Synthesis and Enhanced Capture Properties of a New BioMOF@SWCNT-BP: Recovery of the Endangered Rare-Earth Elements from Aqueous Systems

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1. Introduction

The enormous appetite for resources of modern society[1] (energy, food, and raw materials) is putting under pressure the planet and it is the cause of, at least, half of greenhouse gas emissions and the almost totality of biodiversity loss, together with water stress. The best practices of a circular economy should be applied as necessary condition to reach climate neutrality by 2050, joined with a judicious resource use within planetary boundaries.[2]

In the last years, the demand for raw materials such as rare-earth elements (REEs) has experienced an exponential increase due to their essential uses in circuits of current technology. The extensive use of high-tech devices in our daily life and the consequent reduction of their primary elements make, among others, REEs recovery from secondary sources highly required. For that reason, REEs are attracting attention to legislators and scientists to develop innovative recovery technologies, for sustainable supply of raw materials. The EU 2020 has listed critical...
raw materials on the basis of their economic importance and supply risk, which are the two main parameters used to determine criticality.[3] REEs, divided into light rare-earth and heavy rare-earth elements, appear already among endangered raw materials. Furthermore, REEs, from non-recycled waste materials, are potential pollutants for surface waters. Nevertheless, the recovery of REEs from industrial waste water streams is still highly challenging, due to their very low concentrations. It requires sophisticated and not economically favored processes, requiring several steps, for the efficient recovery of REEs when present in traces.[4–7] Despite the limitations described above, literature reports some examples of REEs recovery.[6,8,9] In this scenario, it is clear that the development of novel, simpler, and less-costly methods for the separation of REEs is highly important from an industrial point of view. After the pretreatment steps for REEs recycling from e-waste, several methods, based on liquid–liquid extraction, ion exchange, adsorption, or chemical precipitation, have been tested to separate REEs.[10] Among them, adsorption methods emerged, and started to show they can be game changers, thanks to high efficiency and wide-ranging applicability. In this context, metal–organic frameworks (MOFs),[11–13] which are porous materials known for a great potential in separation, are demonstrating their high potentiality even in lanthanide separation.[14–17] Water-stable MOFs offer tunable microporosity and the possibility to tailor their channels with the appropriate functionalities to improve affinity for target elements, even in a selective manner.[18–20] Several works related to MOFs and MOF-based materials have been reported for the recovery of lanthanides.[16,17] However, they exhibit important disadvantages such as difficult handling or leaks of fillers, that compromise any industrial process.

Carbon nanotubes (CNTs) are unique nano-structured porous materials with remarkable electronic and mechanical properties. They are proven as promising candidates for a wide range of environmental applications.[21] Free standing or mixed matrix CNTs membranes have shown a great potential in breaking the trade-off between membrane flux and selectivity, while featuring antifouling properties.[22] More recently, buckypapers (BPs) have been proposed as innovative filtration systems alternative to polymer membranes thanks to their lightweight, high-temperature, and chemical resistance.[23–29] They are entangled assembly of CNTs obtained as the result of filtration of CNT (both single-walled CNTs and multiwalled CNTs) dispersions.[30,31] BPs merge the characteristic properties of polymer membranes such as porosity, flexibility, self-standing, and permeation with those of CNTs such as thermal features, mechanical resistance, and enhanced electric characteristics.[12,33] The morphology of BP membranes is characterized by the presence of a porous and highly disordered structure formed by bundles of CNTs interacting via π–π and van der Waals interactions.[34,35]

