Scanning Electron Microscopy – Energy Dispersive X-ray) analysis were employed to elucidate post-adsorption changes in functional groups. Notably, the potential of bergamot pomace for Cd^{2+} adsorption was previously investigated by Irto *et al.* [24], demonstrating effective removal of this cation from aqueous solutions.

The effectiveness of biomasses in adsorbing neodymium(III), lanthanum(III), and dysprosium(III) ions from water and in the presence of NaNO_3 ionic medium was evaluated at various pHs through adsorption kinetics and isotherm studies. Additional tests were carried out in the presence of La^{3+} , enabling comparisons between light and heavy lanthanide ions. Additionally, the suitability of the biomasses for multiple adsorption/desorption cycles was investigated, highlighting their potential reusability through different loading/desorption cycles. This study reports, for the first time, the use of direct ITC (Isothermal Titration Calorimetry) to experimentally determine the enthalpy changes associated with the sorption of Nd^{3+} and Dy^{3+} onto BP. Unlike conventional determinations based on isotherm data collected at different temperatures and analyzed via the van't Hoff equation – a derivative method inherently prone to larger errors [25–28] – ITC enables a more accurate estimation of thermodynamic parameters. Although numerous studies have examined REEs biosorption on agricultural wastes, none have directly quantified sorption enthalpies using ITC, leaving key aspects of the interaction mechanisms unresolved. To fill this gap, the present work investigates the adsorption of Nd^{3+} and Dy^{3+} onto bergamot, grape, and olive pomaces, combining ITC measurements with adsorption modeling, life cycle assessment, and techno-economic analysis. While ITC has previously been applied to dye adsorption systems (e.g., methylene blue onto tangerine peel [29]), its application to REE biosorption remains unexplored. Lastly, LCA (Life Cycle Assessment) and TEA (Techno-Economic Assessment) analyses were also conducted to evaluate the sustainability, in terms of economic and environmental costs, of the BP use as biosorbent under different operational scenarios. Overall, this study demonstrates the potential of waste biomasses as eco-friendly, cost-effective, and scalable adsorbents for critical raw material recovery, contributing to circular economy strategies and sustainable resource management.

Materials and methods

Materials and chemicals

A 5 kg sample of bergamot pomace (*i.e.*, seeds, pulp and deoiled flavedo remaining after essential oil and juice extraction), from the *Femminello* and *Fantastico* cultivars, harvested between November 2021 and January 2022, was supplied by *Capua 1880* company (Reggio Calabria, Italy). A 6 kg sample of grape pomace (*i.e.*, seeds and pulp) from the 2023 harvest of the *Carricante* cultivar was provided by *Azienda Agricola “GIUSEPPE RUSSO”* (Passopisciaro, Catania, Italy). A 10 kg sample of olive pomace constituted by seeds and deoiled pulp post-olive oil extraction, from the *Nocellara dell'Etna* cultivar, harvested in 2022, was supplied by *Frantoio Russo* (Randazzo, Catania, Italy).

Portions of each pristine pomaces were mechanically ground, dried in an oven at $t = 60$ °C until constant weight, and then ground again to obtain a fine powder. An aliquot of the bergamot pomace was also freeze-dried. The resulting solid materials (referred to as RAW pomace) were divided in two fractions and pre-treated with either deionized water or standard solutions of nitric acid, the latter prepared by diluting Riedel–deHäen (Seelze, Germany) concentrated ampoules. These nitric acid solutions were also employed in desorption studies.

$\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (32–37 % La), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (32.0–33.7 % Nd) and $\text{Dy}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (34–37 % Dy) salts (Sigma Aldrich, Milan, Italy) were used for the preparation of the REEs solutions. Standard solutions of La^{3+} , Nd^{3+} and Dy^{3+} ions for instrumental calibration were prepared by diluting 1000 mg/dm³ standard solutions of the REEs ions in 2 % HNO_3 (CPAchem, Bogomilovo, Bulgaria). NaNO_3 salt (purity $\geq 99.0\%$, Sigma-Aldrich, Milan, Italy), previously dried in an oven at $t = 110\text{ }^\circ\text{C}$ for 2 h, was used for the preparation of ionic medium solutions.

Pre-treatments of pomace samples

RAW pomace samples (see Section 2.1) were either used directly or pre-treated exploiting different procedures already reported in the literature [23,24,30–32]. Specifically, weighed amounts of each biomass were put in contact with either deionized water or nitric acid solutions ($C_{\text{HNO}_3} = 0.0983\text{ mol/dm}^3$) at $t = 30\text{ }^\circ\text{C}$, using a solid-to-liquid ratio of 100 g/dm³. Each mixture was centrifuged at 5000 rpm for 5 min at $t = 25\text{ }^\circ\text{C}$ to separate the solid from the liquid phases. The pH was measured by means of a 713-model pH meter equipped with a 6.0233.100 combined glass electrode (Metrohm, Herisau, Switzerland). Then, the supernatant was removed while the solid residues were washed with 25 cm³ of deionized water, then centrifuged again. The pH was checked again, and the washing procedure repeated several times (generally 8 to 10 cycles), until the difference in pH between two consecutive washing cycles was less than 0.05 pH units. Subsequently, the solids residues were dried in an oven at $t = 60\text{ }^\circ\text{C}$ to constant weight (average yield ca. 40 %) and then mechanically ground to obtain a fine powder. A list of sorbent materials used in this study is given in Table 1.

Material characterization

Infrared spectra were obtained from the sorbent samples using a Nicolet iS50 FT-IR (Fourier Transform Infrared) spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts, USA) equipped with an ATR (Attenuated Total Reflectance) diamond window module, operating in the middle infrared range (from 4000 to 400 cm⁻¹). Each spectrum was collected over 32 scans, with a spectral resolution of 4 cm⁻¹. Prior to analysis, the samples were ground to a fine powder using an agate mortar.

The microstructure of the biomasses was investigated using FESEM (Field-Emission Scanning Electron Microscopy) with a JEOL JSM-7610F Plus instrument (JEOL Ltd., Tokyo, Japan), operating at an accelerating voltage of 15 kV and a working distance of 15 mm. To enhance conductivity, samples were coated with a 5 nm layer of gold. The microscope was equipped with an EDXS (Energy-Dispersive X-ray Spectroscopy, Oxford Instruments) system for elemental analysis.

Procedures for equilibrium, kinetic and recycle experiments

Preliminary adsorption tests (i.e., single batch) were conducted on the different pomace-based sorbents (Table 1) to identify the most

Table 1

List of the different pomace-based sorbents tested.

Pristine materials	Pre-treatment	Abbreviations	Symbol
Bergamot pomace	None	RAW BP	A
Bergamot pomace	Freeze-drying	BP LYO	B
Bergamot pomace	Freeze-drying + H ₂ O at $t = 30\text{ }^\circ\text{C}$	BP LYO H ₂ O	C
Bergamot pomace	H ₂ O at $t = 30\text{ }^\circ\text{C}$	BP H ₂ O	D
Bergamot pomace	HNO ₃ at $t = 30\text{ }^\circ\text{C}$	BP HNO ₃	E
Olive Pomace	None	RAW OP	F
Olive Pomace	H ₂ O at $t = 30\text{ }^\circ\text{C}$	OP H ₂ O	G
Olive Pomace	HNO ₃ at $t = 30\text{ }^\circ\text{C}$	OP HNO ₃	H
Grape Pomace	None	RAW GP	I
Grape Pomace	H ₂ O at $t = 30\text{ }^\circ\text{C}$	GP H ₂ O	J
Grape Pomace	HNO ₃ at $t = 30\text{ }^\circ\text{C}$	GP HNO ₃	K

promising pomace samples for the removal of Nd^{3+} and Dy^{3+} ions. In each test, approximately 10 mg of sorbent were added to 50 cm³ Erlenmeyer flasks containing 20 cm³ of REEs solution ($C_{\text{REE}} \sim 0.18\text{ mmol/dm}^3$) at $\text{pH}_i = 5.0$ (subscript “i” stands for initial value). Additional experiments at $\text{pH}_i = 3.0$ and 4.0 were performed for BP H₂O, GP H₂O, RAW OP. Suspensions were stirred for 24 h using an orbital mixer (model M201-OR, MPM Instruments, Bernareggio, Italy) placed in a thermostatted chamber (at $t = 25\text{ }^\circ\text{C}$), and filtered using nylon syringe filters (SPHEROS, pore size = 0.45 μm). Then, the supernatants were collected to measure REE equilibrium concentration (C_e) by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) using an Optima 2100 PerkinElmer instrument (Waltham, Massachusetts, USA), equipped with an autosampler (model AS-90A).

Batch isotherm experiments were carried out to test BP H₂O, RAW OP, and GP H₂O sorption performances towards Nd^{3+} and Dy^{3+} at $\text{pH}_i = 5.0$ in 100 cm³ Erlenmeyer flasks, using varying amounts of sorbent material (10–90 mg) and either 20 or 40 cm³ of REEs solution ($0.18 \leq C_{\text{REE}}/\text{mmol dm}^{-3} \leq 0.36$). The ratio between milliequivalents of sorbent functional sites (estimated from preliminary tests) and metal cation ranged from approximately 1 to 10. All mixtures were stirred for 24 h and filtered as above reported. The supernatants were collected to determine the equilibrium pH (pH_e) using a Metrohm 713-pH meter equipped with a combined glass electrode (model 6.0233.100 from Metrohm, Herisau, Switzerland) and the equilibrium metal ion concentrations (C_e) as above reported. Due to its superior performance, BP H₂O was further studied. In particular, additional isotherm experiments were conducted for La^{3+} , in conditions similar to those for Nd^{3+} , and Dy^{3+} . Moreover, further tests for all the three mentioned cations were also conducted in 0.10 mol/dm³ sodium nitrate solutions (at $\text{pH}_i = 5.0$ and $t = 25\text{ }^\circ\text{C}$).

The sorption capacity (q_e , in mmol/g) at different sorbent/metal ratios was calculated by means of Eq. (1):

$$q_e = \frac{V \cdot (C_0 - C_e)}{m} \quad (1)$$

where V is the volume (in dm³) of batch solutions, C_0 and C_e are the initial and equilibrium metal cation concentration (in mmol/dm³) and m is the sorbent mass (in g).

Kinetic experiments were carried out at $\text{pH}_i = 5.0$ and $t = 25\text{ }^\circ\text{C}$ in a batch mode. Approximately 30 mg of sorbent were added to flasks containing 20 cm³ of the La^{3+} , Nd^{3+} or Dy^{3+} solutions ($C_{\text{REE}} = 0.36\text{ mmol/dm}^3$). Suspensions were stirred at 180 rpm in an orbital mixer and subsequently filtered for solid-to-supernatant separation. Metal cation concentration in solution was measured at various contact times in a timeframe ranging from 0 to 2880 min. Sorption ability as a function of time (q_t , in mmol/g) was measured as for q_e in Eq. (1), but equilibrium concentration C_e was replaced by C_t (Eq. (2)), namely the metal cation concentration measured at any time (t).

$$q_t = \frac{V \cdot (C_0 - C_t)}{m} \quad (2)$$

Sorbent reusability for Nd^{3+} and Dy^{3+} recovery was evaluated via column experiments. Approximately 20 mg of adsorbent were packed into a glass column (diameter = 2 cm, length = 10 cm). A 15 cm³ metal solution ($C_{\text{REE}} = 0.18\text{ mmol/dm}^3$) was flowed at reflux into the column with a flow rate of 6 cm³/min for 17 h using a peristaltic pump (Minipuls 3, Gilson, Cinisello Balsamo, Italy). Desorption was subsequently performed using a 0.10 mol/dm³ HNO₃ solution for 7 h, followed by washing with 100 cm³ of deionized water. Successive adsorption/desorption cycles were conducted under the same conditions. The solutions obtained from each adsorption/desorption step were collected and the metal concentration was determined to calculate both adsorption and desorption capacities.

