



Ion exchange capacity of synthetic zeolite L: a promising way for cerium recovery

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Abstract

The increasing rare earth elements' (REE) demand to meet the market request and the current political scenario show that it is essential to find good solutions to recover these elements from waste (both industrial and mining). Zeolites are microporous materials with high cation exchange capacity, up to now only little investigated for REE recycle. Here, we propose the use of NH_4^+ -exchanged zeolite L for Ce recovery from a very diluted solution (0.002 M), mimicking the Ce^{3+} concentration of the liquors deriving from the leaching of spent catalysts. The aim of this work is twofold: (i) to investigate the exploitability of zeolite L as cation exchanger in the Ce recovery; and (ii) to determine the best working conditions. The investigated process consists of a coupled cation exchange: (1) in the first exchange the NH_4^+ cations — present in the zeolite porosities — are exchanged with the Ce^{3+} ions in the solution; and (2) in the second experiment, the Ce^{3+} trapped into the zeolite is recovered through a further exchange with NH_4 . The best working conditions for Ce^{3+} exchange of NH_4 -zeolite L are: batch system, liquid/solid ratio equal to 90 mL/g and 180 mL/g, 24 h of contact at 25 °C. The resulting Ce adsorption capacity (q_t) is equal to ~25 mg/g and ~39 mg/g and the removal efficiency 100% and 77% for the two tested liquid/solid ratios, respectively. The kinetics was proved to be fast and consistent with industrial timing; no energy cost for temperature setting is required; and the acid pH (~4) of the solutions does not affect the zeolite structure stability and its exchange performance. It has been demonstrated that the zeolite framework is not affected by the exchange so that the same absorbent material can be employed many times.

Keywords Ce recovery · Zeolite L · Cation exchange · Waste recovery · Exchange kinetics

Introduction

Nowadays, the demand for rare earth elements (REE) is increasing due to their extensive use in many technological fields. However, the current political scenario — where REE are considered as strategic resources (Mancheri et al. 2019, Charalampides et al. 2015), the monopoly of only a few countries, the so-called *balance problem* between demand and natural abundance (Binnemans et al. 2018), and the need to limit the environmental costs of their mining (Haque et al. 2014, Suli et al. 2017), stress the necessity of a recycling policy of these elements. In terms of volumes, one of the most exploited REE is Ce (Charalampides et al. 2015, Binnemans et al. 2018), which is exploited in a huge number of devices such as NiMH batteries (Porvali et al. 2020), fluid catalytic cracking (FCC) catalysts (Innocenzi et al. 2015), redox support for three-way automotive catalysts and other metal catalysts (Gorte 2010), glass polishing and glass films

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(Borra et al. 2018) and fluorescent lamps (Tunsu et al. 2016, Yurramendi et al. 2019). These materials contain a variable amount of REEs; for example, Ce dioxide reaches 40–99 wt% in glass polishing waste (Meshram and Abhilash, 2020) — where Ce is the most abundant REE, being at least 65 wt% of the whole REE content (Binnemans et al. 2013) — and 5.3 wt% in automotive catalysts (Zhao et al. 2020), while in FCC Ce is 0.2–0.3 wt% (Meshram and Abhilash, 2020), only 10 wt% of the total REE amount (Binnemans et al. 2013). The liquors obtained by leaching these exhausted components can present Ce concentrations ranging from ~0.02 M for the leached solutions coming from the residual waste of exhausted automobile catalysts (Ilyas et al. 2021) to 0.002 M for FCC (Innocenzi et al. 2015). A strategy for the extraction of Ce from these acid solutions is mandatory for the efficient recycling of this metal. Different methods were already tested for REE recovery such as precipitation (double salt precipitation, oxalate precipitation, carbonate precipitation, hydroxide precipitation), solvent extraction (Meshram and Abhilash, 2020), adsorption (de Farias et al. 2021), or ion exchange (Royen & Fortkamp 2016). This last is usually applied using metal-organic frameworks (MOF) materials or resins; however, efficient recycling can be achieved using other porous materials such as zeolites.

Zeolites are microporous natural and synthetic materials characterized by: (i) porous open structures, which makes them good molecular sieves; (ii) ion exchange capacity; (iii) catalytic properties; (iv) adsorption capacity; and (v) reversible dehydration. Due to these properties, they can be exploited for energy storage purposes (Eroshenko et al. 2001, Soulard and Patarin, 2011, Krajnc et al. 2017, Confalonieri et al. 2018, Confalonieri et al. 2020), as agriculture amendments (Ramesh et al. 2011, Eroglu et al. 2017, Nakhli et al. 2017, Mendez-Arguello & Lira-Saldivar 2019), in medicine as drug delivery systems (Stylianou 2012, Bacakova et al. 2018), as scaffolds for organic molecules (Calzaferrri et al. 2003, Gigli et al. 2018, Fabbiani et al. 2021) for CO₂ adsorption (Hong et al. 2014, Coudert & Kohen 2017, de Aquino et al. 2020), in catalysis (Corma 2003, Čejka et al. 2010), etc.