2. Results and Discussion

In this context, with the aim to make a step forward on MOF-based technologies for element recovery and water remediation, we present a novel, flexible, and self-standing MOF-based single-walled carbon nanotube buckypaper[33,36] (BioMOF@SWCNT-BPs) as a new and highly performant material in REEs recovery (Figure 1). The highly crystalline bioMOF, previously reported by us[17] and prepared from the natural amino acid L-threonine, has been homogeneously dispersed within a thin (150 µm) membrane, made with an entangled CNT network and produced by multiple steps of dispersion and filtration for lanthanide recovery from water. Among the different MOF subfamilies, bioMOFs,[37,38] constructed using biomolecule derivatives as building blocks and often affording water stable materials, emerge as valuable systems to study the capture properties and application in water remediation, either for their chemical functionalization or for being eco-friendly porous materials.[37,39] The presence of such MOF with formula \( \text{Sr}^{2+}\text{Cu}^{2+}([S,S]-\text{threonine})_{\text{z}}(\text{OH})_{\text{z}}(\text{H}_{2}\text{O})_{\text{z}} \cdot 36\text{H}_{2}\text{O} \) BioMOF (where threomox = bis([S]-threonine)oxalyl diamide)[37] featuring hexagonal functional channels decorated with the \( –\text{CH(OH)} \) \( \text{CH}_{3} \) amino acid residues, which point toward the accessible void spaces, unambiguously boosted the capture properties of the final BP membrane, providing the appropriate adaptable functional environment to interact with lanthanides (Figure 2).

Figure 1. a) Graphical idea of the filtration process to recover REEs by means of a BioMOF@SWCNT-BP membrane in low ion concentration regimes. b) Details of the interaction sites between cerium and functional groups decorating MOF channels and sections of SWCNTs.
As a consequence, BioMOF@SWCNT-BP membrane, exploiting the well-known affinity of O atoms for lanthanides, was capable to adsorb, to a certain degree, CeCl$_3$ and equimolar mixtures of lanthanide chlorides from model solutions.

Recently, a number of carbon-based nanomaterials have been applied in adsorption processes for this purpose.\cite{23,26,40,41} Literature shows the studies of the recovery of REEs also using CNTs composites; but SWCNT-based membranes have been only barely explored.\cite{40,42} Up to date, the material with the highest maximum adsorption capacity of REEs reported in the literature is an imprinted chitosan/CNT composite, which exhibits a maximum theoretical recovery of 121.51 mg g$^{-1}$.\cite{43}

Most studies on CNT composites have mainly focused, so far, on sorption experiments using CNTs with several functionalizations which improves their efficiency but increase the number of steps required for their recovery and re-use.\cite{23,24} To the best of our knowledge, no MOF-based SWCNT-BP have been reported so far for the recovery of metal species from water. Herein, we present a green material with potential application in the recovery of lanthanides present in small quantities, for low chemical consuming technologies. This material’s preparation presents also a potential for large-scale application. After an initial study on a mono-elemental system with cerium as target ion, investigated both in static and dynamic adsorption regime with both SWCNT-BP and MOF@SWCNT-BP composites, we focused on REE recovery study in a multi-elemental system under dynamic conditions.\cite{44,45}

In this work, we show that the integration of a suitable MOF in a BP, with a specifically designed morphology, yields a membrane that combines the superior capture properties of the MOF, boosting the intrinsic assets of SWCNT-based membrane with improved applicability. The main scope of this work is, indeed, to define, for the first time, a viable protocol to immobilize task-specific MOFs, with a high potential for capturing metal ions, which is related to the high affinity of oxygen atoms toward lanthanides onto a porous and robust support which allows easy manipulation and operability. This particular MOFs, for instance, due to their extremely hydrophilic properties and the presence of functional groups containing oxygen atoms, has already demonstrated its capability as receptor toward lanthanides and great affinity, underpinned by X-ray crystallography, for Cerium$^{3+}$ (Figure 3).\cite{17}

In this work, the MOFs has been homogenously dispersed in a highly robust support as a BP for a successful approach to a stable and handy composite, which guarantees high-water fluxes, that is, productivity, and an efficient separation process, that is, purity of the final products.