Models for adsorption kinetic and isotherm experiments

The experimental data of the REEs adsorption kinetics (t and q_t) onto BP, OP and GP were fitted with different kinetic models, namely PFO (pseudo-first order, Eq. (3)), PSO (pseudo-second order, Eq. (4)), PGO (pseudo-n order, Eq. (5)), and DEM (double exponential model, Eq. (6)) equations [33–36]:

$$q_t = q_e \cdot (1 - e^{-k_1 \cdot t}) \quad \text{PFO} \quad (3)$$

$$q_t = \frac{q_e^2 + k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t} \quad \text{PSO} \quad (4)$$

$$q_t = q_e \cdot \frac{q_e}{\left(1 + q_e^{(n-1)} \cdot k_n \cdot t \cdot (n-1)\right)^{\frac{1}{n-1}}} \quad \text{with } n \neq 1 \quad \text{PGO} \quad (5)$$

$$q_t = q_e [1 - \alpha \cdot e^{-k_{p1} \cdot t} - (1 - \alpha) \cdot e^{-k_{p2} \cdot t}] \quad \text{with } 0 < \alpha \leq 1 \quad \text{DEM} \quad (6)$$

where k_1 (1/min), k_2 [g/(mmol·min)], k_n [(1/min)(g·mmol)⁽ⁿ⁻¹⁾], k_{p1} (1/min) and k_{p2} (1/min) are the rate constants of adsorption according to the various models, n is the order of the PGO model, α accounts for the relative contribution of each exponential term to the overall adsorption amount ($0 < \alpha < 1$) in the DEM model [37], whereas q_t and q_e were defined above.

Additionally, the Boyd model was employed to further investigate the mass transfer mechanism and to identify the rate-limiting step of the adsorption process [38]. This model helps distinguish whether external film diffusion or intraparticle diffusion governs the overall adsorption kinetics. The fractional attainment of equilibrium (F) was calculated using the following expression:

From the F values, the time-dependent Boyd function B_t was derived using the following equations:

$$F = \frac{q_t}{q_e} \quad (7)$$

When $F \leq 0.85$

$$B_t = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 \cdot F}{3}} \right)^2 \quad (8)$$

When $F > 0.85$

$$B_t = \ln \frac{\pi^2}{6} - \ln(1 - F) \quad (9)$$

The values of B_t were then plotted as a function of time (t) to evaluate the linearity and intercept of the curve. According to the model, a linear plot of B_t vs. t that passes through the origin (the point with 0,0 coordinates) indicates that intraparticle diffusion is the rate-limiting step. Conversely, if the fitting line does not pass through the origin, film diffusion is the dominant mechanism controlling the adsorption rate [39].

The experimental data obtained from batch isotherm adsorption experiments (C_e and q_e) were processed with Freundlich (Eq. (10)) and Langmuir (Eq. (11)) isotherm model equations [40–42]:

$$q_e = K_F \cdot C_e^{1/n} \quad (10)$$

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (11)$$

where K_F (dm^{3/n}·mmol^(1-1/n)/g) and K_L (dm³/mmol) are the affinity constants for the Freundlich and Langmuir models, respectively; q_m is the maximum adsorption capacity (in mmol/g) according to the Langmuir model.

In order to evaluate the recovery and reuse performance of the bio-

sorbents, adsorption–desorption cycles were performed and quantified. The adsorbed amount of REEs after each cycle was calculated using Eq. (1). The amount of metal desorbed during the regeneration phase was determined from the concentration of metal released in the acidic effluent:

$$q_{des} = \frac{V_{des} \cdot C_{des}}{m} \quad (12)$$

The recovery efficiency (R%) for each cycle was then calculated as:

$$R(\%) = \frac{q_{des}}{q_e} \cdot 100 \quad (13)$$

These values were used to track both the stability of the material and the effectiveness of REE recovery over successive reuse cycles.

Calorimetric measurements

With the aim of investigating the thermodynamic parameters of the sorption process, ITC experiments were carried out at $t = 25.0000 \pm 0.0001$ °C using a TAM III thermostat (TA Instruments, New Castle, Delaware, USA) equipped with a nanocalorimeter (1 cm³ cell volume) and an automatic titration Hamilton syringe of 0.25 cm³. The TAM III device is featured by two stainless steel cells: one designed for the sample and the other for the reference (*i.e.*, deionized water and 10 mg of BP). Each titration experiment consisted of ten consecutive injections of 0.01 cm³ of Nd³⁺ or Dy³⁺ aqueous solution ($C_{Nd} = 0.0540$ mol/dm³, $C_{Dy} = 0.0538$ mol/dm³) into 0.75 cm³ of deionized water containing a weighed sorbent amount (approx. 10 mg). The blank experiments were performed by injecting the REEs cation solutions into 0.75 cm³ of deionized water in the absence of the biosorbent. A delay time of 60 mins was set between two consecutive injections. The sample cell was stirred constantly at 50 rpm using a gold helix.

The adsorption enthalpy change ($\Delta_{sor}H$) was calculated by Eq. (14):

$$\Delta_{sor}H = \frac{(q_{i,sor} - q_{dil})}{n_i} \quad (14)$$

where: $q_{i,sor}$ is the heat measured during the titration experiment as a consequence of the REE sorption by the material, q_{dil} is the dilution heat, obtained from the titration of Ln³⁺ solutions in water, and n_i is the number of moles of Ln³⁺ adsorbed after each injection, calculated from the parameters of the isotherm model equation.

The free Gibbs energy ($\Delta_{sor}G$) and entropy ($\Delta_{sor}S$) changes for Nd³⁺ and Dy³⁺ adsorption processes were calculated using the following equations (Eqs. (15) and (16)):

$$\Delta_{sor}G = -R \cdot T \cdot \ln K_C = -R \cdot T \cdot \ln(55.5 \cdot 1000 \cdot AM \cdot K_L) \quad (15)$$

$$\Delta_{sor}S = (\Delta_{sor}H - \Delta_{sor}G)/T \quad (16)$$

where R is the universal gas constant ($R = 8.314$ J/(mol·K)), T is the temperature in Kelvin (K) scale, K_C is a dimensionless sorption parameter, 55.5 is the number of pure water moles for each liter, AM is the atomic mass (g/mol) of each lanthanide, K_L is the Langmuir affinity constant (see Eq. (11)) converted in dm³/mol using a 1000 conversion factor [29,42].

Life Cycle Assessment (LCA) and Techno-Economic Assessment (TEA)

A Life Cycle Assessment was conducted according to ISO 14040 [43] and ISO 14044 [44] standards to evaluate the environmental profile of BP H₂O. The functional unit was defined as 1 kg of biosorbent produced. A gate-to-gate system boundary was used, including feedstock preparation, manufacturing, regeneration. Being an agrowaste, the production of raw BP was excluded from the analysis. The end-of-life phase, transportation, and lab infrastructure impacts were excluded from the system boundaries due to the localized, bench-scale nature of the system, consistent with LCA practices for early-stage processes [45,46].

Inventory data, detailed in Table 2, were obtained from lab measurements and supplemented by the Ecoinvent v3 database [47]. The environmental impacts were assessed using SimaPro software, applying the ReCiPe 2016 Midpoint method (H), focusing on the most relevant areas of the system: GW (Global warming, in kg CO₂ eq), WC (Water Consumption, in m³), and CED (Cumulative Energy Demand, in MJ). In addition to the lab-scale scenario, three alternative scenarios were modelled: S1 with improved drying efficiency of 0.7 kWh/kg [48], S2 performing four regeneration cycles with acidic desorption, and S3 combining both efficient drying and regeneration. To support the environmental analysis, a preliminary TEA was conducted within the same boundaries as the LCA to estimate production costs. The analysis focused solely on upstream and processing stages, excluding labor costs, which are often uncertain at early research and development stages [49]. Cost estimation considered direct expenses related to raw materials, energy use, and consumables, expressed per unit of functional output, defined as 1 kg of dried biosorbent. Electricity costs were estimated based on the average supply costs to non-domestic customers, at 0.30 €/kWh [50]; deionized water costs were estimated from the laboratory inventory, 60 € for 1000 dm³ filter, or 0.06 €/dm³; nitric acid costs were 100 € for 1 dm³ of 10 mol/dm³ nitric acid solution, or 0.5 €/0.1 mol/dm³ [51]. Sensitivity analyses aligned with those of the LCA were performed to facilitate comparison of environmental and economic performance. This limited-scope TEA offers an initial indication of the process' economic feasibility and highlights potential routes for future process optimization and scaling up [52].

This table summarizes the Life Cycle Inventory of lab-scale production of BP H₂O (B1), with S1 using a more efficient drying process, S2 regenerating the Spent BP H₂O over 4 adsorption–desorption cycles with a 9 % efficiency drop from the first to the fourth cycle, and S3 performing both efficient drying and regeneration. A flow diagram of the system boundaries and life cycle stages across the four scenarios considered is given in Fig. S1.

Results and discussion

Preliminary adsorption tests

The results obtained from preliminary tests, in terms of measured q_e , at pH_i = 5.0 are shown in Fig. 1 and the numerical values of measured q_e for each test are listed in Table S1. The RAW bergamot pomace samples – whether oven-dried (BP RAW) or freeze-dried (BP LYO) – exhibited limited adsorption capacities for Nd³⁺ and Dy³⁺, with the freeze-dried ones performing the poorest. In contrast, water pre-treated samples (BP LYO H₂O, and BP H₂O) demonstrated a notable improvement in adsorption capacity compared to raw counterparts. Between the two dehydration techniques tested, freeze-drying and thermal, the latter performed better for sorption of both metal cations. The pre-treatment with HNO₃ also proved to be effective for increasing sorption capacity, however the corresponding q_e values ($q_e \sim 0.22$ mmol/g) were lower than those recorded for the H₂O-treated counterparts ($q_e \sim 0.27$ mmol/g). In the case of grape pomace, the RAW biomass displayed lower q_e

Table 2

Life Cycle Inventory of lab-scale production of BP H₂O.

Input	B1	S1	S2	S3	Unit
Raw Bergamot Pomace	4.16	4.16	1.04	1.04	Kg
Drying electricity consumption	11.96	1.4	3	0.35	kWh
Grinding electricity consumption	0.023	0.023	0.006	0.006	kWh
Centrifuge electricity	0.14	0.14	0.035	0.035	kWh
Distilled water	166.66	166.6	41.67	41.67	dm ³
Nitric acid (0.1 mol/dm ³)	0	0	0.75	0.75	dm ³
Output					
BP H ₂ O	1	1	1	1	kg

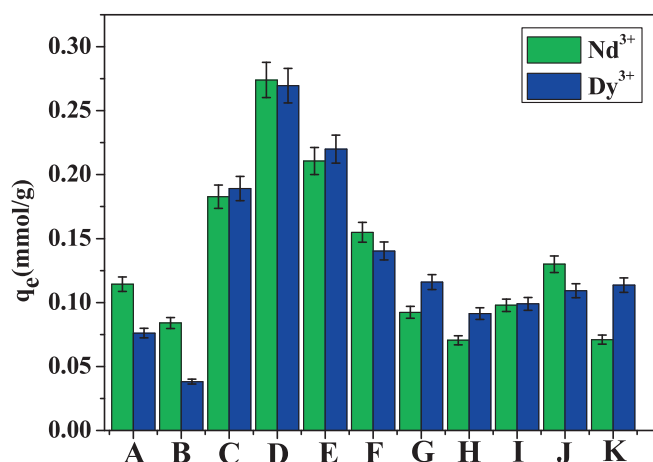


Fig. 1. Screening of the sorption capacity of all the tested BP (A-E), GP and OP-based materials towards Nd³⁺ and Dy³⁺.

values ($q_e \sim 0.10$ mmol/g) than the H₂O-treated samples ($q_e \sim 0.11$ mmol/g), yet higher than those pre-treated with nitric acid ($q_e \sim 0.09$ mmol/g), with both metal cations. Olive pomace, on the other hand, exhibited good adsorption performance as RAW material ($q_e \sim 0.15$ mmol/g), but the q_e value decreased for samples pre-treated with either H₂O or HNO₃.

The differences in adsorption performance among bergamot, grape, and olive pomaces can be likely attributed to their overall chemical composition and surface acid–base properties. Bergamot pomace is richer in polysaccharides bearing carboxyl and hydroxyl groups, which are known to promote the interaction with REE cations through complexation and ion-exchange mechanisms. In contrast, grape and olive pomaces contain higher proportions of lignin and phenolic moieties, which may hinder the accessibility or reactivity of such functional groups [23,53,54].