Despite the promising ion exchange properties of zeolites, just a few preliminary works investigated their use for REEs recycling (Faghihian et al. 2005, Duploux 2016, Barros et al. 2019, Mosai et al. 2019) thus, their potential application to recover these elements from acid-leached liquors of industrial waste should be deeper explored.

In the present paper, we tested the efficiency of NH₄⁺-exchanged zeolite L (NH₄-L) in Ce recovery from acid solutions. Zeolite L was reported as a promising candidate, among various tested zeolites (FER and FAU), for REE recovery (Duploux 2016). A recent study by our group investigated the Ce exchange capacity of three different cationic forms of zeolite L and proved the efficacy of this

zeolite in exchanging Ce³⁺ from highly concentrated solutions (Confalonieri et al. 2021). The structural study gave new insight on the sites involved in the exchange and showed that after the Ce exchange, of the NH₄⁺ zeolite L, the Ce recovery from the porosities was complete.

For the above-mentioned reasons, in the present work a NH₄⁺-exchanged form of zeolite L, was chosen to test the effectiveness in exchanging Ce from a very diluted solution ([Ce³⁺] = 0.002 M), which mimics the concentration reported for residual liquor of FCC waste (Innocenzi et al. 2015). We experimented different liquid/solid (l/s) ratios while, to follow the requirements of a green process, the temperature was maintained at 25 °C. In fact, several tests performed at higher (but mild) temperature did not indicate improvements in the cation exchange process. In a second step, the extraction of Ce from the Ce-exchanged L zeolite is obtained through a reverse exchange in a NH₄⁺ solution. This final exchange is proposed to recover the Ce ions for further utilization by fully exploiting the reversibility of cation exchange in zeolites (Fig. 1).

This work is part of a wider project aimed at exploiting zeolite cation exchange properties to recover REE from waste, to move toward a green circular economy model. In fact, although some conventional adsorbents display high adsorption capacity, they have several limitations, including expensive production and difficult regeneration. Using zeolites for REE recovery will offer the possibility to exploit a material that can be recycled many times (probably for infinite cycles) and that does not need to be regenerated, since once the REE is recovered, the powder can be immediately reused.

We started by testing synthetic zeolites, since the use of pure materials allows a clearer understanding of the process occurring during the exchange and an easier following of the exchange kinetics. The further step of the project, to pursue a greener process, will be the exploitation of natural zeolites, this in fact will allow the use of cheap materials, without

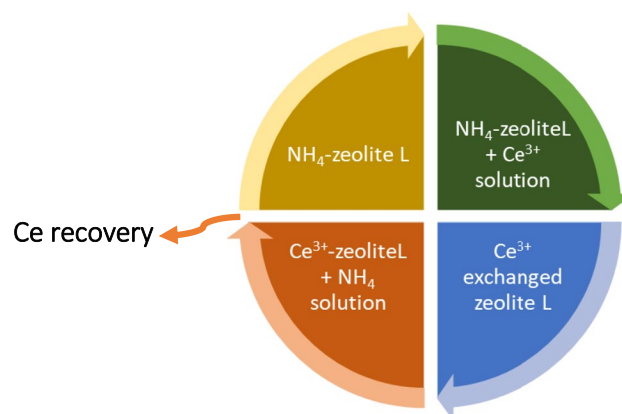


Fig. 1 Nutshell of the process

the need of a dedicated synthesis, allowing further energy saving. In addition, the use of an NH_4^+ solution for the first and final exchange will allow the use of the same solution for several exchange cycles, so to avoid waste of chemicals during the treatment stages.