Polycrystalline samples of MOF (Figure 2) have been prepared even in multigram scale and characterized as previously reported (see Experimental Section in Supporting Information). A polycrystalline sample of the MOF, with particle dimensions averaging 0.1 µm, was embedded in a SWCNT BP by dispersing in an optimized CNT water solution of SWCNTs and carboxylic acid functionalized SWNTs (COOH-SWCNTs) using

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**Figure 2.** Perspective view of the 3D open-framework of BioMOF along the c axis. Cu and Sr atoms are represented by cyan and blue spheres, respectively, whereas the ligands are depicted as sticks. The oxygen atoms from the L-threonine residues are represented as red spheres. Hydrogen atoms and the crystallization water molecules are omitted for clarity.

**Figure 3.** Host–guest interactions at the origin of cerium-MOF affinity previously unveiled by X-ray crystallography: a) Perspective views along the crystallographic c axis of a single pore in the CeCl$_3$@MOF crystal structure.\cite{17} b) Details of the Ce···O interaction. Spheres: copper–cyan; calcium–blue; cerium–yellow; oxygen–red; carbon from methyl groups–grey. Sticks: Carbon, nitrogen, and oxygen atoms from the ligand. Free water solvent molecules are omitted for clarity.
an ultrasonic bath. Then, the solution was filtered through the PTFE disks with a vacuum pump, washed several times with methanol and, finally, dried at room temperature yielding a novel mixed membrane named BioMOF@SWCNT-BP (Figure 4b). The detailed procedure is given in the Supporting Information.

TGA analysis assessed the thermal stability of both SWCNT-BPs and BioMOF@SWCNT-BPs. The TGA curves demonstrate that the presence of MOF in BP membrane does not significantly influence the pattern of the neat BP decomposition, showing only slight changes (Figure S1, Supporting Information). The most appreciable variation is probably related to the hydrophilic nature of the MOF and thus to its water content, which is reflected in a weight loss in the temperature range of 50–450 °C for BioMOF@SWCNT-BP. Above 450 °C, there is ≈50% mass loss for both BioMOF@SWCNT-BP and neat SWCNT-BP membrane, which accounts for the partial decomposition of BP (Figure S1, Supporting Information).

As reported in the Experimental Section in Supporting Information several factors influence the integrity and self-standing properties of SWCNT-BP and BioMOF@SWCNT-BP membranes including, in particular, the SWCNT mixture composition (amount of SWCNTs and COOH-SWCNTs) and the percentage of BioMOF loading. After several trials, self-sustaining SWCNT-BPs and BioMOF@SWCNT-BPs were obtained with the weight ratio SWCNT:COOH-SWCNT = 1:2 and 25 wt% of BioMOF.

Figure 4a,b shows SWCNT-BP and BioMOF@SWCNT-BP membranes obtained under the abovementioned optimal conditions. Such circular membranes are characterized by an average thickness of 150 ± 5 μm and an active average diameter of either 41 ± 1 or 37 ± 1 mm (average mass of the disks 40 ± 2 mg) accordingly if they were used in static or dynamic experiments. Both membranes show similar density and porosity values (around 0.60 ± 0.03 g cm⁻³ and 70 ± 5%, respectively).

The morphology of SWCNT-BP and BioMOF@SWCNT-BP membranes was assessed by scanning electron microscopy (SEM). Figure 4c shows the typical microscopic texture of a SWCNT-BP, characterized by bundles and clusters of SWCNTs arising from π-π and van der Waals interactions. The addition of the bioMOFs in SWCNT-BPs is evidenced in Figure 4d by the presence of small spherical aggregates with an average size lower than 1 μm and formed by smaller primary particles with an average diameter of about 0.1 μm. The highly porous and outstanding stable structure of SWCNT-BPs, firmly hosting the nanosized BioMOF particles (no leakage was observed at the end of both static and dynamic experiments), guarantees a high permeability and a large surface area for the contact and successive adsorption of lanthanides present in the test solutions.

