Ion Exchange Capacity of Synthetic Zeolite L: A Promising Way for Cerium Recovery

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Abstract

Due to the increasing demand for Rare Earth Elements (REE) and the current political scenario, it is essential to recover these elements from industrial or mining waste. Zeolites are microporous materials little investigated for REEs recycle. Here, we propose the use of NH_4^+ -exchanged synthetic zeolite L for cerium recovery from a solution mimicking the Ce^{3+} concentration of the liquors deriving from the recovery of spent catalysts (0.002 M). A NH_4^+ -exchanged sample was used since the presence of only ammonium as exchangeable cation in the zeolite porosities greatly simplifies the Ce recovery once the exchange is accomplished. The aim of this work is twofold, in fact we want to investigate the exploitability of zeolite L as cation exchanger in the Ce recovery and determine the best working conditions. The investigated process consists of a coupled cation exchange: 1) $\text{Ce}^{3+}(\text{solution}) + 3\text{NH}_4^+(\text{zeolite}) \leftrightarrow \text{Ce}^{3+}(\text{zeolite}) + 3\text{NH}_4^+(\text{solution})$. In the first exchange the NH_4^+ cations - present in the zeolite porosities- are exchanged with the Ce^{3+} of the solution and in the second experiment the Ce^{3+} trapped into the zeolite is recovered through a further exchange with the NH_4^+ of a rich solution. The best working conditions for Ce^{3+} exchange of $\text{NH}_4\text{-L}$ are: batch system, liquid/solid ratio equal to 90 mL/g and 180 mL/g, 24 h of contact at 25 °C. The resulting cerium 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. At these conditions, cerium of the solution was first incorporated into the zeolite porosities and then completely recovered. It has been demonstrated that the zeolite framework is not affected by the exchange so that the same absorbent can be employed many times.

1. 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 in the export of these materials, 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 and of their recovery from industrial and mining waste. In terms of volumes, one of the most exploited REE is cerium (Charalampides et al. 2015, Binnemans et al. 2018), which is employed 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-ways automotive catalysts and other metal catalysts (Gorte 2010), glass polishing and glass films (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, cerium dioxide reaches 40–99 wt % in glass polishing waste (Meshram & Abhilash 2020) -where cerium is the most abundant REE, being at least 65 wt % of the whole REEs content (Binnemans et al. 2013)- and 5.3 wt % in automotive catalysts

(Zhao et al. 2020), while in FCC cerium is 0.2-0.3 wt % (Meshram &Abhilash 2020), only 10 wt % of the total REEs amount (Binnemans et al. 2013). The liquors obtained by leaching these exhausted components can present, thus, different cerium concentrations, 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 REEs recovery such as precipitation (double salt precipitation, oxalate precipitation, carbonate precipitation, hydroxide precipitation), solvent extraction (Meshram &Abhilash 2020), adsorption (de Farias et al. 2021) or ion exchange (Royen &Fortkamp 2016). This last is usually applied using MOF or resin, however, efficient recycling can be achieved using other porous materials such as zeolites.

Zeolites are microporous natural and synthetic materials with various frameworks and pore systems and characterized by: i) open structures, which makes them good molecular sieves; ii) ion exchange capacity; iii) catalytic properties; iv) adsorption capacity; v) reversible dehydration. Due to these properties, they can be exploited for energy storage purposes (Eroshenko et al. 2001, Souldard &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 (Calzaferri et al. 2003, Gigli et al. 2018, Fabbiani et al. 2021) (in many technological applications, 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 a NH₄⁺- exchanged zeolite L (NH₄-L) in Ce recovery from acid solutions. Zeolite K-L was reported in a work of Duploux as a promising candidate, among various tested zeolites (FER and FAU), for REEs recovery (Duploux 2016). A recent study by our group investigated the Ce exchange capacity of three different cationic forms of zeolite L through chemical analyses and X Ray Powder Diffraction (XRPD) structural investigations (*i.e.* original as synthesized K⁺, and Na⁺ and NH₄⁺ exchanged forms) (Confalonieri et al. 2021) and proved the efficacy of this zeolite in exchanging Ce³⁺ from highly concentrated solutions. The structural study gave new insight on the sites involved in the exchange, and even if it demonstrated that cation exchange capacity for Ce is not influenced by the nature of the extraframework cations, showed that for the NH₄⁺ exchanged sample, the Ce recovery from zeolite porosities is complete.