Experimental section

Zeolite L

The synthetic zeolite L has formula $(\text{K}_6\text{Na}_3(\text{H}_2\text{O})_{21}\text{Al}_9\text{Si}_{27}\text{O}_{72})$, $a = 18.4 \text{ \AA}$ $c = 7.52 \text{ \AA}$, $\gamma = 120^\circ$ and LTL framework type (Baerlocher and McCusker, n.d.). This framework is composed by small cages and two mono-dimensional channels both running along the c axis of the unit cell: a channel built by connection of rings of 12 tetrahedra (12MR) and a smaller elliptical one delimited by rings of 8 tetrahedra (8MR). In the as-synthesized K form, cations occupy different crystallographic positions: two of them participate to the cation exchange — being hosted in the channels — whereas those hosted in the cages cannot be exchanged. The NH_4^+ exchanged form of synthetic K-L zeolite ($\text{NH}_4\text{-L}$ from now on), with chemical formula $\text{K}_{2.25}(\text{NH}_4)_{6.86}\text{Si}_{26.91}\text{Al}_{9.08}\text{O}_{72}\cdot 17.07(\text{H}_2\text{O})$, was fully characterized in Confalonieri et al. (2021). In the exchanged form, NH_4^+ ions substitute $\sim 75\%$ of the original K and are hosted just in the two channels (Fig. 2). NH_4^+ -exchanged form was chosen for this study since, once the Ce exchange will be obtained, the zeolite will be further NH_4^+ exchanged to recover Ce from the pores. In this way, the presence of NH_4^+ as unique exchangeable cation in the starting material will allow to obtain a final recovery solution

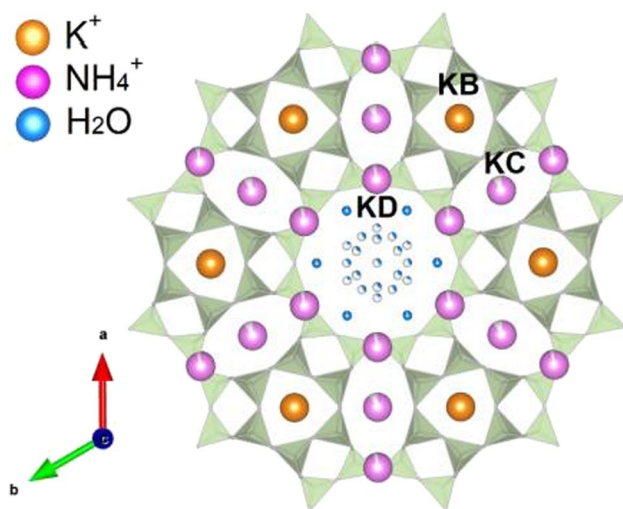


Fig. 2 Structure of NH_4^+ -exchanged zeolite L with chemical formula $\text{K}_{2.25}(\text{NH}_4)_{6.86}\text{Si}_{26.91}\text{Al}_{9.08}\text{O}_{72}\cdot 17.07(\text{H}_2\text{O})$. The extra framework species are drawn showing the fractional occupancy of their crystallographic sites (Confalonieri et al., 2021)

containing only NH_4^+ (easily removable and recyclable by evaporation) and Ce ions.

Ce exchange

A 0.002 M Ce^{3+} solution was prepared dissolving $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (Cerium(III) nitrate hexahydrate, REActon®, 99.5% (REO) — Alfa Aesar) into double-distilled water. $\text{NH}_4\text{-L}$ zeolite was put in contact for 72 h with the solution at 25°C under stirring. The pH was initially set to 4.3 using HNO_3 to avoid Ce compound precipitation and to mimic the acid conditions of a real industrial waste liquor. The stability of the zeolite framework at this pH condition was tested in order to exclude the possibility of a dealumination process or structural modifications. The pH of the solution was constantly monitored showing a maximum variation from 4.3 to 4.9 after 72 h of contact with the zeolite. No buffer solution was used to avoid competition in the zeolite ion exchange. Various experiments were performed using different liquid/solid ratios (30, 60, 90, 180, 290, 750 mL/g) and the same contact time of 72 h. Several tests were performed at higher temperatures (up to 80°C , data not reported), but, since they did not indicate improvements in the cation exchange process, we decided to work at room temperature. The exchanged samples were labelled Ce-X , where X is the liquid/solid ratio in mL/g. At the end of the process, all the exchanged zeolites were rinsed three times with double-distilled water using an ALC multi-speed centrifuge PK 121, operated at 5000 rpm for 10 min. The samples were finally dried at 60°C for 24 h.

Ce recovery

All the Ce-exchanged zeolites, obtained as described in the previous section, were contacted for 24 h under stirring, at room temperature, with a solution $[\text{NH}_4^+] = 0.8 \text{ M}$, prepared dissolving NH_4NO_3 (ammonium nitrate, 99%, Carlo Erba) in double-distilled water. The liquid/solid ratio was 60 mL/g; pH was not set. Zeolite samples so obtained are identified with the prefix *Rev*. At the end of the NH_4^+ -exchange, the powders were washed, dried following the procedure reported above, and analysed to check the Ce recovery.