These trends are consistent with potentiometric titration data previously reported in our earlier work [23], in which the concentration of surface carboxylic groups was quantified to be 1.10 ± 0.02 meq/g for BP H₂O, 0.23 ± 0.01 meq/g for GP H₂O, and 0.21 ± 0.01 meq/g for OP H₂O. The higher abundance of carboxylic groups in BP H₂O likely contributes to its superior adsorption capacity observed in Fig. 1. Based on the outcomes of the preliminary adsorption tests, one sorbent sample was selected for each pristine material. Accordingly, BP H₂O, GP H₂O, and RAW OP were identified as the best-performing materials and subsequently tested further. In particular, to assess the best pH conditions for REE adsorption, single-batch experiments were also carried out at pH_i = 3.0 and pH_i = 4.0. The results are summarized in Fig. 2, in which the data at pH_i = 5.0 are those already reported in Fig. 1. The results showed that the adsorption capacity increased as the initial pH (pH_i) increases. This behavior could be attributed to the competition between REE cations and H⁺ ions for the binding to active sorption sites. At pH_i = 3.0, the high concentration of H⁺ ions significantly hindered REE uptake, reducing the adsorption efficiency of the tested material. Conversely, the highest adsorption capacity for Nd³⁺ and Dy³⁺ was observed at pH_i = 5.0, which was therefore selected as the optimal pH condition for further adsorption isotherm experiments.

Spectroscopic and morphological investigations

ATR FT-IR analysis was employed to identify the functional groups in BP H₂O, GP H₂O, and RAW OP potentially involved in the adsorption of Nd³⁺ and Dy³⁺.

The spectra of these materials were previously discussed in detail [23,24]. In particular, the FT-IR profiles exhibited broad bands at 3310–3330 cm⁻¹, corresponding to O–H stretching [55], and a weak

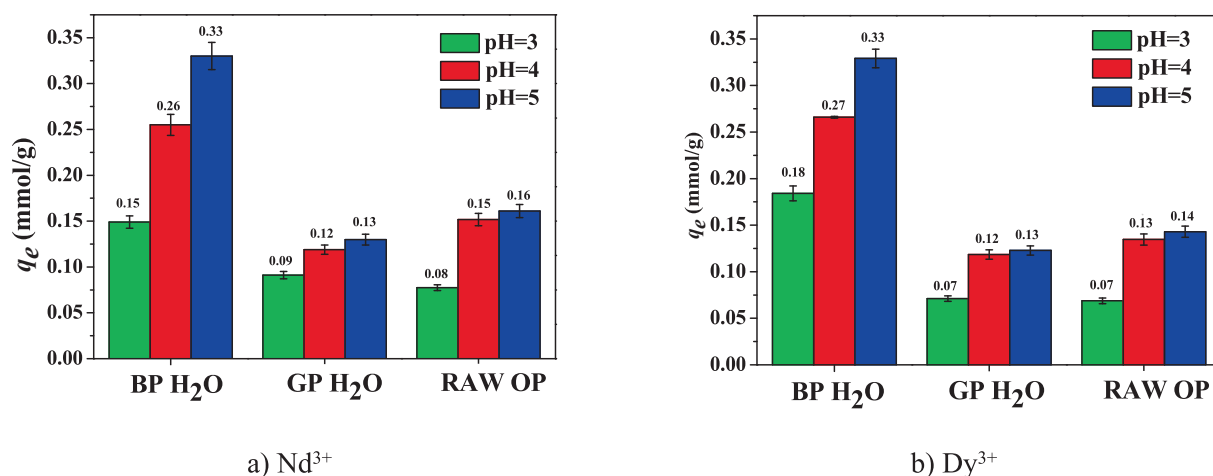


Fig. 2. q_e values of Nd^{3+} (a) and of Dy^{3+} (b) adsorption onto BP H_2O , GP H_2O and RAW OP in aqueous solution, at $\text{pH}_i = 3.0, 4.0$ and 5.0 at $t = 25^\circ\text{C}$. Experimental conditions: ~ 0.01 g of adsorbent in 20 cm^3 of REEs solution ($C_{\text{REE}} \sim 0.18\text{ mmol/dm}^3$).

peak at 3010 cm^{-1} attributed to aromatic C–H stretching [56]. Bands at ~ 2920 and 2850 cm^{-1} were assigned to methylene and methyl stretching vibrations [57]. A band in the $1710\text{--}1740\text{ cm}^{-1}$ range was attributed to C=O stretching of non-ionic carboxylic groups [58]. The peaks at $\sim 1610\text{--}1650$ and $1420\text{--}1440\text{ cm}^{-1}$ were assigned to the asymmetric and symmetric stretching modes of carboxylates [23]. Bands at $1510\text{--}1526\text{ cm}^{-1}$ were associated with aromatic C–C ring vibrations, characteristic of polyphenols [59]. Weak bands in the $1310\text{--}1350\text{ cm}^{-1}$ region were attributed to C–O bending vibrations of methylene and alcoholic groups [60]. Finally, a weak band at 1230 and a more intense band at 1030 cm^{-1} were assigned to C–O, O–C–O, and C–O–C stretching, as well as $-\text{CH}_2$ bending vibrations modes [24,61].

The infrared spectrum of BP H_2O is reported in Fig. 3 before (black line) and after adsorption of Nd^{3+} (blue line) and Dy^{3+} (red line). Similar spectral comparisons for the other biomasses are given in the Supporting Information (Fig. S2).

After Nd^{3+} and Dy^{3+} sorption (Figs. 3 and S2), the three materials exhibited variations in the intensity of bands mainly associated to O–H, C–H, C=O, COO^- and C–O–C vibrational modes, in accordance with Lapo and coworkers findings [19], who investigated the interactions of

banana wastes and peels with various lanthanide ions, such as Nd^{3+} , Dy^{3+} , Eu^{3+} , and Tb^{3+} . Additionally, the sorption process induced shifts in the wavenumber (ν , in cm^{-1}) of maxima for bands attributed to both non-ionic and ionic carboxylic groups. The observed shifts ($\Delta\nu = \nu_{\text{REE}+\text{biomass}} - \nu_{\text{biomass}}$) ranged between 3 and 12 cm^{-1} , suggesting a possible involvement of these functional groups in the adsorption process, a hypothesis in line with Torab-Mostaedi *et al.* [28,62] who studied the La(III) and Ce(III) adsorption by orange and grapefruit peels. Comparable shifts were also reported by Yushin *et al.* [63] for Er^{3+} adsorption onto *Arthospira platensis*, and Oliveira *et al.* [64], who examined interactions between COO^- groups in *Sargassum* sp.-based adsorbents, and La(III), Nd(III), Eu(III), Gd(III) ions. They also introduced the Δ parameter, defined as the difference between the asymmetric ($\nu_{\text{a}(\text{COO}^-)}$) and symmetric ($\nu_{\text{s}(\text{COO}^-)}$) stretching wavenumbers, in the range of $213\text{--}216\text{ cm}^{-1}$ for REE-carboxylate complexes. In the case of BP H_2O (Fig. 3) and RAW OP (Fig. S2b) samples, comparable shift values ($\Delta = 200\text{--}230\text{ cm}^{-1}$) were determined. In addition, the bergamot-based materials spectra showed an increase in the relative intensity ratios of the intensity the peaks at $\sim 1619\text{--}1650$ and $\sim 1730\text{--}1735\text{ cm}^{-1}$, as a further possible consequence of the BP H_2O -metal cations interaction. Specifically, the calculated $\nu_{\text{a}(\text{COO}^-)}/\nu_{\text{s}(\text{COO}^-)}$ ratios were 1.70 and 1.75 with Nd^{3+} and Dy^{3+} , respectively, compared to 1.36 in the absence of M^{3+} . Furthermore, the presence of new bands, as shown in the inset of Fig. 3, was observed in the samples recorded after the sorption of Nd^{3+} (at $\sim 421\text{ cm}^{-1}$) and Dy^{3+} (at $\sim 418\text{ cm}^{-1}$). These bands were attributed to stretching vibrations associated with the coordination of rare earth ions to the biosorbent surface functional groups [19,65].

To investigate morphological changes, the surface of BP H_2O , GP H_2O , and RAW OP were analyzed by SEM-EDX before and after REEs adsorption at a magnification of $1000\times$. As shown in Fig. 4a, the BP H_2O displayed a rough and heterogeneous surface, with fibrous and porous structures typical of lignocellulosic biomass. EDX analysis confirmed the presence of only carbon and oxygen. After Nd^{3+} adsorption (Fig. 4b), SEM images revealed a smoother and more compact surface, suggesting interaction between neodymium and surface functional groups. EDX analysis confirmed the presence of Nd^{3+} through its characteristic peaks ($\sim 1.0, 4.2,$ and 5.2 keV). For Dy^{3+} adsorption (Fig. 4c), the BP surface appeared less altered than that of the BP-Nd sample, retaining visible fibrillar features. However, EDX spectra clearly showed Dy^{3+} peaks ($\sim 1.0, 6.5,$ and 7.8 keV), confirming effective ion adsorption. Similar morphological changes and elemental signals were also observed for RAW OP and GP H_2O , as reported in the Supplementary Figs. S3 and S4, respectively. These findings confirmed the ability of both biomasses mentioned above to be used as sorbent materials for both Nd^{3+} and Dy^{3+} ions, with the former generally inducing more pronounced surface

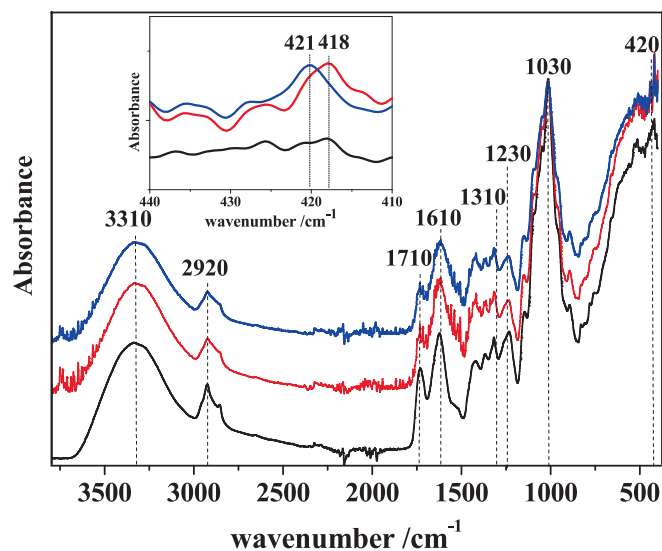


Fig. 3. ATR FT-IR spectra of BP H_2O before (black line, [24]), and after sorption with Nd^{3+} (blue line), and Dy^{3+} (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