For the above-mentioned reasons, in the present work, zeolite L, precisely NH₄⁺- exchanged form, was chosen to test the effectiveness in exchanging cerium 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, and 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 cations exchange process. This work aims to target the optimum experimental setting to remove Ce^{3+} from the solution, concentrating it inside the zeolite pores. In a second step, the extraction of cerium from the Ce-exchanged LTL is obtained through a reverse exchange in a NH_4^+ solution. This final exchange is proposed to recover the cerium ions for further utilization by fully exploiting the reversibility of cation exchange in zeolites (Figure 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 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.

2. Experimental Section

2.1. 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 & McCusker). This framework is composed by small cages (cancrinite 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, while 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 (Figure 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 cerium from inside the zeolite porosities. In this way, the presence of NH_4^+ as unique exchangeable cation in the starting material will allow to obtain a final

recovery solution containing only ammonium (easily removable and recyclable by evaporation) and cerium.

2.2. Cerium 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 cerium compound precipitation and to mimic the acid conditions of a real industrial waste liquor. The stability of the zeolite framework in 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 cations 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.

2.3. Cerium 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 cerium recovery.

2.4. 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 μm) and properly diluted. ICP analysis was performed using a Perkin Elmer Optima 4200 DV to measure the cerium content. Three analyses were performed for each sample and the initial solution with $[\text{Ce}^{3+}] = 0.002 \text{ M}$ 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 detected 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 15kV, five analyses for each sample were performed scanning the beam to avoid dehydration and cation migration in the zeolite and the 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 a13 Si(111) analyser crystals. Powder patterns were collected in Debye-Scherrer geometry.

3. Results And Discussion

3.1. Cerium exchange of NH_4 -L

The results of elemental (Table S1) and SEM-EDS (Table S2) analyses, performed on the exchanged zeolite samples are reported in the Supporting Information, while thermogravimetric analyses and chemical formulas are shown in Figure 3 and Table 1 respectively.

Table 1. Chemical formula of Ce-exchanged NH_4 -L zeolites calculated from EDS analysis with nitrogen and H₂O content determined by elemental and TG analysis, respectively. Error of the analyses is calculated as reported in (Gottardi &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 -LTL	$K_{2.25}(NH_4)_{6.86}Si_{26.91}Al_{9.08}O_{72} \cdot 17.07 H_2O$	-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

As evident in Table 1, the H₂O content increases with the cerium amount. This is because i) Ce³⁺ has a larger solvation sphere in comparison to NH₄⁺ (~ 9.1 (Lutz et al. 2012) *versus* ~5.8 (Chang & Dang 2003) H₂O molecules in the first hydration shell, respectively); ii) due to the reduced number of cations (trivalent Ce vs monovalent cations), in the samples with a higher amount of cerium more space is available in the main 12MR channel (Confalonieri et al. 2021). The weight loss imputable to H₂O (the first peak of the DTG curves (Figure 3) corresponds to 11.7 wt %, 11.7 wt %, 12.4 wt %, 12.8 wt %, 12.9 wt % and 12.9 for samples *Ce-30*, *Ce-60*, *Ce-90*, *Ce-180*, *Ce-290* and *Ce-750*, respectively. The shift at higher temperature of the first peak of DTG as a function of the liquid/solid ratio is related to the higher cerium content of the samples. 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 for each exchange experiment carried out (Figure 4 and Table S3).