Analytical methods

Inductively coupled plasma (ICP) analysis

The kinetic of Ce^{3+} exchange was monitored daily analysing the exchange solutions with ICP-OES technique. A small fraction of supernatants was withdrawn from the solutions, filtered by cellulose nitrate membrane ($0.45 \mu\text{m}$) and properly diluted. ICP analysis was performed using a Perkin Elmer Optima 4200 DV to measure the Ce content. Three

analyses were performed for each sample, and the initial solution with $[Ce^{3+}] = 0.002\text{ M}$ was also analysed and used as reference.

Thermogravimetric analysis (TG)

Seiko SSC/5200 thermal analyser was employed to perform thermogravimetric analysis. The temperature range was room temperature (r.t.) –1050 °C with a ramp of 10 °C/min under air flow.

Elemental analysis

Nitrogen content of zeolite samples was analysed through Flash 2000 CHNS/MAS200R instrument. “FLASH” dynamic combustion (modified Dumas method) allows to treat the sample at 1800 °C. Released elementary gases are separated through a chromatographic column and detected by a highly sensitive thermal conductivity (TCD) detector.

SEM-EDS analysis

Chemical analyses of the exchanged zeolites were performed by a scanning electron microscope (SEM) Nova NanoSEM 450 equipped with X-EDS Bruker QUANTAX-200 detector. Samples were prepared compressing the zeolite powders into thin self-supporting discs, then coated with gold. The instrument operated at 15 kV; five analyses for each sample were performed scanning the beam to avoid dehydration and cation migration in the zeolite. The obtained intensities were corrected using the phi-rho-Z method.

X-ray powder diffraction (XRPD)

Diffraction patterns of the original NH_4-L (Confalonieri et al. 2021), $Ce-90$, $Ce-180$, $Rev-Ce-90$, and $Rev-Ce-180$ were collected at ID22, high resolution beamline, of European Synchrotron Radiation Facility, Grenoble, using the new extremely brilliant source (EBS). Wavelength was set at 0.35426696 Å; diffraction intensities were recorded by an Eiger2 X CdTe 2M-W detector preceded by 13 Si(111) analyser crystals. Powder patterns were collected in Debye-Scherrer geometry.

Results and discussion

Ce exchange of NH_4-L

The results of elemental (Table S1) and SEM-EDS (Table S2) analyses of the exchanged zeolite are reported in the Supporting Information, while thermogravimetric curves

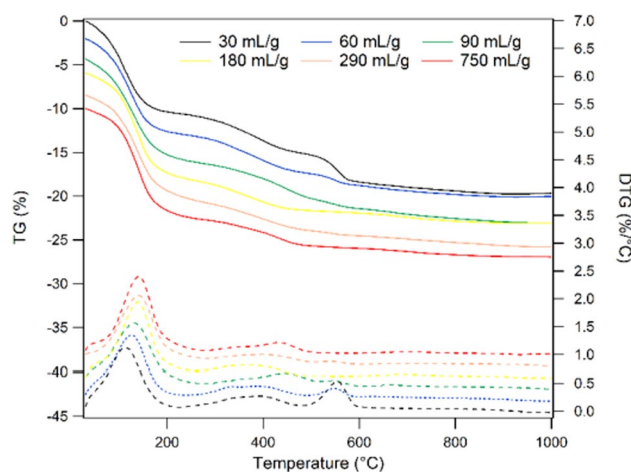


Fig. 3 TG (solid line) and DTG (dotted line) curves for zeolite samples exchanged with Ce. For a more readable figure, every TG curve is progressively shifted along the y axis of about –2%, while the corresponding DTG one is shifted progressively along the y axis of about 0.2%/°C.

Table 1 Chemical formula of Ce-exchanged NH_4-L zeolites calculated from EDS analysis with nitrogen and H_2O content determined by elemental and TG analysis, respectively. Error of the analyses is calculated as reported in Gottardi and Galli (1985), using the following formula: $Error\% = \frac{Al-K-NH_4-3Ce}{K+NH_4+3Ce} \cdot 100$