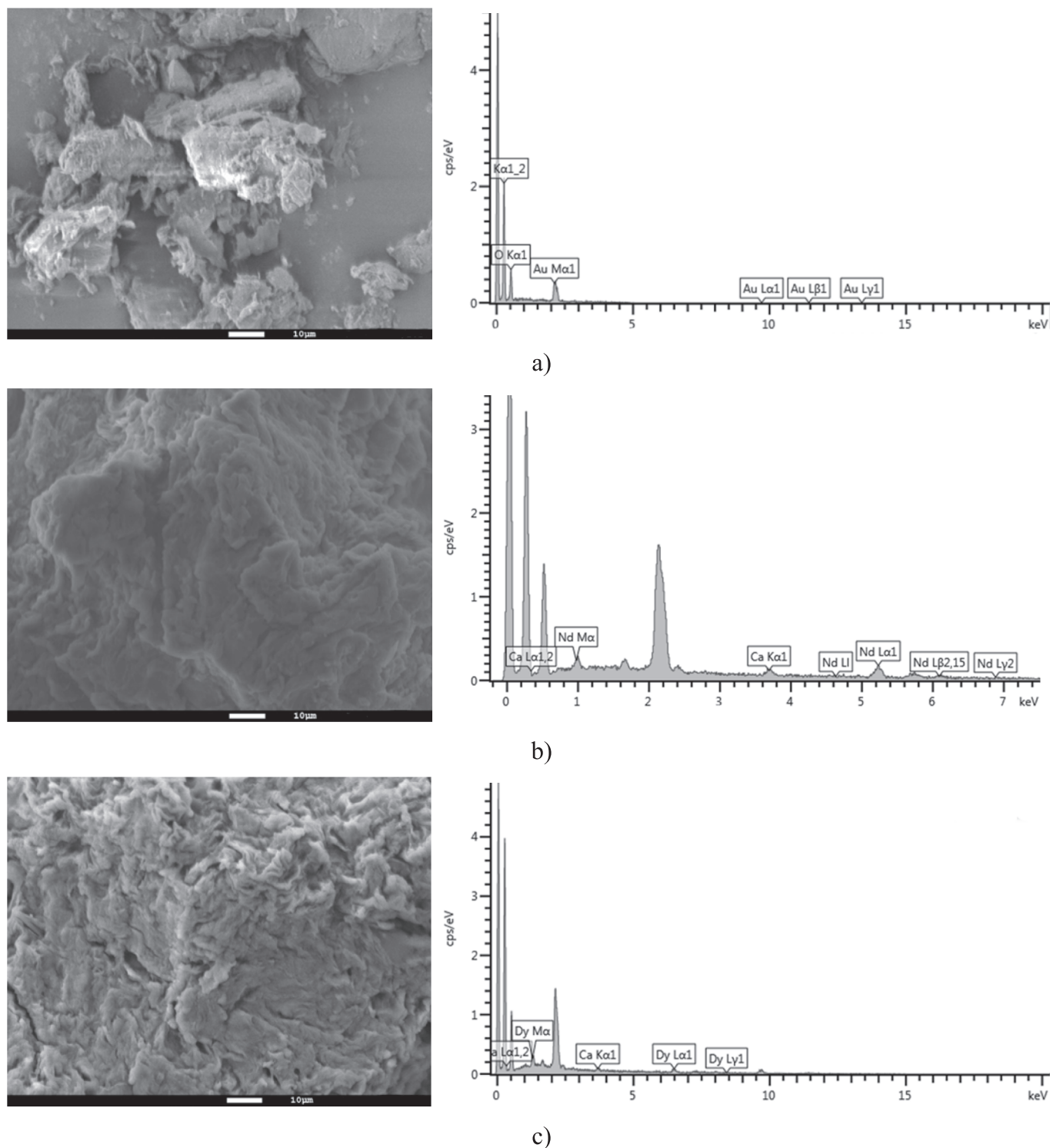


Fig. 4. SEM images of a) BP H₂O before adsorption experiments and after adsorption of b) Nd, c) Dy. On the right the elemental analysis.

modifications [19].

Adsorption kinetics

The adsorption kinetics of Nd³⁺ and Dy³⁺ ions onto BP H₂O, RAW OP and GP H₂O was investigated in the absence of ionic medium. The experimental data (t and q_t) were analyzed using five kinetic models, namely PFO (Eq. (3)), PSO (Eq. (4)), PGO (Eq. (5)), DEM (Eq. (6)), and Boyd (Eqs. (7)–(9)). The results obtained with the five models were

compared based on their fitting parameters, to identify which best reproduced the experimental data. As the PSO model provided the best fitting performances, the results obtained with this model, including the rate constant (k_2), equilibrium adsorption capacity (q_e), and fitting statistics (R^2 and RMSE), are reported in Table 3. The corresponding values for the PFO, PGO, DEM and Boyd models are reported in Tables S2–S5, respectively. Although the PSO model consistently provided better correlation coefficients ($R^2 > 0.98$) and more accurate predictions of q_e , the PFO model was included for comparison purposes, as it remains

Table 3

Parameters of PSO kinetic equation for the adsorption of Nd^{3+} and Dy^{3+} from aqueous solutions at $\text{pH}_i = 5.0$ and $t = 25^\circ\text{C}$.

M^{3+}	Adsorbent	q_e^a	k_2^b	R^2	RMSE ^c
Nd^{3+}	RAW OP	0.11 ± 0.01	18 ± 4	0.9850	0.0047
	GP H ₂ O	0.08 ± 0.01	8 ± 1	0.9837	0.0037
	BP H ₂ O	0.32 ± 0.03	0.29 ± 0.03	0.9929	0.0073
Dy^{3+}	RAW OP	0.12 ± 0.01	17 ± 3	0.9863	0.0047
	GP H ₂ O	0.09 ± 0.01	4 ± 1	0.9848	0.0027
	BP H ₂ O	0.25 ± 0.01	0.70 ± 0.10	0.9839	0.0117
La^{3+}	BP H ₂ O	0.29 ± 0.04	0.32 ± 0.01	0.9739	0.0165

^a mmol/g \pm std. dev.

^b g/(mmol·min) \pm std. dev.

^c Root Mean Square Error, mmol/g.

widely reported in biosorption literature for rare earth elements [19,38,50]. However, the PFO model is generally more appropriate for systems governed by simple physisorption or initial diffusion-controlled uptake mechanisms. Scatter plots comparing the experimental and fitted data using the PSO model are displayed in Fig. 5, while those obtained from the other kinetic models are shown in Figs. S5–S9.

In many cases, the PSO model exhibited the best fitting performance. For example, for Nd^{3+} adsorption onto BP H₂O, correlation coefficients were $R^2 = 0.9819, 0.9929, 0.9915,$ and 0.9807 for PFO, PSO, PGO, and DEM, respectively. Similar trends were observed for RMSE values, which were $0.0118, 0.0073, 0.0079,$ and $0.0094,$ respectively. In other cases (e.g., Dy^{3+} on BP H₂O), the PGO and DEM models showed good statistical parameters; however, the strong correlation between parameters in these models often led to unreliable estimates (e.g., $kp_1 = 0.05 \pm 0.07$ 1/min, Table S4), thus limiting their applicability to our system. The analysis through the Boyd model revealed that, although none of the systems displayed perfect linearity, the regression lines did not pass through the origin, which strongly suggests that intraparticle diffusion cannot be considered the sole rate-limiting mechanism. Specifically, for Nd^{3+} and La^{3+} adsorption onto BP H₂O, moderate correlations were observed, with R^2 values of 0.788 and $0.789,$ respectively, and non-zero intercepts of 0.13 ± 0.06 and $0.19 \pm 0.09.$ Similarly, Dy^{3+} on BP H₂O showed an R^2 of 0.616 with an intercept of $0.15 \pm 0.05.$ For the other biosorbents, lower R^2 values were obtained e.g., 0.391 for Nd^{3+} on OP RAW and 0.397 for Nd^{3+} on GP H₂O and the intercepts were consistently non-zero. These results point to external film diffusion as the predominant mass transfer limitation, rather than intraparticle diffusion, across

all tested systems.

This interpretation is consistent with recent findings reported in literature, where Boyd modeling applied to multicomponent systems also indicated film diffusion as the controlling step, even under competitive adsorption conditions [39].

A visual inspection of Figs. 5 and S5–S8 confirms that PFO was generally inadequate, whereas PSO can be regarded as the most suitable model for describing REE adsorption kinetics on the tested biosorbents. For both Nd^{3+} and Dy^{3+} ions, equilibrium was reached within 20 min on RAW OP and GP H₂O, with a rapid initial uptake followed by a slower plateau region. This two-step kinetic behavior is typical for adsorption processes and has been observed in numerous studies [18,26,28,62,66–69], where the initial phase corresponds to the availability of abundant active sites, and the later stage reflects site saturation and possible diffusional limitations [62]. In contrast, the BP H₂O sample required a longer equilibrium time (ca. 120 min) and showed the lowest k_2 values among the tested biosorbents (Table 3). These findings were further confirmed by kinetic tests conducted with La^{3+} under identical conditions. Also in this case, the data were best fitted by the PSO model (Fig. S8), although the k_2 value for La^{3+} on BP H₂O was lower than those observed for Nd^{3+} and Dy^{3+} adsorption on OP RAW and GP H₂O. The k_2 values obtained in this study for $\text{La}^{3+}, \text{Nd}^{3+},$ and Dy^{3+} on BP H₂O were $0.32, 0.29,$ and 0.70 g/(mmol·min), respectively (Table 3). The trend among the k_2 values may be related to differences in ionic radii of the REE ions: 1.045 \AA (La^{3+}), 0.983 \AA (Nd^{3+}), and 0.912 \AA (Dy^{3+}) [70]. The smaller radius of Dy^{3+} could enhance its mobility and affinity toward the active sites on the biosorbent surface, explaining the higher adsorption rate. This was further supported by comparisons of k_2 values with literature data on rare earth adsorption onto various biomasses [11,26,62,67–69,71–75], reported in Table 4. Despite the slower

Table 4

Pseudo-second-order rate constants (k_2) for rare earth adsorption onto various lignocellulosic biosorbents.

Adsorbent	REE	k_2^a	Ref.
BP H ₂ O	Nd^{3+}	0.29	This work
BP H ₂ O	Dy^{3+}	0.70	This work
BP H ₂ O	La^{3+}	0.32	This work
Banana waste	Nd^{3+}	0.027	[19]
Banana peel	Dy^{3+}	0.019	[19]
Orange peel	La^{3+}	0.017	[28]
Grapefruit peel	Ce^{3+}	0.020	[62]
Grape stalk	La^{3+}	0.008	[11]

^a g/(mmol·min) \pm std. dev.

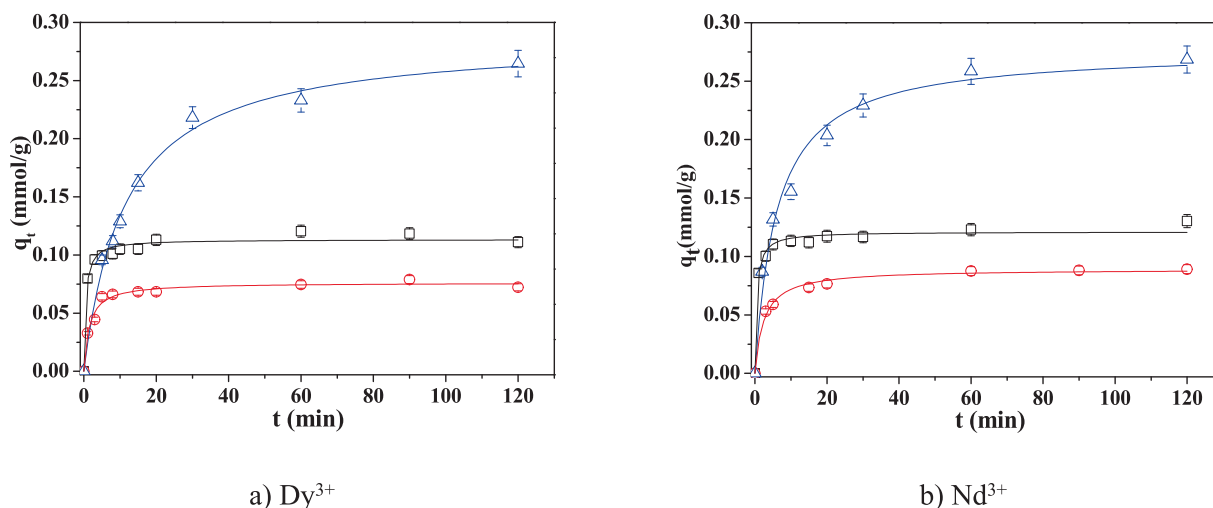


Fig. 5. PSO kinetics of adsorption of Dy^{3+} (a) and Nd^{3+} (b) ions on BP H₂O (Δ), RAW OP (\square), and GP H₂O (\circ) samples.

kinetics of BP H₂O compared to OP and GP in this study, its k_2 values remain higher than those reported for other unmodified lignocellulosic biosorbents [11,19,28,62]. For example, the pseudo-second-order rate constants (k_2) for BP H₂O are 0.29, 0.70, and 0.32 g/(mmol·min) for Nd³⁺, Dy³⁺, and La³⁺, respectively, whereas k_2 values reported for banana peel and orange peel range from 0.017 to 0.027 g/(mmol·min) [19,28]. These results highlight the relatively fast adsorption kinetics of BP H₂O under the tested conditions, making it a promising candidate for practical application in continuous flow systems. While engineered sorbents show higher capacities, the use of unmodified fruit pomace offers clear advantages in terms of waste valorization, cost, and environmental impact, as also highlighted in the LCA and TEA sections.

