1 **USE OF NATURAL CLAYS AS SORBENT MATERIALS FOR RARE**

2 **EARTH IONS: MATERIALS CHARACTERIZATION AND SET UP OF THE**

3 **OPERATIVE PARAMETERS**

4 Elena Maria Iannicelli-Zubiani[1*], Cinzia Cristiani[1], Giovanni Dotelli[1], Paola Gallo Stampino[1],

5 Renato Pelosato[1], Ernesto Mesto[2], Emanuela Schingaro[2], Maria Lacalamita[2]

6 [1] Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta",

7 Piazza Leonardo Da Vinci 32, 20133 Milano, Italy

8 [2] Università degli Studi di Bari "Aldo Moro", Dipartimento di Scienze della Terra e Geoambientali,

9 Via E. Orabona 4, 70125 Bari, Italy

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20 *Corresponding author:

21 Elena Maria Iannicelli Zubiani

22 Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta",

23 Piazza Leonardo Da Vinci 32, 20133 Milano, Italy

24 Phone: +390223993234

25 Fax: +390270638173

26 Email: elenamaria.iannicelli@polimi.it

Abstract

Two mineral clays of the montmorillonite group were tested as sorbents for the removal of Rare Earths (REs) from liquid solutions. Lanthanum and neodymium model solutions were used to perform uptake tests in order to: (a) verify the clays sorption capability, (b)to investigate the sorption mechanisms and (c)to optimize the experimental parameters, such as contact time and pH. The desorption was also studied, in order to evaluate the feasibility of REs recovery from waters. The adsorption-desorption procedure with the optimized parameters was also tested on a real wastewater obtained by dissolution of a dismantled NdFeB magnet of a hard-disk. The clays were fully characterized after REs adsorption and desorption by means of X-ray powder diffraction (XRPD) and X-ray photoelectron spectroscopy (XPS); the liquid phase was characterized via inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses. The experimental results show that both clays are able to capture and release La and Nd ions, with an ion exchange mechanism. The best efficiency (capture $\approx$ 50%, release $\approx$ 70%) is obtained when the uptake and release processes are performed at pH = 5 and pH = 1 respectively; in real leached scrap solutions, the uptake is around 40% but release efficiency is strongly decreased passing from a mono-ion system to a real system (from 80 to 5%). Furthermore, a strong matrix effect is found, with the matrix largely affecting both the uptake and the release of neodymium.

1. Introduction

Water is a key resource for industrial and manufacturing processes, but generated wastewater can cause environmental damage when discharged without any treatment (Luna et al., 2007). The increasing awareness about water preservation, revealed also by the high attention paid by EU Framework Programme for Research and Innovation research Horizon 2020 (Walsh et al., 2015), has resulted in stricter limits to contaminants concentrations in wastewater.

Industrial pollutants in water generally contain heavy metals (Goi et al., 2006) whose removal is compulsory but requires the application of processes that, although essential, are complex and expensive (see for instance the Italian emission limits in surface and sewage water in Supplementary materials).

The processes currently used for the removal of heavy metals from inorganic effluents (i.e. conventional chemical precipitation, ion exchange, electrochemical separation) have significant disadvantages: incomplete removal, high-energy requirements, production of toxic sludge (Barakat, 2011). Recently, numerous approaches have been explored to develop cheaper and more effective technologies in decreasing the amount of produced wastewater and improving the quality of the effluents. In particular, adsorption has become one of the alternative treatments (Rao et al., 2008), being a simple and potentially low cost process. Indeed, technical applicability and cost-effectiveness are the key factors in the selection of the treatment technology (Nurchi and Villaescusa, 2012). One of the open points regarding the use of adsorption technology is related to the kind of solid matrix used. Extraction resins combine the advantages of high selectivity, typical of solvent extraction, with high efficiency typical of chromatographic separation. In addition, they are characterized by large surface area, require minimal use of organic solvents (and thus are environmentally friendly) and phase separation phenomena do not occur (Soylak and Yilmaz, 2010). Nanostructured materials such as nanotubes are advantageous for their large specific surface area, excellent mechanical strength, and high chemical stability (Addo Ntim and Mitra, 2012). However, in both materials, the high costs and issues about the global sustainability of the process push towards the investigation of alternative solid sorbents. In this respect, the use of natural materials as sorbents gained a significant interest in the last years, mainly thanks to the high selectivity demonstrated for certain heavy metal ions, the low cost and the characteristic of being intrinsically environmentally friendly themselves (Kyzas et al., 2015). In the above scenario, clays have been suggested as a green alternative, having low cost, good mechanical properties, good tolerance towards harsh chemical environment, convenient solid-liquid separation and excellent

reusability. Furthermore, clay minerals show a well-known adsorption behaviour towards metals (Brigatti et al., 2013; Moldoveanu and Papangelakis, 2012).