Sample	Chemical formula	Error (%)
NH_4-L	$K_{2.25}(NH_4)_{6.86}Si_{26.91}Al_{9.08}O_{72} \cdot 17.07 H_2O$	–0.3
$Ce-30$	$K_{2.15}NH_{4\ 6.30}Ce_{0.18}Si_{26.80}Al_{9.24}O_{72} 17.56 H_2O$	2.90
$Ce-60$	$K_{2.19}NH_{4\ 5.95}Ce_{0.37}Si_{26.77}Al_{9.21}O_{72} 17.71 H_2O$	–0.47
$Ce-90$	$K_{2.16}NH_{4\ 5.47}Ce_{0.55}Si_{26.79}Al_{9.15}O_{72} 18.90 H_2O$	–1.59
$Ce-180$	$K_{2.11}NH_{4\ 4.97}Ce_{0.87}Si_{26.67}Al_{9.19}O_{72} 19.92 H_2O$	–6.29
$Ce-290$	$K_{1.97}NH_{4\ 4.62}Ce_{0.93}Si_{26.70}Al_{9.26}O_{72} 20.00 H_2O$	–1.59
$Ce-750$	$K_{1.89}NH_{4\ 4.44}Ce_{0.97}Si_{26.69}Al_{9.30}O_{72} 20.09 H_2O$	0.82

and chemical formulas are shown in Fig. 3 and Table 1, respectively.

As evident in Table 1, the H_2O content increases with the Ce amount. This is because: (i) Ce^{3+} has a larger solvation sphere in comparison to NH_4^+ (~9.1 (Lutz et al. 2012) versus ~5.8 (Chang & Dang 2003) H_2O molecules in the first hydration shell, respectively); and (ii) due to the reduced number of cations (trivalent Ce vs monovalent cations), more space is available in the channel (Confalonieri et al. 2021). The weight loss imputable to H_2O corresponds to the first peak of the derivative thermogravimetric analysis — DTG — curves. From Fig. 3, it is possible to observe a

shift at higher temperature of this peaks as a function of the liquid/solid ratio used in the exchange. This is related to the increase of exchanged Ce with increasing liquid/solid ratio used. In fact, being the bonds between the H₂O molecules and Ce stronger with respect to those with ammonium ions, the H₂O molecules are released at higher temperature (Confalonieri et al. 2021). The weight losses above 300 °C are related to the NH₄⁺ loss. TG results suggest a slightly higher NH₄⁺ content for samples with low liquid/solid ratio, corresponding to a lower Ce exchange, in agreement with elemental analyses (Table S1).

The kinetics of the Ce³⁺ exchange was monitored every 24 h (Fig. 4; Table S3).

From ICP results (Fig. 4; Table S3), it appears that the Ce³⁺ concentration into the solution decreases for all the liquid/solid ratios tested, so confirming that NH₄-L zeolite extracts Ce³⁺ from the solutions. The exchange occurs mainly in the first 24 h (Fig. 4, bottom panel) and affects

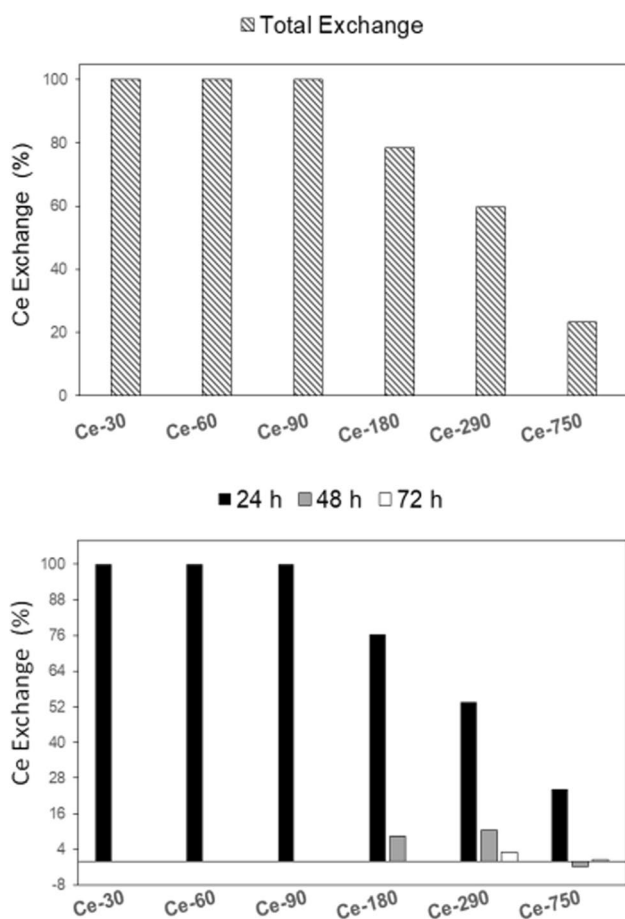


Fig. 4 Percentage of Ce withdrawn from the solution (i.e. exchanged) by the zeolite after 3 days of contact with the solutions at various liquid/solid ratios. The total percentage of exchanged Ce is reported in the top panel, while in the bottom one, the Ce percentage after 24, 48, and 72 h is shown. The anomalous behaviour of sample Ce-750 is explained in Table S3.