Adsorption isotherms

The adsorption equilibria of Nd³⁺ and Dy³⁺ ions onto BP H₂O, RAW OP, and GP H₂O were first studied in aqueous solutions at pH_i = 5.0, at low ionic strength and $t = 25$ °C. The collected data (q_e vs. C_e) were subjected to regression analysis by both the Langmuir and Freundlich isotherm equations. Diagrams reporting scatter plots and corresponding lines representing the two isotherm equation models are depicted in Fig. 6, whereas the fitting parameters for the Langmuir and Freundlich models are collected in Table 5 and Table S6, respectively.

As a preliminary observation, the best fit was achieved by means of the Langmuir model. Although the strongest agreement with a specific isotherm model does not necessarily indicate the uptake mechanism of the REE ions, analysing the isotherm parameter values serves as a valuable tool for predicting and optimizing sorption processes. Considering the q_m data (0.38 mmol/g for Nd³⁺, 0.45 mmol/g for Dy³⁺, Table 5) at pH_i = 5.0, BP H₂O resulted to be the best adsorbent material for both the Ln³⁺ ions, followed by RAW OP and GP H₂O for Nd(III), by GP H₂O and RAW OP for Dy(III), respectively. The highest adsorption capacity of the water-treated bergamot pomace could be attributed to its acid-base properties, as already discussed in a previous work [23]. Indeed, among the tested materials, BP H₂O showed the highest acidity, with a protonation constant value of $\log^1 K^H = 3.65$ at $t = 25$ °C, compared to 4.30 and 4.29 for GP H₂O and RAW OP, respectively, in all the cases consistent with the presence of carboxylic groups [23]. Furthermore, the concentration of these active sites is higher in BP H₂O (1.10 meq/g) with respect to GP H₂O (0.23 meq/g) and RAW OP (0.43 meq/g). Consequently, under the investigated conditions, BP H₂O likely exhibited the highest abundance of ionized carboxyl groups, potentially enhancing their interaction with REE ions.

In addition, as shown in Table 5, at pH_i = 5.0 RAW OP exhibits the

Table 5

Langmuir isotherm parameters for the Nd³⁺, Dy³⁺ and La³⁺ ions from aqueous solutions adsorption onto RAW OP, GP H₂O and BP H₂O at $t = 25$ °C, pH_i = 3.0 to 5.0, low ionic strength (absence of ionic medium) and in NaNO₃ 0.10 mol/dm³.

M ³⁺	Adsorbent	pH _i ^a	pH _e ^b	q_m ^c	K_L ^d	R ²	RMSE ^e
Nd ³⁺	RAW OP	5.0	4.1	0.18 ± 0.01	48 ± 6	0.9905	0.0054
	GP H ₂ O	5.0	4.0	0.17 ± 0.01	11 ± 2	0.9835	0.0052
	BP H ₂ O	5.0	3.4	0.38 ± 0.01	27 ± 3	0.9915	0.0105
	BP H ₂ O	5.0 ^f	3.6	0.16 ± 0.02	16 ± 4	0.9723	0.0079
La ³⁺	BP H ₂ O	5.0	3.6	0.35 ± 0.01	38 ± 4	0.9927	0.0100
	BP H ₂ O	5.0 ^f	3.4	0.21 ± 0.01	20 ± 4	0.9757	0.0105
Dy ³⁺	RAW OP	5.0	4.1	0.14 ± 0.01	81 ± 17	0.9699	0.0076
	GP H ₂ O	5.0	4.0	0.16 ± 0.01	17 ± 6	0.9240	0.0106
	BP H ₂ O	5.0	3.2	0.45 ± 0.02	12 ± 1	0.9912	0.0112
	BP H ₂ O	5.0 ^f	3.4	0.16 ± 0.02	30 ± 10	0.9134	0.0167
Nd ³⁺	BP H ₂ O	4.0	3.3	0.28 ± 0.01	130 ± 20	0.9793	0.0121
Dy ³⁺	BP H ₂ O	4.0	3.6	0.29 ± 0.02	90 ± 20	0.9372	0.0211
Nd ³⁺	BP H ₂ O	3.0	2.9	0.24 ± 0.01	70 ± 30	0.9941	0.0069
Dy ³⁺	BP H ₂ O	3.0	2.9	0.18 ± 0.01	400 ± 100	0.9891	0.0066

^a initial pH value of REE ions solutions.

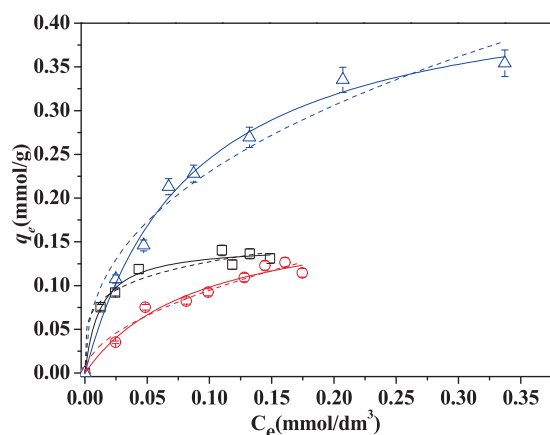
^b mean pH value at adsorption equilibrium.

^c in mmol/g ± std. dev.

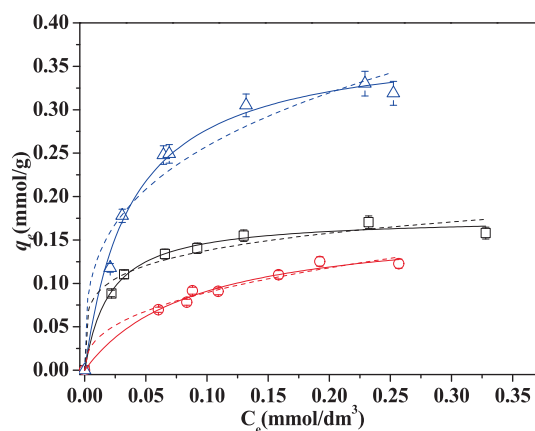
^d in dm³/mmol ± std. dev.

^e Root Mean Square Error.

^f adsorption isotherm carried out in NaNO₃ 0.10 mol/dm³.



a) Dy³⁺



b) Nd³⁺

Fig. 6. Adsorption isotherms of Dy³⁺ (a) and Nd³⁺ (b) ions onto BP H₂O (△), RAW OP (□), and GP H₂O (○) in aqueous solutions and $t = 25$ °C. The experimental data were processed using the Langmuir (solid line) and Freundlich (dotted line) models.

highest values of K_L , indicating a greater affinity of the material for the REEs. The use of this waste biomass could enhance the marketability of the recovery process, as it is an inexpensive, biodegradable, and widely available material. These are significant advantages for adsorption compared to other extraction techniques used for the recovery/removal of metals from aqueous solutions (e.g., solid–liquid extraction, flotation, coagulation, flocculation, solvent extraction, ion exchange, coprecipitation), which typically involve hazardous chemical reagents [18].

The mean equilibrium pH values of isotherm experimental points (pH_e) are reported in Table 5. In all the investigated systems, the pH_e was lower than pH_i of the REE ions solution as the result of an exchange reaction involving metal cation and proton bound to carboxylate on the pomace surface.

Furthermore, given its higher adsorption capacity, the effect of pH on Nd^{3+} and Dy^{3+} adsorption onto BP H₂O was further investigated carrying out isotherm experiments in aqueous solutions at $t = 25\text{ }^\circ\text{C}$, $\text{pH}_i = 3.0, 4.0$. The scatter plot of experimental data (q_e vs. C_e), together with lines representing Langmuir and Freundlich isotherm model equation are given in Fig. 7. Refined parameters (q_m and K_L) together with fitting quality parameters (R^2 and RMSE) of the Langmuir and Freundlich models are summarized in Table 5 and Table S6, respectively. Consistently, the Langmuir model provided the best description of the experimental data, as evidenced by the highest R^2 and lowest RMSE values. Furthermore, the q_m values obtained for each metal ion at the different pH levels confirmed the single batch experiment findings (see section 3.1), showing a reduction in maximum adsorption capacity of $\sim 37\%$ for Nd^{3+} and $\sim 60\%$ for Dy^{3+} comparing the q_m values at $\text{pH}_i = 3.0$ and 5.0 . In all cases, the sorption capacity of the material towards metal cations increased with pH. As the active site of the material ($\log K^H \approx 3.5$) is increasingly deprotonated ($\approx 25\%$ at $\text{pH} = 3$, $\approx 75\%$ at $\text{pH} = 4$, and $\approx 95\%$ at $\text{pH} = 5$), then metal binding is favored when the sites are in deprotonated (anionic) form. As regards Nd^{3+} and Dy^{3+} , their chemical speciation is quite similar. In the experimental conditions given, below $\text{pH} = 5$, cation hydrolysis is negligible, and they are present as hydrated cations.

The adsorption capacity of the most effective material was further examined by assessing the influence of an ionic medium on the adsorption of Dy^{3+} and Nd^{3+} . To this purpose, batch adsorption isotherm experiments were carried out in 0.10 mol/dm^3 NaNO_3 solutions at $\text{pH}_i = 5.0$ and $t = 25\text{ }^\circ\text{C}$. The experimental data were well described by the Langmuir model (Figs. S10 and S11 of the Supporting Materials). A comparison between q_m calculated in the presence of

sodium nitrate and that obtained without background salt revealed a significant decline in adsorption ability. This reduction could be attributed to the shielding effect exerted by the ions resulting from NaNO_3 dissociation, as well as the competitive adsorption of Na^+ ions, which are present at a concentration of five orders of magnitude higher than that of the cations. Furthermore, the potential formation of ion pairs between nitrate anions and trivalent REE cations should be considered [70], as this interaction may partially neutralize the positive charge of the metal ions, thereby reducing their affinity for the adsorbent.

The adsorption ability of BP H₂O was also evaluated towards La^{3+} ions carrying out other adsorption isotherm experiments at $t = 25\text{ }^\circ\text{C}$, $\text{pH}_i = 5.0$, at low ionic strength and in 0.10 mol/dm^3 NaNO_3 solution, to evaluate its adsorption ability towards another light REE ion (analogously to Nd^{3+}) in the presence and absence of an ionic medium. Once again, in both conditions, Langmuir model well described the collected data (Fig. S11).

By comparing the Langmuir parameters obtained for La^{3+} with those for Nd^{3+} and Dy^{3+} (this latter a heavy REE) collected in Table 5, a comprehensive understanding of the adsorption of REEs ions onto BP H₂O has been achieved. The maximum adsorption capacity values without ionic medium addition were observed towards Dy^{3+} , followed by Nd^{3+} and La^{3+} , respectively, while the Langmuir constant values

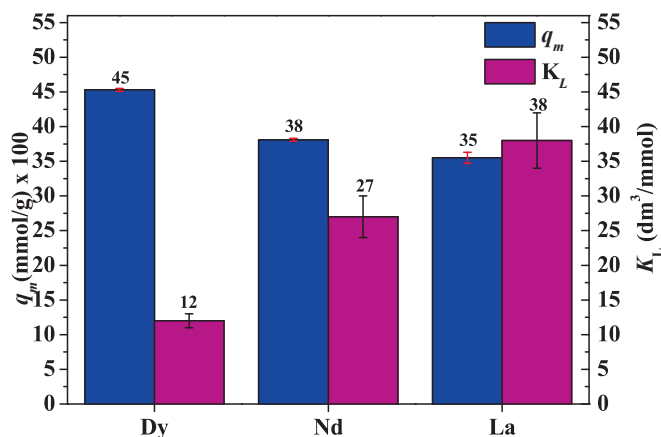


Fig. 8. q_m and K_L values of REEs adsorption onto BP H₂O at $\text{pH}_i = 5.0$, without ionic medium and $t = 25\text{ }^\circ\text{C}$.