Given the high efficiency of MOFs in cerium capture previously demonstrated in their powder form,[17] we started to evaluate the capture properties of BioMOF@SWCNT-BP and compare them with those of the neat SWCNT-BP membrane by experimental set-up reported in Figure 5. The study of the Ce⁺ capture efficiency of both neat SWCNT-BP and BioMOF@SWCNT-BP membranes has been performed by static adsorption in batch (Figure 5a) and dynamic adsorption during permeation, adapting a microfiltration round test cell (Figure 5b, flow rate = 5 mL min⁻¹, feed pressure = 3 bar). In the last case, solutions containing the target ion have been allowed to recirculate through the neat SWCNT-BP and BioMOF@SWCNT-BP membrane, using a peristaltic pump.
In our initial screening, performed under static conditions and different pH values (5, 6, and 8), we found that the pH did not affect in a remarkable way the binding performance, as hydroxyl (of bioMOF) and carboxylic acid groups (of SWCNT) are protonated and deprotonated, respectively, in the whole pH range studied. The Ce$^{3+}$ capture by a SWCNT-BP or a BioMOF@SWCNT-BP disk (diameter 41 mm) during soaking in aqueous solutions of 3.5 ppm Ce$^{3+}$ (volume 80 ml) at different pH values (5, 6, and 8) in the 0–24 h interval is reported in Figure 6 and Tables S1 and S2, Supporting Information. As it is evident from the time behavior of the Ce$^{3+}$ adsorption static experiments, there is no particular difference among the tested pH conditions for both used membranes: SWCNT-BPs and BioMOF@SWCNT-BPs are able to reduce the initial 3.5 ppm Ce$^{3+}$ concentration to values lower than 20 ppb in 1000 min and to around 0 ppb in 1400 min. A slightly faster adsorption can be noticed by a BioMOF@SWCNT-BP at pH 5, and, consequently, we set the pH value of our solutions for the successive tests under dynamic conditions at 5, which unveiled the best capture properties. In addition, there is no evidence that the presence of MOFs within the BP membranes could meaningfully increase the removal efficiency of the neat SWCNT-BP membranes at all tested pH values.

In the experiments under dynamic conditions two different solutions were used: a Ce$^{3+}$ aqueous solution at different concentrations (1.35, 3, 10, 30, and 50 ppm) in order to unveil if MOFs could enhance capture capacity of the composite material versus the neat SWCNT-BP and a multi-elements solution (REEs standard solution containing Sc$^{3+}$, Y$^{3+}$, La$^{3+}$, Ce$^{3+}$, Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$, Tm$^{3+}$, Yb$^{3+}$, and Lu$^{3+}$ ions, total concentration 13.4 ppm around 835 ppb for each element) to assess eventually the presence of a selective recovery of REEs by a SWCNT-BP or a BioMOF@SWCNT-BP. Solutions were recirculated in a small continuous plant and the residual concentration values were monitored through ICP-MS analysis, which allowed to follow the adsorption as a function of time.

Under dynamic experiments and at lower Ce$^{3+}$ concentrations (1.35 and 3 ppm), no difference was observed in the adsorption rates of both SWCNT-BP and BioMOF@SWCNT-BP.
The initial lanthanide concentrations fall to less than 10 ppb in 1400 min and to about 0 ppb in 4320 min. No difference in the adsorption rates between a net SWCNT-BP and a BioMOF@SWCNT-BP is again evident.

For larger Ce\(^{3+}\) concentrations (10, 30, and 50 ppm) a different behavior is observed in the recovery efficiency by a neat SWCNT-BP and a BioMOF@SWCNT-BP is again evident.

(Figure 7a,b and Table S3, Supporting Information). The initial lanthanide concentrations fall to less than 10 ppb in 1400 min and to about 0 ppb in 4320 min. No difference in the adsorption rates between a net SWCNT-BP and a BioMOF@SWCNT-BP is evident.