mainly the NH₄⁺ ions (Table 1). A slight decrease in the K content with respect to starting NH₄-L sample is observed (Table 1), indicating that some residual K can be further exchanged by Ce (see discussion below). The data after 72 h of contact is stable enough to be considered as equilibrium values (Table S3), and the experiments with different residual Ce³⁺ amounts in solution allow to establish an experimental Ce³⁺-NH₄⁺ exchange isotherm, as shown in Fig. 5. The experimental points are expressed as Az vs As, where Az = 3 Ce³⁺ / Al (molar) in the zeolite and As = C (Ce³⁺) / initial C (NH₄⁺) (equivalents) in solution. The isotherm can be fitted by a constant separation factor model $Az = (K As Az_{max}) / (1 + K As)$, in which $K = \alpha_B^A - 1$, where $\alpha_B^A = (Az / As) / (Bz / Bs)$ is the separation factor, in which Bz = NH₄⁺ / Al (molar) in the zeolite and Bs = C (NH₄⁺) / initial C (NH₄⁺) (equivalents) in the solution (LeVan et al. 1997) (Breck 1984). The value of the separation factor of the exchange of Ce for ammonium is 67, indicating a much higher affinity of NH₄-L for Ce than for ammonium. Such a value is not uncommon in the exchange of multivalent- monovalent cations in zeolites (Breck 1984). The isotherm reaches an asymptotic value of Az_{max} at 0.31. This corresponds to a clear limit of Ce content at ~1 Ce atom p.u.c. This value is very close to the 1.17 Ce p.u.c. reported for the NH₄-L using a highly concentrated Ce solution, which represents the maximum Ce adsorption in zeolite L and involves only sites positioned in the main channel (Confalonieri et al. 2021).

In conclusion, Ce cannot saturate all the anion sites of zeolite L; however, the aim of this work is not to obtain the complete cation exchange of the zeolite, but rather to define the best conditions to recover Ce from a very diluted liquor. In particular, we would like to: (1) obtain an efficient uptake

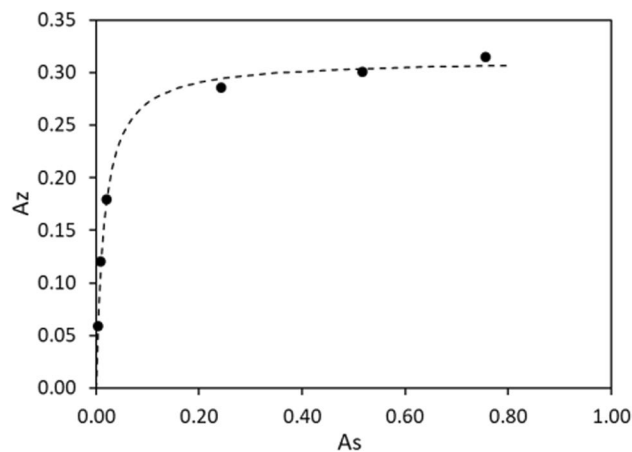


Fig. 5 Ce-NH₄ exchange isotherm in NH₄-L. The experimental points are expressed as Az vs As, where Az = 3 Ce³⁺ / Al (molar) in the zeolite and As = C (Ce³⁺) / initial C (NH₄⁺) (equivalents) in solution

of Ce, reducing at the minimum the Ce left in the solution and, in the meantime (2) achieve a high concentration of Ce in the zeolite to reduce the number of uptake-recovery cycles; and (3) prove that the same zeolite powder can be used many times to recover Ce from solutions. Among the tested systems, two demonstrated to be the most suitable for these purposes: *Ce-90* and *Ce-180*, showing an uptake of 100% and 77% of the Ce in the solution the first 24 h (Fig. 4; Table S3)

Ce recovery

The Ce recovery from the Ce exchanged zeolites was fulfilled through a further exchange with a NH_4^+ 0.8 M solution.

As reported in Table 2 (and in Tables S4 and S5), an almost complete release of Ce is obtained for all the samples.