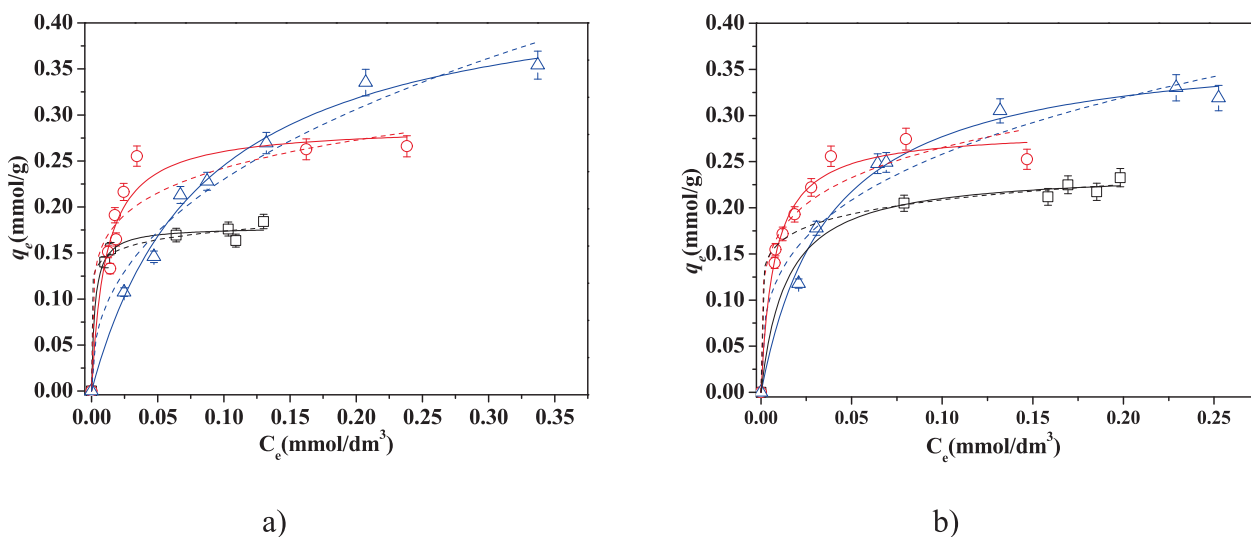


Fig. 7. Adsorption isotherms of Dy^{3+} (a) and Nd^{3+} (b) onto BP H₂O in aqueous solutions, at $t = 25\text{ }^\circ\text{C}$, at $\text{pH}_i = 5.0$ (Δ), 4.0 (\circ) and 3.0 (\square). The experimental data were processed using the Langmuir (solid line) and Freundlich (dotted line) models.

exhibited an opposite trend (Fig. 8).

Despite their common trivalent charge and similar coordination chemistry, REEs display adsorption behaviors strongly influenced by subtle differences in ionic radius, hydration energy, and coordination geometry. The observed q_m and K_L trends likely reflect variations in hydration shell structure: La^{3+} (1.045 Å) > Nd^{3+} (0.983 Å) > Dy^{3+} (0.912 Å) [70,76]. Larger ions, such as La^{3+} , possess more diffuse hydration shells with lower desolvation energies, enabling direct coordination with carboxylates on BP and higher K_L values. Conversely, smaller ions like Dy^{3+} form compact, strongly bound hydration shells that enhance electrostatic interactions with carboxylate and hydroxyl groups, producing denser adsorption layers (higher q_m) but incurring greater desolvation penalties. Similar size–hydration effects, favoring heavy REEs, have been reported for lignocellulosic biosorbents such as banana peel–derived adsorbents [19]. The role of the hydration shell on the adsorption of REE ions onto water-treated bergamot pomace is further supported by analyzing the q_m values obtained in the presence of sodium nitrate (Table 5). The introduction of Na^+ ions lead to a general decrease in the adsorption capacity due to above-mentioned competitive adsorption processes. However, La^{3+} exhibited the highest q_m values, indicating that its lower solvation energy enables more effective interaction with BP H_2O sites despite the presence of sodium ions.

In order to evaluate the results obtained in this paper for BP H_2O within the framework of waste biomass used for the same purpose of recovering REEs, a comparative analysis of adsorption capacities (q_m) is provided in Table 6, including also data for Ce^{3+} , Eu^{3+} , Pr^{3+} , Sm^{3+} , and Tb^{3+} , which were not considered in this work. To make comparisons among different metal cations, which are featured by different atomic weights, the q_m values were reported, both for experimental and literature data, in mmol/g instead of mg/g. The table is organized grouping results metal by metal and values are ordered from the highest to the lowest and also contains information of which equation was used for the modelling of the kinetic and isotherm experiments.

The sorption performance of BP H_2O lies within the typical range reported for lignocellulosic materials. As far as La^{3+} cation is considered, BP H_2O exhibited a maximum adsorption capacity of 0.35 ± 0.01 mmol/g, lower than that of grapefruit peel (1.24 mmol/g [62]) and orange peel (1.13 mmol/g [28]), but higher than grape stalk (0.26 mmol/g [11]). For Nd^{3+} , BP H_2O reached 0.38 ± 0.01 mmol/g, surpassing banana peel (0.33 mmol/g [19]) and bone powder (0.08 mmol/g, [67]) although still lower than banana waste (0.72 mmol/g [19]). The best adsorption result was recorded for Dy^{3+} , with 0.45 ± 0.02 mmol/g, outperforming banana peel (0.36 mmol/g [19]), but lower than banana waste (0.81 mmol/g, [19]). A general evaluation of these results indicated that the diversity of performance depends on the sorbent nature. For example, prawn carapace, which is a chitin-based material, resulted very efficient for the recovery of Ce^{3+} (7.13 mmol/g [75]), activated biochar (at pH = 6.5) from cactus fibers, which is a material obtained through a thermal treatment of waste biomass, was capable to recovery Sm^{3+} (2.33 mmol/g [73]). Considering all the differences among the possible waste biomass, the sorption capacities achieved by BP H_2O towards La^{3+} , Nd^{3+} and Dy^{3+} fall within an average value.

Adsorption processes thermodynamic parameters

ITC is a highly sensitive and accurate technique allowing a direct quantification of the heat exchanged during a chemical process. Although it is widely employed for the investigation of chemical solution equilibria (see, e.g., [77–79]), to the best of the authors knowledge no papers have been published yet using the mentioned technique to obtain thermodynamic parameters of interaction between a solid sorbent and metal cations. Adsorption enthalpy change ($\Delta_{\text{sor}}H$) is usually indirectly calculated by means of the Van't Hoff equation, considering the temperature dependence of the Langmuir constant, as observable in the case of studies reported on Yb(III), La(III), Ce(III), Sm(III) and Nd(III) adsorption onto Spirulina biomass [27], orange peel [28], activated

Table 6

Literature data reported for the adsorption of rare earths by different biomasses.

Adsorbent	REEs	Isotherm model	Kinetic model	q_m (mmol/g)	Ref.
Prawn carapace	Ce^{3+}	L	N/A	7.13	[75]
Corn style	Ce^{3+}	L	N/A	1.78	[75]
Fish scales	Ce^{3+}	L	N/A	1.43	[75]
Neem sawdust	Ce^{3+}	L	N/A	1.43	[75]
Eggshell	Ce^{3+}	L	N/A	1.19	[75]
Orange peel	Ce^{3+}	L	PSO	1.16	[28]
Grapefruit peel	Ce^{3+}	L	PSO	1.14	[62]
Pineapple crown	Ce^{3+}	L	N/A	1.02	[75]
Crab shell	Ce^{3+}	L	N/A	0.65	[75]
Orange peel	Ce^{3+}	L	N/A	0.51	[75]
Grape stalk	Ce^{3+}	L	PSO	0.27	[11]
Banana waste	Dy^{3+}	L	PSO	0.81	[19]
BP H_2O	Dy^{3+}	L	PSO	0.45	This work
Banana peel	Dy^{3+}	L	PSO	0.36	[19]
Bone powder	Eu^{3+}	L	N/A	1.33	[67]
Crab shell	Eu^{3+}	L	PSO	0.65	[68]
Banana waste	Eu^{3+}	L	PSO	0.56	[19]
Banana peel	Eu^{3+}	L	PSO	0.12	[19]
Modified cactus fibers (MnO ₂ -coated)	Eu^{3+}	L	PFO	0.08	[74]
Modified cactus fibers	Eu^{3+}	L	PFO	0.02	[74]
Raw cactus fiber	Eu^{3+}	L	PFO	0.01	[74]
Prawn carapace	La^{3+}	F	N/A	1.44	[69]
Grapefruit peel	La^{3+}	L	PSO	1.24	[62]
Orange peel	La^{3+}	L	PSO	1.13	[28]
Eggshell	La^{3+}	F	N/A	0.72	[69]
Pineapple crown	La^{3+}	F	N/A	0.72	[69]
Crab shell	La^{3+}	F	N/A	0.65	[69]
Corn style	La^{3+}	F	N/A	0.55	[69]
BP H_2O	La^{3+}	L	PSO	0.35	This work
Grape stalk	La^{3+}	L	PSO	0.26	[11]
Banana waste	Nd^{3+}	L	PSO	0.72	[19]
BP H_2O	Nd^{3+}	L	PSO	0.38	This work
Banana peel	Nd^{3+}	L	PSO	0.33	[19]
Bone powder	Nd^{3+}	L	N/A	0.08	[67]
Crab shell	Pr^{3+}	L	PFO	0.48	[66]
Orange peel	Pr^{3+}	L	PSO	0.42	[66]
Activated biochars from cactus fibers (pH = 6.5)	Sm^{3+}	L	PFO	2.33	[73]
Activated biochars from cactus fibers (pH = 3.0)	Sm^{3+}	L	PFO	0.60	[73]
Banana peel	Tb^{3+}	L	PSO	0.14	[19]

L: Langmuir; F: Freundlich; PSO: Pseudo-second-order kinetic model; PFO: Pseudo-first-order kinetic model.

carbon derived from soybean pods [25], biochar fibers from *Opuntia Ficus Indica* [26], chitosan–polyethylene glycol–polyvinyl alcohol hybrid membrane [80]. However, some authors have highlighted significant discrepancies between the values obtained via Van't Hoff analysis and those directly measured by ITC, due to the inherent limitations and assumptions of the indirect approach [61]. On the contrary, the mentioned analytical technique allows the determination of more robust and independent thermodynamic parameters, as demonstrated by Batista *et al.* [29], who investigated the adsorption of methylene blue by tangerine peel pre-treated with a 0.10 mol/dm³ sodium hydroxide solution.

The Nd^{3+} and Dy^{3+} adsorption enthalpy change ($\Delta_{\text{sor}}H$) onto BP H_2O was determined by ITC and the experimental data elaborated using Eq. (14). In addition, Eqs. (15) and (16) were employed for the calculation of the corresponding free Gibbs energy ($\Delta_{\text{sor}}G$) and entropy ($\Delta_{\text{sor}}S$) change values associated to the sorption process. The results, reported in Table 7 together with literature values on similar systems obtained by the Van't Hoff equation, suggest that the REEs adsorption is a spontaneous ($\Delta_{\text{sor}}G < 0$ kJ/mol) and endothermic process ($\Delta_{\text{sor}}H > 0$ kJ/mol),

Table 7

Literature data reported for thermodynamic parameters for the adsorption of rare earths by different biomasses and methodologies (ITC or Van't Hoff) used.