(Figure 7c–e and Tables S4 and S5, Supporting Information). SWCNT-BPs show a higher plateau after 72 h in the final Ce\(^{3+}\) concentration (3 ppb, 3.79, and 23.64 ppm) than that shown by BioMOF@SWCNT-BPs in similar conditions (≈ 0 ppb, 1.91, and 20.78 ppm, respectively). The recovery efficiencies at 10, 30, and 50 ppm by SWCNT-BPs were, respectively, 99.97%, 87.72%, and 53.77% (calculated uncertainties of ±2%) while the corresponding BioMOF@SWCNT-BP efficiencies were ≈100%, 93.92%, and 59.94%. In order to be sure that the setup did not absorb cerium, Ce\(^{3+}\) solutions were recirculated through the cell used in dynamic adsorption conditions without any membrane. There was no meaningful drop in Ce\(^{3+}\) concentrations during all test procedures, confirming that there was no considerable Ce\(^{3+}\) adsorption by the tubes, pump, or other parts of the experimental setup. These results clearly situate the BioMOF@SWCNT-BP as a potential material for Ce\(^{3+}\) capture from water streams. Dynamic experiments using a solution of [Ce\(^{3+}\)] = 50 ppm, recirculating for a week, showed that SWCNT-BP and BioMOF@SWCNT-BP exhibit a maximum adsorption capacity of about 157 and 263 mg g\(^{-1}\), respectively, which is an adsorption value twice larger than that shown by current most performing carbon-based membranes (chitosan-CNT composite with a maximum theoretical and measured recovery of 121.51 and 88 mg g\(^{-1}\), respectively, at 303.15 K).[43] The perfectly synergistic action of threonine arms of the MOF and the −COOH groups of the functionalized SWCNTs added

![Figure 7. Effect of initial concentrations on the Ce\(^{3+}\) capture by SWCNT-BP and BioMOF@SWCNT-BP disks (diameter 37 mm) under dynamic experimental conditions for solutions with a Ce\(^{3+}\) concentration of: a) 1.35 ppm, b) 3 ppm, c) 10 ppm, d) 30 ppm, and e) 50 ppm. The solid lines in the figures are guides for the eye. The experiments were carried out in triplicate.](image)
to not-functionalized SWCNTs in the preparation of SWCNT-BP, outperform the state-of-the-art giving the best performant material for adsorption of REEs. These results not only prove the validity of our approach, but also allow producing a new robust and efficient composite of potential application in the real-world of membranes. Thus, the obtained recovery efficiencies shown by BioMOF@SWCNT-BPs under different Ce$^{3+}$ concentrations demonstrate the suitability of these membranes for the recovery of cerium from water. The maximum recovery capacity reaches 263 mg g$^{-1}$ thanks to the higher surface area of BioMOFs added in SWCNT-BPs, which contributes with a further recovery after the initial adsorption on SWCNT membrane.

Overall, even if, at lower Ce concentrations no significant differences can be observed between SWCNT-BP and BioMOF@SWCNT-BP membranes, BioMOF@SWCNT-BP outperforms SWCNT-BP at higher Ce$^{3+}$ concentrations, which is most likely due to its larger adsorption capacity, that has special relevance when adsorption sites of SWCNT bundles are saturated.

Aiming at evaluating the efficiency of these two novel materials in the neat adsorption of lanthanides, an equimolar multi-element standard solution of ScCl$_3$, YCl$_3$, LaCl$_3$, CeCl$_3$, PrCl$_3$, NdCl$_3$, SmCl$_3$, EuCl$_3$, GdCl$_3$, TbCl$_3$, DyCl$_3$, HoCl$_3$, ErCl$_3$, TmCl$_3$, YbCl$_3$, and LuCl$_3$ when using an equimolar standard solution—is/are almost totally recovered by both SWCNT-BP and a BioMOF@SWCNT-BP membranes, confirming the suitability of both neat BP and MOF-loaded BP for the recovery of lanthanides from water by a simple recirculation through the same membrane for less than one day. In addition, it is evident the fundamental role of the MOFs in the increase of lanthanides recovery.