Table 2 Ce oxide (wt%) in zeolite samples before and after NH_4^+ exchanges (i.e. after Ce recovery), from EDS analysis

Name	Ce ₂ O ₃ (wt%)	Name	Ce ₂ O ₃ (wt%)
<i>Ce-30</i>	1.35 (8)	<i>Rev-Ce-30</i>	0.16 (11)
<i>Ce-60</i>	2.71 (2)	<i>Rev-Ce-60</i>	0.15 (5)
<i>Ce-90</i>	3.95 (6)	<i>Rev-Ce-90</i>	0.35 (32)
<i>Ce-180</i>	6.20 (15)	<i>Rev-Ce-180</i>	0.29 (12)
<i>Ce-290</i>	6.55 (60)	<i>Rev-Ce-290</i>	0.23 (10)
<i>Ce-750</i>	6.83 (32)	<i>Rev-Ce-750</i>	0.20 (10)

The effectiveness of the final exchange is also shown by the nitrogen content, which recovers the original value of $\text{NH}_4\text{-L}$. To test the impact of these treatments on the zeolite structure and evaluate the possible reuse of the same zeolite powder in further cycles of Ce recovery, X ray powder diffraction patterns before and after the whole process were collected for the two most promising samples. In Fig. 6, the diffraction pattern of the original $\text{NH}_4\text{-L}$ (Confalonieri et al. 2021) is compared with that of samples *Ce-90* and *Ce-180* before and after the Ce recovery. The two samples containing Ce clearly show differences in the peak intensity ratios related to the incorporation of the REE in comparison to the original $\text{NH}_4\text{-L}$ (Fig. 6, left panel). These changes disappear completely after the second exchange with NH_4^+ solution (Fig. 6, right panel), demonstrating a complete recovery of Ce. Neither structure modifications nor loss of crystallinity was detected.

Comparison with other adsorbent materials

The adsorption capacity of the two most promising samples was calculated as in Zhao et al. (2019):

$$q_t = (C_0 - C_t)V/m$$

where C_0 and C_t are the initial concentration and the residual concentration (mg/L) of Ce in the solution; V is the volume of Ce^{3+} solution (L), and m is the weight of the zeolite (g).

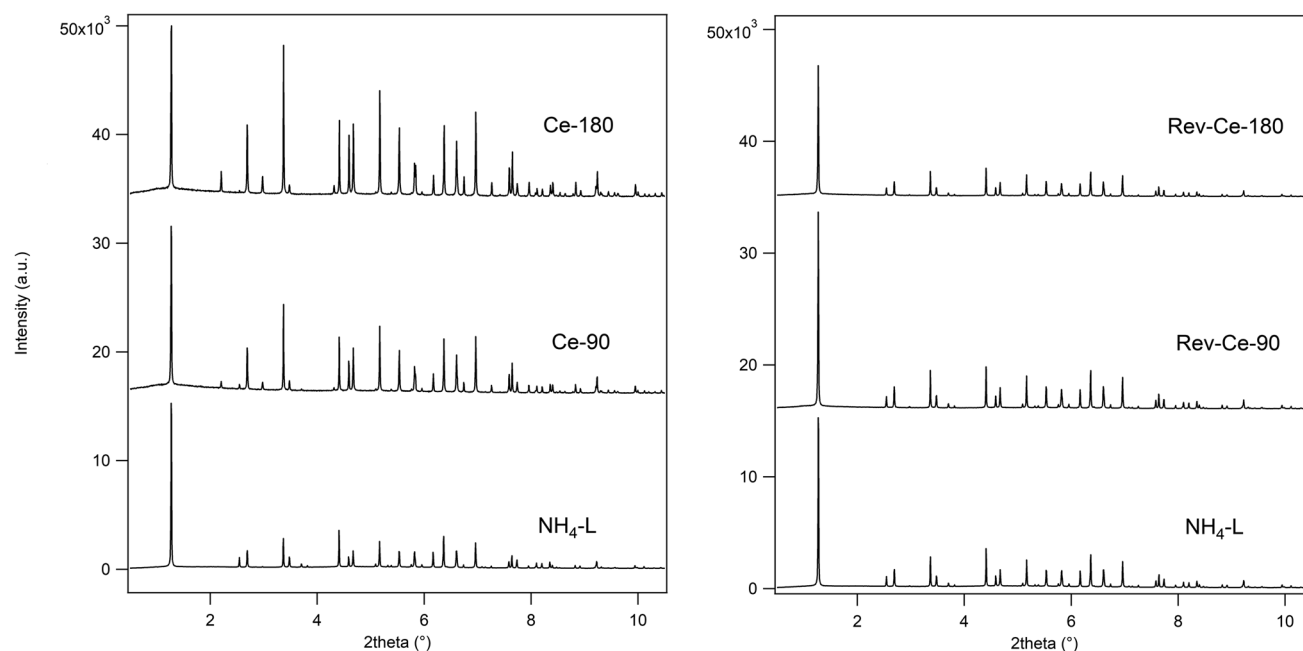


Fig. 6 Comparison between XRPD patterns of $\text{NH}_4\text{-L}$ (Confalonieri et al. 2021) and of the samples *Ce-90* and *Ce-80* before (left panel) and after (right panel) Ce recovery