Metal Ion	Adsorbent	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol·K))	Method	Ref.
Nd ³⁺	BP H ₂ O	35 ± 8 ^a	−48 ± 17 ^a	278 ± 63 ^a	ITC	T. W. ^b
Dy ³⁺	BP H ₂ O	65 ± 16	−46 ± 6	371 ± 58	ITC	T. W. ^b
La ³⁺	Tangerine Peel	28.57	−23.29	170.85	Van't Hoff	[28]
Ce ³⁺	Tangerine Peel	38.34	−24.13	206.18	Van't Hoff	[28]
Eu ³⁺	Cactus Fibers	39.7	−31.1	237	Van't Hoff	[26]
Eu ³⁺	Phosphorylated Cactus Fibers	80.9	−38.2	397	Van't Hoff	[26]
Eu ³⁺	MnO ₂ -coated Cactus Fibers	73.6	−29.5	342	Van't Hoff	[26]
Yb ³⁺	Dried Spirulina Powder	0.41	−3.09	11.72	Van't Hoff	[27]
Ce ³⁺	Zeolite ZSM-5	98.2	−31.68	−223.1	Van't Hoff	[25]
La ³⁺	Zeolite ZSM-5	73.3	−27.49	−155.5	Van't Hoff	[25]
Nd ³⁺	Zeolite ZSM-5	96.8	−33.72	−211.6	Van't Hoff	[25]

^a ± std. dev.

^b This work.

indicating that the sorption would be favoured with a temperature increase. The ITC-derived enthalpy changes for Nd³⁺ (+35 ± 8 kJ/mol) and Dy³⁺ (+65 ± 16 kJ/mol) fall above the range typically associated with physisorption ($\Delta H = -5$ to -20 kJ/mol) and approach values reported for chemisorption (-40 to -120 kJ/mol) as noted in general adsorption reviews [81,82]. The values obtained for the sorption of REE cations onto BP in this work, exhibiting positive $\Delta_{\text{sor}}H$ (+35 and + 65 kJ/mol, for Nd(III) and Dy(III), respectively) and high $\Delta_{\text{sor}}S$ values (+278 and + 371 J/(mol·K), same order) suggest entropy-driven mechanisms involving inner-sphere surface complexation and partial dehydration of REE aquo-complexes. In fact, Choppin [83–86] reports that when inner sphere complexes of 4f cations are formed, the primary hydration sphere is sufficiently disrupted that its contribution exceeds that of the cation–ligand interaction, resulting in an endothermic enthalpy change and a positive entropy change. Moreover, the greater enthalpy change value obtained for Dy³⁺ compared to Nd³⁺ reflects the lanthanide contraction, which results in a lower ionic radius and a more compact and strongly bound hydration sphere, as also above suggested when discussing data on Langmuir constants (Fig. 8). The release of water molecules from the hydration sphere into the bulk increases the number of accessible microstates, resulting in a significant entropic increase, which balances the positive enthalpy change values and makes the process spontaneous ($\Delta_{\text{sor}}G < 0$). This suggests a specific and direct adsorption on the oxygenated sites of the biomass, in agreement with the hard behaviour of lanthanides, according to Pearson [87]. The results reported by Batista [29] showed that the process was exothermic ($\Delta_{\text{sor}}H \sim -20$ to -25 kJ/mol) and entropy-driven by the release of solvation water from hydrophobic domains, resulting in a modest $\Delta_{\text{sor}}S$ (~ 35 J/(mol·K)). In contrast, the adsorption of Nd³⁺ and Dy³⁺ onto bergamot pomace required a significantly higher energy input for dehydration ($\Delta_{\text{sor}}H > 30$ kJ/mol) accompanied by much higher entropy gain ($\Delta_{\text{sor}}S > 270$ J/(mol·K)), which reflects the breakdown of structured hydration shells and the formation of inner-sphere surface complexes. These differences underscore the strong dependence of thermodynamic behaviour on the chemical nature of the adsorbate and confirm the distinct adsorption pathways involved in metal–biosorbent versus dye–biosorbent systems.

To better contextualize our findings, in Table 7 our ITC results are

compared with van't Hoff-derived data from literature for the sorption on REE cations onto biosorbents.

REE adsorption process is always endothermic, even though enthalpy changes vary considerably depending on the biosorbent. Our results ($\Delta H = +35$ to $+65$ kJ/mol) are comparable or higher than values obtained for lanthanide sorption on tangerine peel (28–38 kJ/mol), cactus fibers (39–80 kJ/mol), and much lower than those for Zeolite ZSM-5 (up to 98 kJ/mol), suggesting that the pomace materials interact with REEs via relatively strong, selective, and energetically demanding processes, most likely involving coordination to carboxylate and hydroxyl groups after partial disruption of the hydration shell.

As far as entropy change values are concerned, most of the values are largely positive, except for what found in the case of Zeolite ZSM-5 that were found to be negative.

The $\Delta_{\text{sor}}G$ values could also provide insight into the adsorption mechanism: according to thermodynamic criteria [88], since the data obtained using BP H₂O range between -48 to -46 kJ/mol, the Nd³⁺ and Dy³⁺ adsorption processes could potentially occur by means of a combination of physical and chemical-type electrostatic interactions.

These results suggest that the REE–biomass interactions in this case involve a combination of electrostatic attraction and weak coordination to functional groups, consistent with the absence of major spectral shifts in FT-IR [81,82]. It should be emphasized that ΔH alone is not sufficient to classify the adsorption mechanism. In this study, the endothermic nature of the process, combined with high $\Delta_{\text{sor}}S$ values, lack of strong FT-IR band shifts, and fast PSO-type kinetics, suggests that the mechanism involves entropy-driven, non-covalent interactions likely comprising electrostatic attraction and weak coordination rather than true chemisorption.

Reuse and recovery

The cost and environmental footprint of REEs recovery can be significantly minimized by regenerating and reusing adsorbent materials. To investigate this aspect, a series of four adsorption/desorption cycles was carried out. A 0.1002 mol/dm³ HNO₃ solution was employed as the desorbing agent. The adsorption capacity in each cycle was calculated using Eq. (1), while the amount of REE cation desorbed was obtained by Eq. (12); data obtained for the adsorption/desorption steps are reported in Fig. S13(a–f). The desorption efficiency for each cycle was determined using Eq. (13). These parameters were used to monitor both the stability of the biosorbent and the effectiveness of REEs recovery over consecutive reuse cycles. As shown in Fig. 9 (9a for Dy³⁺ and 9b for Nd³⁺), BP H₂O exhibited the highest stability in recovery performance across the four cycles. For Dy³⁺, the recovery efficiency decreased only from 98.8 % in the first cycle to 90.2 % in the fourth, while for Nd³⁺ it lowered from 97.0 % to 88.9 %. This corresponds to an overall loss of less than 9 %, demonstrating the strong potential of the material for multiple use without the need for pre-treatment. In contrast, GP H₂O showed a more pronounced decrease (Dy³⁺: from 92.2 % to 52.0 %; Nd³⁺: from 96.2 % to 35.3 %), while RAW OP suffered the steepest decline (Dy³⁺: from 91.4 % to 45.0 %; Nd³⁺: from 95.3 % to 24.8 %). Nevertheless, the desorption with nitric acid ensured the complete recovery of the adsorbed metals at each step. These findings confirm BP H₂O as a sustainable and durable biosorbent for the repeated recovery of Nd³⁺ and Dy³⁺ from aqueous solutions.

In literature, Lapo and colleagues [19] checked one cycle of Nd³⁺, Dy³⁺, Eu³⁺ and Tb³⁺ desorption by banana waste biomass using 0.01 mol/dm³ EDTA and 0.10 mol/dm³ HCl solutions as desorbing agents. The author obtained a desorption efficiency of 97 % and 40 % by testing the chelating agent and the inorganic acid, respectively. Varshini *et al.* [69] evaluated the reusability of orange peel for the Pr³⁺ adsorption/desorption employing a 0.10 mol/dm³ NaOH solution for the metal elution, observing that the biomass could be efficiently reused for 7 cycles, with a desorption efficiency of 94–95 % for each of them. Birungi and Chirwa [71] used freshwater algal biomasses for La(III)

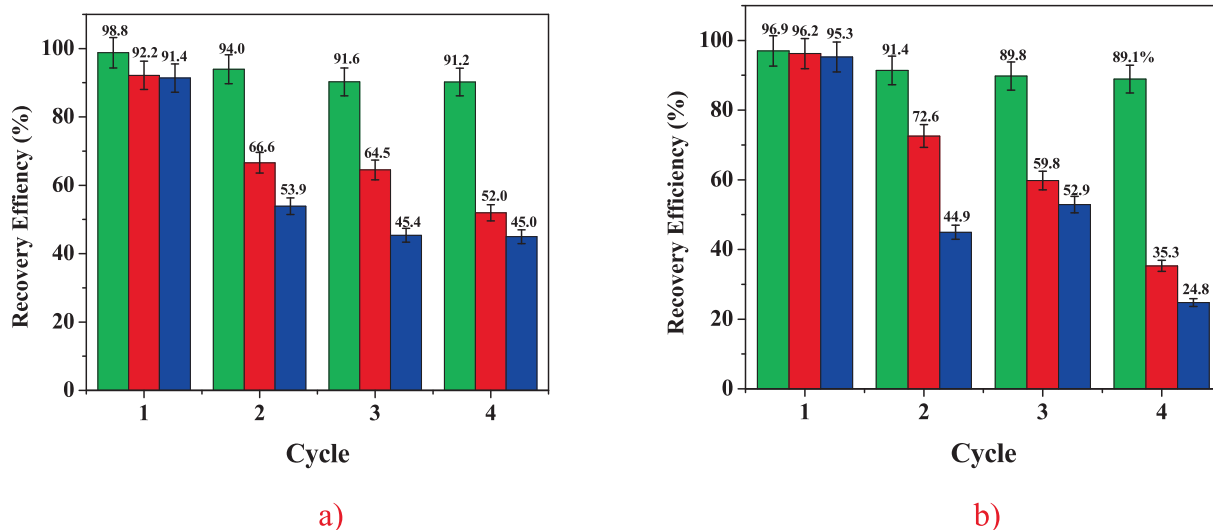


Fig. 9. Recovery efficiencies (RE%) of (a) Dy³⁺ and (b) Nd³⁺ over four consecutive adsorption/desorption cycles using BP H₂O (green), GP H₂O (red), and RAW OP (blue) as biosorbents. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adsorption and checked the metal recovery with a 0.10 mol/dm³ HNO₃ solution in three elution cycles, finding that the *Desmodosmus multivariabilis* was the most efficient with a recovery of ~99.6 %. Hussien

[73] carried out three cycles of La³⁺ desorption experiments in the presence of *Pleurotus ostreatus* biosorbent and dilute hydrochloric and nitric acid solutions (C_{H+} = 0.10, 0.20, 0.30 mol/dm³), determining that