From ICP results (Figure 4 and Table S3) it is clear 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 (Figure 4, bottom panel) and affects mainly the NH₄⁺ ions (Table 1). A slight decrease in the K content with respect to starting *NH₄-L* sample is observed (Table 1), showing 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, shown in Figure 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 cerium for ammonium is 67, indicating a much higher affinity of *NH₄-L* for cerium 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 cerium 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⁺-exchanged zeolite L using a highly concentrated cerium 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, cerium 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: 1) to obtain an efficient uptake of cerium, reducing at the minimum the cerium left in the solution and, in the meantime 2) to achieve a high concentration of Ce in the zeolite to reduce the number of uptake-recovery cycles; 3) to 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*, that show an exchange of the cerium from the solution equal to the 100% and 77% (Figure 4 and Table S3) in the first 24 h and incorporating in zeolite porosities 0.55 and 0.87 cerium ions p.u.c., respectively (Table 1).

3.2. Cerium recovery

The cerium recovery from the Ce exchanged zeolites was fulfilled through a further exchange with a NH_4^+ 0.8 M solution. The chemical composition of the zeolite samples recovered after the final NH_4^+ -exchange is reported in Table S4, while the comparison between Ce_2O_3 and N wt% present in the zeolite channels before and after the Ce recovery process (*i.e.* NH_4^+ exchange) is shown in Tables 2 and S5, respectively.

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

Name	Ce_2O_3 (wt %)	Name	Ce_2O_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)

An almost complete release of cerium is obtained for all the samples. The effectiveness of the final exchange is also shown by the nitrogen content (Table S5), which recovers the original value of $\text{NH}_4\text{-LTL}$. 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 Figure 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 cerium recovery. The two samples containing cerium clearly show differences in the peak intensity ratios related to the incorporation of the REE in comparison to the original $\text{NH}_4\text{-L}$ (Figure 6 left panel), structural modifications are described elsewhere (Confalonieri et al. 2021). These changes

disappear completely after the second exchange with NH_4^+ solution (Figure 6 right panel), demonstrating a complete recovery of cerium. Neither structure modifications nor loss of crystallinity was detected.

3.3 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), m is the weight of the zeolite (g).

Ce-90 and *Ce-180* show a cerium 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 & 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 cerium 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)/attapulgit (205,48 mg/g), where the final cerium recuperation 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), etc. (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, moreover, it could be considered that this work can pave the way to the use of natural zeolites (zeolitites) for REE recovery, and this will further improve the sustainability of the process. No energy cost for temperature setting is required and NH_4^+ solution can be recycled over different cycles. Zeolites proved to have high framework stability at low pH, compatible with the acidity of industrial leached liquor and this, along with their effectiveness in releasing all the exchanged cations, allows their use for several cycles.

4. Conclusions

NH_4^+ -exchanged zeolite L demonstrated to be a suitable candidate for cerium recovery from a diluted solution ($[\text{Ce}^{3+}] = 0.002 \text{ M}$), which mimics the leached liquor from the residual waste of some industrial processes. Our work indicates that 100% of cerium 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 exchanged in 24 h by NH_4^+ of the zeolite and the zeolite approaches its maximum capacity, being ready for an effective counter-exchange cycle. In complete cycles of uptake and release of cerium, the counter-exchange of NH_4^+ for Ce^{3+} allowed the complete cerium 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.

Declarations

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Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

All 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.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

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

Data and materials

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

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Figures

Figure 1

Nutshell of the process.

Figure 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 extraframework species are drawn showing the fractional occupancy of their crystallographic sites (Confalonieri et al. 2021).

Figure 3

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

Figure 4

Percentage of Ce withdrawn from the solution (*i.e.* exchanged) by the zeolite after three 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, 72 h is shown. The anomalous behaviour of sample Ce-750 is explained in Table S3.

Figure 5

Cerium-ammonium exchange isotherm in NH_4 -LTL. The experimental points are expressed as Az vs As, where Az = $3 \text{ Ce}^{3+} / \text{Al}$ (molar) in the zeolite and As = $C(\text{Ce}^{3+}) / \text{initial } C(\text{NH}_4^{+})$ (equivalents) in solution.

Figure 6

Comparison between XRPD patterns of NH_4 -L (Confalonieri et al. 2021) and of the samples *Ce-90* and *Ce-80* before (left panel) and after (right panel) cerium recovery.

Supplementary Files

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