Anyway, a further prove of the cooperative mechanism of capture can be inferred by SEM coupled with energy dispersive X-ray (EDX) measurements carried out for SWCNT-BP and BioMOF@SWCNT-BP after the recovery of CeCl$_3$ (Figure S6, Supporting Information). The EDX color mapping images of the two membranes after their use show a homogeneous distribution of red dots in SWCNT-BP membrane arising from the Ce(III) adsorption, while in BioMOF@SWCNT-BP the BioMOF particles (green dots) are close together and overlapping in some cases to red dots from cerium. Such results suggest that cerium atoms are linked to the alcohol groups of threonine, as previously unveiled by X-ray crystallography,[47] confirming the relevant role of MOFs in the capture properties of the final composite and that such a mechanism is still operating when MOFs are within the SWCNT-BP membrane.

The stability of the membrane for a potential regeneration process was also evaluated, in order to test their potentiality in industrial applications. In that perspective, the development of extremely efficient, reusable, and selective sorbents is needed.[46]

It is known that both SWCNT-BP[33] and BioMOF in polymer matrices[47] are stable after regeneration processes showing integrity and reusability over several successive cycles of adsorption and regeneration. Such properties were also confirmed for BioMOF@SWCNT-BPs, which were reused thrice after regeneration in 250 mL ethanol for the release of adsorbed lanthanides. Both SWCNT-BP and BioMOF@SWCNT-BP membranes showed still significant efficiency recovery after each regeneration process, losing less than 5% of the original adsorption capacities and confirming the suitability of such BPs in industrial applications (data in Table S14, Supporting Information).

Finally, experiments evaluating the selectivity of SWCNT-BP and BioMOF@SWCNT-BP membranes toward competing ions such as Fe$^{3+}$ and Al$^{3+}$, as well as the kinetic profile of these processes, were designed and carried out in duplicate. Membranes of 3.7 cm as diameter were soaked in 10 ppm aqueous solutions of CeCl$_3$, containing also 10 ppm of other salts usually competing in water such as FeCl$_3$ and AlCl$_3$, respectively.
during 72 h at pH = 5. ICP-MS analyses indicated that the cerium salt was adsorbed by SWCNT-BP and BioMOF@SWCNT-BP with a modest selectivity toward Fe(III) (Figure 8 and Table S15, Supporting Information). Results indicate two main features, the first is that, for both SWCNT-BP and BioMOF@SWCNT-BP membranes, the Al(III) is the most competing ion and Ce(III) moderately separated from Fe(III) at low concentrations. The second one is related to different degree of selectivity; while BioMOF@SWCNT-BP confirms its better adsorption capacity with respect to SWCNT-BP membrane (Figure 8), it is scarcely performant in terms of selectivity, being able to recover Ce(III) versus Fe(III) in somewhat degree, but failing when compared with Al(III), which is captured almost efficiently as Ce(III). Despite the extraordinary affinity of Fe(III) and Al(III) for oxygen atoms, these preliminary results show a sufficient selectivity at least versus iron(III) metal ion. The kinetic profiles suggest also some insights about possible mechanisms implied, which is most likely indicative of a fast adsorption of first row transition metal ions by −COOH chemical functionalization of CNT, leaving MOF’s threonine moieties for further uptake of lanthanide ions. The interaction of lanthanide ions with the carboxylate functional groups decorating the surface of the SWCNT-BP is likely to be the kinetically favored step. These hard acid−hard base interactions mainly driven by Coulombic forces[48] can be easily established between the lanthanide ions and the freely exposed carboxylate groups. On the contrary, the adsorption within the BioMOF structure most likely encompasses a surface adsorption/diffusion step within the porous network, followed by the establishment of interactions between the Ce(III) cations and both the OH− groups from the threonine residue and a carboxylate oxygen atom from the exomate network, as already proven by crystal structure determination.[49] Experimental results (see Figure 7) suggest that the first mechanism predominates at low lanthanide concentration and in the very early stages of adsorption/filtration experiments, while the second one mainly contributes in improving the overall membrane performances observed at higher REEs concentration.