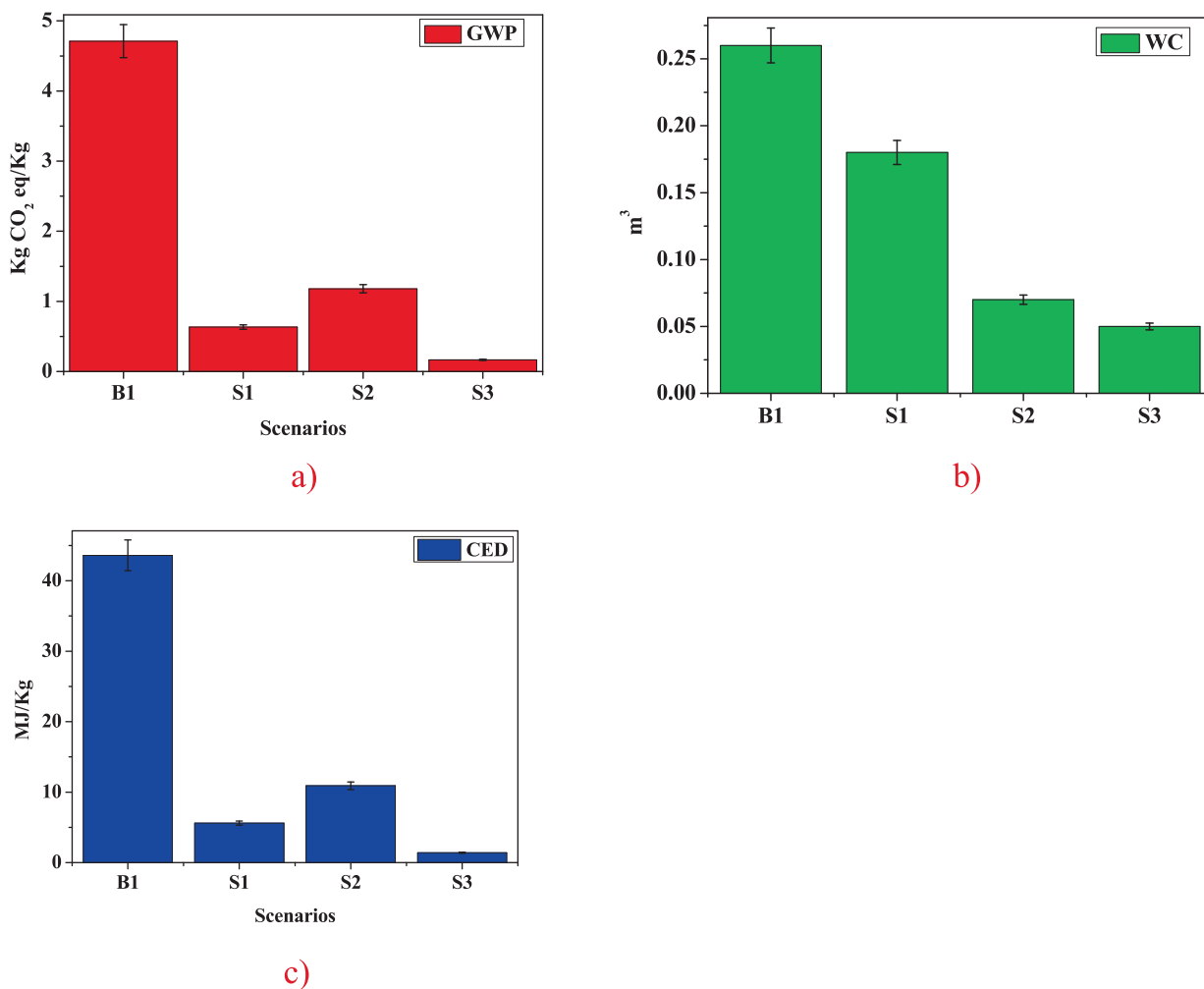


Fig. 10. Bar plot of Global Warming (a), Water Consumption (b) and Cumulative Energy Demand (c) for the production of 1 kg of biosorbent under all the four scenarios.

0.10 mol/dm³ HNO₃ solution was the most suitable, with elution efficiencies between 67 % and 97 %.

Environmental and economic evaluation

In recent years, the development and application of alternative sorbents derived from industrial and agricultural by-products, such as biochar and activated carbon, have gained global interest. Several LCA studies have evaluated the environmental impacts of biochar production [48,89,90]. These studies highlight that feedstock-type, pyrolysis technology and processing temperature play significant roles in determining overall environmental performance. Moreover, as stated by Alipanah *et al.* [91], REEs adsorption capacity and reusability of biosorbents are critical to their environmental and economic viability. In this context, biosorbents derived from agricultural by-products, particularly those requiring minimal processing energy, offer promising potential for sustainable resource recovery.

As a part of this study, the environmental and economic performance of BP H₂O produced under laboratory-scale conditions was evaluated. Experimental inventory data were analyzed through both LCA and TEA methodologies, providing a dual-perspective assessment of BP H₂O sustainability for REEs recovery. Fig. 10a and b summarize GW, WC and CED scores associated to the production of 1 kg of BP H₂O, evaluated across the four scenarios.

The real case (B1) yields the highest environmental impact (GW: 4.22 kg CO₂ eq; WC: 0.26 m³; CED: 43.6 MJ), primarily due to inefficient drying process. Scenario S1, which implements an improved drying method, significantly reduced GW, WC and CED to 0.55 kg CO₂ eq, 0.18 m³ and 5.6 MJ, respectively. Scenario S2, which involves biosorbent regeneration, offers moderate improvements over the real case, although not as effective as the energy-efficient drying in S1. The optimized scenario (S3), simulating the industrial-scale drying of BP H₂O together with its regeneration, achieves the lowest environmental burdens (GW: 0.14 kg CO₂ eq; WC: 0.05 m³; CED: 1.4 MJ). Notably, the trend in GW closely mirrors that of CED, indicating that electricity consumption is the dominant contributor to carbon emissions, while the impacts from water and chemical use remain minimal.

Following the environmental assessment, a TEA was conducted to estimate production costs in €/kg of BP H₂O, as shown in Fig. 11.

The real case (B1) shows the highest estimated cost at 13.64 €/kg, whereas the optimized scenario (S3) reduces it significantly to 2.99 €/kg. The acid required for regenerating BP H₂O, used in the S2 and S3 scenarios, had minor economic relevance. Notably, water consumption

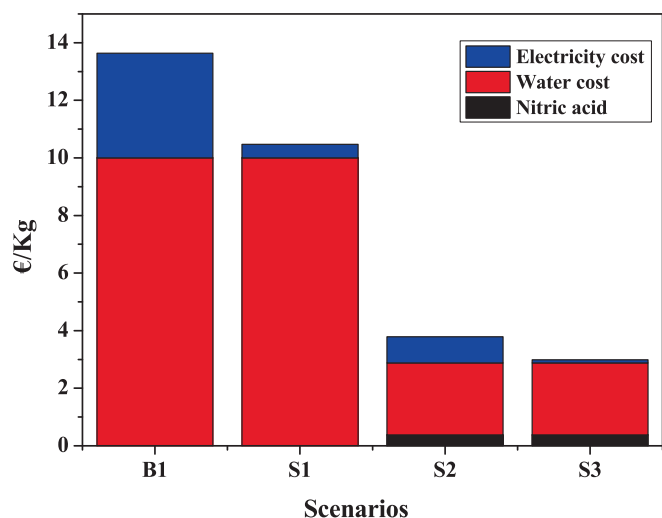


Fig. 11. Bar plot of Techno-Economic Assessment (TEA) for the production of 1 kg of biosorbent under all the four scenarios.

emerged as the most impactful economic factor; its reduction in S2 and S3 proved more cost-effective than solely implementing improved drying (S1). These results highlight the importance of water management, energy efficiency and sorbent reuse in optimizing the cost-performance ratio. When compared to conventional biosorbents, BP H₂O demonstrates competitive performance. Activated carbon typically exhibits GWP values around 6.6 kg CO₂ eq/kg and CED above 97 MJ/kg due to its high-temperature processing requirements. In contrast, biochar, owing to its lower energy demand, tends to have a smaller environmental footprint and may even become carbon-negative when applied to soil [48]. From an economic standpoint, the production of BP H₂O demonstrates promising cost performance, particularly when extrapolated to industrial-scale scenarios. In the optimized scenario (S3), production costs fall within or below the range reported in the literature: activated carbon and biochar average 5.6 \$/kg and 5 \$/kg [89], respectively, with some sources citing values as low as 1.06 \$/kg for date palm biochar and 1.34 \$/kg for activated carbon [48].

From all of the above, the preliminary techno-economic and environmental assessment suggests that BP H₂O is a viable and competitive biosorbent for REEs recovery. Its potential is particularly strong in applications where low-cost agricultural residues and energy-efficient processing strategies can be leveraged to minimize both economic and environmental impacts.

Conclusions

This study explored the valorization of agri-food industrial waste biomasses, specifically bergamot, grape and olive pomaces, for the recovery of rare earth elements (REEs), such as Nd³⁺, La³⁺ and Dy³⁺ ions, from aqueous solutions. The adsorption performance varied among the tested biomasses, likely influenced by their surface properties and functional groups. The sorption process followed pseudo-second order kinetic, with equilibrium reached in approximately 120 min. The isotherm batch experiments were modeled by means of a Langmuir model equation. Among the tested materials, BP H₂O exhibited the highest adsorption capacity, particularly for Dy³⁺ at pH_i = 5.0 in the absence of ionic medium ($q_m = 0.45 \pm 0.02$ mmol/g), followed by Nd³⁺ ($q_m = 0.38 \pm 0.01$ mmol/g) and La³⁺ ($q_m = 0.35 \pm 0.01$ mmol/g). The sorption efficiency decreased upon the addition of ionic medium and the acidification of solutions. The interaction between metal cations and biosorbent was confirmed by SEM-EDX and ATR FT-IR spectroscopies. The former technique allowed the investigation of morphology variation induced by contact with REEs cations and ascertained the presence of both Nd³⁺ and Dy³⁺ on the pomace surface. The latter revealed a new band at ~ 420 cm⁻¹ in the spectra of BP H₂O samples after sorption with Nd³⁺ and Dy³⁺, absent in the starting samples, attributed to the interaction between the metal cations and O-donor groups on the pomace surface. Adsorption isotherm modeling using Langmuir equation showed excellent fits with the experimental data, suggesting the homogeneous distribution of surface adsorption sites. Thermodynamic parameters of interaction between sorbent and REEs cations were directly determined by ITC providing, for the first time and addressing a critical knowledge gap in the field, a more robust and accurate alternative to the traditional Van't Hoff approach. The results suggested that REE cation sorption processes are spontaneous, endothermic and entropic in nature. The adsorption process investigated here showed a better fit with the PSO model, which is often associated with systems where chemisorption or complexation phenomena are involved. Nevertheless, the thermodynamic analysis performed via ITC revealed positive enthalpy changes ($\Delta_{\text{sor}}H = +35 \pm 8$ kJ/mol for Nd³⁺ and $+65 \pm 16$ kJ/mol for Dy³⁺), indicating an endothermic process. This, together with high positive entropy values and the absence of major FT-IR spectral shifts, suggests an entropy-driven adsorption mechanism, likely involving a combination of electrostatic interactions, weak surface complexation, and partial desolvation of REE ions upon interaction with surface sites of BP.

Besides converting waste material into a valuable resource, in view of the possible scaling up of the process, the reusability of the sorbent material through multiple adsorption/desorption cycles was verified to enhance the overall sustainability of the process. Desorption experiments demonstrated successful biomass regeneration across four adsorption/desorption cycles, with a negligible performance contraction (~9 %). This is very significant since when planning an integrated protocol for the continuous recovery of valuable materials, both q_m values and reusability features must be taken into account. A combined environmental (LCA) and economic (TCA) assessment of the BP H₂O production revealed that, while lab-scale impacts are significant, scalability may lead to substantial improvements. In the optimized scenario (S3), GWP and CED were reduced by over 85 %, while production costs dropped below 2.99 €/kg. Further research is required to validate these findings on a pilot scale and to assess performance in real matrices.

These findings, integrated with desorption and reuse analysis and comprehensive environmental and techno-economic evaluations, provide a holistic perspective on the feasibility and sustainability of this approach, contributing valuable insights into eco-efficient strategies for the recovery of CRMs, such as Nd³⁺, La³⁺ and Dy³⁺, ranking bergamot pomace as a promising sustainable resource.

CRedit authorship contribution statement

Salvatore Giovanni Michele Raccuia: Writing – original draft, Resources, Methodology, Investigation, Formal analysis. **Emanuele Zanda:** Writing – original draft, Validation, Methodology, Formal analysis, Data curation. **Clemente Bretti:** Validation, Resources, Methodology, Formal analysis, Data curation. **Mauro Formica:** Writing – original draft, Visualization, Methodology, Formal analysis, Data curation. **Eleonora Macedi:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Andrea Melchior:** Writing – original draft, Resources, Methodology, Formal analysis, Data curation. **Marilena Tolazzi:** Writing – original draft, Validation, Methodology, Formal analysis, Data curation. **Alberto Pettignano:** Writing – original draft, Validation, Methodology, Formal analysis, Data curation. **Nicola Muratore:** Validation, Software, Resources, Investigation, Formal analysis. **Davide Lascari:** Software, Investigation, Formal analysis, Data curation. **Edoardo Teresi:** Methodology, Investigation, Formal analysis, Data curation. **Cristian Chiavetta:** Writing – original draft, Methodology, Investigation, Data curation. **Giovanna De Luca:** Writing – original draft, Visualization, Resources, Methodology, Conceptualization. **Anna Irto:** Writing – original draft, Validation, Methodology, Formal analysis, Data curation, Conceptualization. **Concetta De Stefano:** Visualization, Validation, Software, Resources, Conceptualization. **Paola Cardiano:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Funding acquisition, Conceptualization. **Gabriele Lando:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

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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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jiec.2025.09.008>.

Data availability

Data will be made available on request.

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