Ce-90 and *Ce-180* show a Ce adsorption capacity (q_t) equal to ~ 25 mg/g and ~ 39 mg/g, respectively, for an initial Ce^{3+} concentration of 280 mg/L. Interesting evaluations can be made comparing the value calculated for *Ce-180* with those obtained for other materials in similar conditions, such as those described in the review by De Farias et al. (2021). Our sample displays higher adsorption capacity than some reported adsorbents such as poly- γ -glutamic acid crosslinked with polyvinyl alcohol (Gao et al. 2015), which was, by the way, studied at lower concentration (100 mg/L), cyanobacteria of the genus *Arthrospira* (Sadovsky et al. 2016), as well as for some treated olive pomace (Akbas and Yusan, 2020). Similar performances, instead, are obtained by a novel hybrid inorganic materials $\text{H}_n\text{PMo}_{12}\text{O}_{40}@\text{Fe(III)}_x\text{Sn(II)}_y\text{Sn(IV)}_{1-x-y}$ (Yousefi et al. 2015), only if compared in similar experimental conditions (temperature, 25 °C, pH, ~ 4 , while the concentration is lower, 100 mg/L). Differently, higher Ce adsorption capacity is shown by HKUST-1 metal-organic framework (MOF) (353 mg/g), but the subsequent process for REE recovery (methanol washing) is not able to completely remove the absorbed Ce^{3+} . A high value is also displayed by monolithic multi-porous carboxymethyl cellulose-g-poly (acrylamide)/attapulgite (205.48 mg/g), where the final Ce recovery was obtained using HCl solution, while the material was regenerated through NaOH solution with the need of neutralisation and formation of salt wastes (Wang et al. 2020).

Even if other materials showed adsorption capacity similar or higher than those shown by our systems (i.e. marine algae (Vijayaraghavan et al. 2010), polymers (Maruthapandi et al. 2020) (de Farias et al. 2021), the use of zeolites has many advantages and indicates them as potential interesting adsorbents to be exploited for a green recovery of REE. In fact, first of all, cationic zeolite syntheses are easy and do not require exotic and expensive organic chemicals to be realized. This work can, in addition, pave the way to the use of natural zeolites for REE recovery further improving the sustainability of the process.

Conclusions

NH_4^+ -exchanged zeolite L demonstrated to be a suitable candidate for Ce recovery from a diluted solution ($[\text{Ce}^{3+}] = 0.002$ M), which mimics the leached liquor from the residual waste of some industrial processes. Our work indicates that 100% of Ce can be already extracted in batch from the solution at room temperature, with a liquid/solid ratio of 90 mL/g and 24 h of contact between zeolite and solution. With a liquid/solid ratio of 180 mL/g, 77% Ce^{3+} in solution is drawn in 24 h and the zeolite approaches its maximum capacity, being ready for an effective counter-exchange cycle. In complete cycles of uptake and release of Ce, the counter-exchange of

NH_4^+ for Ce^{3+} allowed the complete Ce recovery. The kinetics of the process was proved to be fast and consistent with industrial timing; no energy cost for temperature setting is required; and acid conditions of the solutions do not affect the zeolite structure. Despite the $\text{NH}_4\text{-L}$ should be tested in a more complex system (i.e. with a multicomponent solution), which better simulates a leached liquor, the obtained results are very promising for future industrial applications. This work can pave the way for the use of zeolites as “green tools” to recover REE from liquor of different nature in a circular economy perspective.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11356-022-20429-1>.

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Author contribution All the authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Giorgia Confalonieri, Vittorio Gozzoli and Laura Maletti. The first draft of the manuscript was written by Giorgia Confalonieri, and all the authors commented on the previous versions of the manuscript. All the authors read and approved the final manuscript.

Data availability All the data are available in the supporting information file. Further data can be requested to the authors.

Declarations

Ethical approval Not applicable

Consent to participate Not applicable

Consent for publication All the authors agreed with the content and that all gave explicit consent to submit. They obtained consent from the responsible authorities at the institute/organization, where the work has been carried out.

Competing interests The authors declare no competing interests.

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