In order to characterize surface properties, hydrophilic, and hydrophobic characteristics of the given SWCNT-BP and BioMOF@SWCNT-BP membranes, contact angle have been determined by measuring the contact angle. The hydrophilic character of SWCNT-BP and BioMOF@SWCNT-BP top surfaces was confirmed, measurements gave average contact-angle values of 50.8° ± 0.5° and 51.5° ± 0.5°, respectively (Figures S7a and S7b, Supporting Information), highly desirable for water treatment membranes.[49]

3. Conclusions

In summary, in this paper the preparation, characterization, and potential applications of SWCNT-BPs and BioMOF@SWCNT-BPs in the recovery of REEs from model water solutions were reported. Flexible and self-standing BPs were obtained by simple filtration of SWCNT and BioMOF/SWCNT solutions and characterized by SEM, TGA, porosimetry, XRD, EDX, and contact angle measurements. The ability of SWCNT-BPs and BioMOF@SWCNT-BPs in recovering lanthanides from water solutions was investigated both in static and dynamic conditions as a function of pH values and initial lanthanide concentrations. These experiments showed that the adsorption is not influenced by pH of lanthanide solutions and BioMOFs in SWCNT-BPs play a beneficial role in the increase of Ce(III) recovery at higher concentrations thanks to the alcohol functionalities of threonine, decorating the MOF pores. We found a relative recovery percentage after a week recirculation in higher concentration (50 ppm of cerium) solutions—recirculating through the same membrane—with a 263.30 mg of cerium adsorbed per gram of BioMOF@SWCNT-BP.

Although this worthy result is achieved only after a large recirculation time, suggesting that binding to supported MOF is kinetically slow, it represents a good background to further improve the preparation of kinetically faster adsorbent materials. As previously stated, the interaction of lanthanide ions with the −COOH functional groups of the SWCNT-BP is likely to be the kinetically favored step, then followed by MOF uptake. The self-standing and re-use features with the possibility of an easy up-scale can make SWCNT-BPs and BioMOF@SWCNT-BPs an effective and cheap solution for the minimization of toxic pollutants from environment and waste and boost the recovery of rare elements such as lanthanides from water. The potential of BioMOF-containing BPs in recovery of REEs from water have been demonstrated for the first time. The overall behavior of here reported membranes presents some advantages but also weakness comparable to other ion-exchange materials such as resins, for which moderate selectivity was obtained as well, and further optimization of the resin preparation conditions is needed and expected to improve the final material performances.[50] However, herein, we have described a new and successful strategy for the preparation of a BP embedding a MOF carefully designed by us for a specific purpose. We showed an unprecedented BioMOF@SWCNT-BP built up with SWCNTs and a bioinspired MOF highly performing in the recovery of ions and possessing intrinsic chemical affinity for oxygen atoms. It outperforms the state-of-the-art representing the carbon-based material with the highest maximum adsorption capacity of REEs reported so far. The strategy reported is sustainable, effective, and cheap and can represent a viable solution to be extended to the whole recovery of REEs family from water streams. As indicated from EC, recovery technologies for critical raw materials are highly deliverable to boost the best practice of a circular economy. The potential of application of BioMOF@SWCNT-BPs on water streams, after the first steps of REEs recovery from e-waste, has been demonstrated here at lab-scale. Its performance is undoubtedly related to both the exquisite control of the threonine moieties decorating the MOF pores that are used, and the intrinsic affinity of SWCNTs for lanthanides. The performed dynamic capture experiments, rarely reported, bring this new composite material closer to a large-scale application. These last results represent a step forward toward the synergistic exploitation of MOFs and carbon-based materials, reporting one of the rare examples of MOF-carbon-based materials in applications dealing with recovery and environmental remediation.

4. Experimental Section

See Supporting Information for a detailed description of MOFs and membranes preparation, their characterization and capture experiments.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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metal–organic frameworks, nanotube membranes, rare-earth elements recovery, single-walled carbon nanotubes, water remediation

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