Although the primary purpose of the adsorption technologies is the reintegration in the environment of water with pollutant concentration compatible with ecosystem receptors, more and more attention is paid to the prospect of using the same processes also for recovering materials of economic interest (i.e. valuable metals). In this perspective, wastewaters generated by hydrometallurgical processes of Waste Electric and Electronic Equipment (WEEE) treatment could be a potential target of this kind of processes, since they contain a large amount of valuable metals (Behnamfard et al., 2013; Menad et al., 2013; Mueller et al., 2015). The main available technologies for metal recovery are electrodeposition (Fogarasi et al., 2015), solvent extraction (Akcil et al., 2015) or precipitation (Behnamfard et al., 2013); they are able to purify and recover noble metals as copper, gold or silver, but they are still quite unsatisfying for what concerns Rare Earths (REs) (Binnemans et al., 2013). By the way, REs content in electronic devices is constantly increasing (Gutiérrez-Gutiérrez et al., 2015) and their supply is critical (Smith Stegen, 2015; Tunsu et al., 2015). The use of natural clays in treating aqueous wastes containing heavy metals and organic matter has been previously reported in other works (Ijagbemi et al., 2009; Sdiri et al., 2011) but still lacks in the literature a deep investigation of REs recovery from aqueous wastes.

For all these reasons, the present work focuses on the adsorption of REs, specifically lanthanum and neodymium, from liquid solutions (in order to evaluate the uptake capability of the natural clays towards these RE metals) and also investigates the possibility of recovering these metal ions from wastewaters.

At the best of the Authors' knowledge, no experiments have been performed on the adsorption of Nd onto clay minerals. Few studies, instead, deal with the La uptake on bentonite (Chegrouche et al., 1997; Chen et al., 2012; Spencer et al., 2007) and on modified montmorillonite (Bruque et al., 1980; Iannicelli Zubiani et al., 2013b).

Regarding bentonite, Chegrouche et al. (1997) found that the temperature decrease (from 50 to 20°C) has favourable effect upon adsorption. Spencer et al. (2007), instead, reported that the retention of La in bentonite was not affected by saline conditions. Chen et al. (2012) observed that the adsorption of La onto a sample of Na-bentonite, named GMZ bentonite, carries on quickly (after 30 min of contacting time), increases with increasing the bentonite concentration in the solution, and raises gradually from pH = 2 to pH = 8. Finally, the Authors found that adsorption proceeds throughout exchange reaction between La^{3+} in the aqueous solution and the Na^+, K^+, Ca^{2+} and Mg^{2+} of the bentonite.

Regarding montmorillonite, Bruque et al. (1980) studied the H^+-La^{3+} exchange reaction for a modified H-montmorillonite whereas Iannicelli-Zubiani et al. (2013b) intercalated two different polymers in Ca- and Na- natural montmorillonite, obtaining organo-clays which were found effective in both lanthanum adsorption and release processes. They also found that the contact time does not seem to affect the La adsorption.

In this study adsorption tests were carried out on two model solutions of lanthanum and neodymium salts, using two natural smectite clay minerals, with the aim of selecting a system with good uptake efficiency for the pollutant abatement in wastewaters. The adsorption mechanism and the effect of the experimental conditions (such as contact time and pH) on the adsorption efficiency were investigated, and the clay sorbents characterized. Furthermore, the release (desorption) of REs from clays was also studied, in order to evaluate the feasibility of REs recovery from wastewaters. The adsorption-desorption procedure with the optimized parameters was also tested on a real wastewater obtained by dissolution of a dismantled NdFeB magnet of a hard-disk. The studied smectites were characterized before and after the adsorption tests combining the results of X-ray powder diffraction (XRPD) and X-ray photoelectron spectroscopy (XPS) whereas the solutions were analysed by means of Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).

2. Experimental

2.1 Materials and Characterization techniques

Two natural smectite samples were used as sorbents, namely a Ca-montmorillonite (STx-1b which stands for "State of Texas", STx in the following) and a Na-rich montmorillonite (SWy-2, which stands for "State of Wyoming", SWy in the following) which were provided by the Clay Minerals Society. The chemical composition is:

$^{IV}Si_{4.0}{}^{VI}(Al_{1.21}Fe^{3+}{}_{0.05}Mg^{2+}{}_{0.36}Ti_{0.02})^{XII}(Ca_{0.14}Na_{0.02}K_{0.01})O_{10}(OH)_2$ for the STx sample and

$^{IV}(Si_{3.99}Al_{0.01})^{VI}(Al_{1.51}Fe^{3+}{}_{0.21}Mg^{2+}{}_{0.27}Mn_{0.01}Ti_{0.01})^{XII}(Ca_{0.11}Na_{0.16}K_{0.01})O_{10}(OH)_2$ for the SWy sample. The average grain size of STx and SWy was 20 ± 10 μm and 30 ± 15 μm, respectively, and was measured by a laser particle size analyser (Cilas 1180).

In order to develop and validate a REs adsorption process, two model solutions were adopted: lanthanum and neodymium were selected as model ions for this purpose; the process was studied and developed with La-containing solutions; once the process parameters were set on the basis of the lanthanum results, the approach was replicated with neodymium solutions. Also the desorption

1. mechanism was evaluated, and at the end the entire process was applied to a real wastewater

2. coming from a dismantled NdFeB magnet of a hard disk.

3. Together with clays, the reactants used in this study were lanthanum nitrate ($La(NO_3)_3 \cdot 5H_2O$

4. 99.99%, Sigma Aldrich), neodymium nitrate ($Nd(NO_3)_3 \cdot 6H_2O$ 99.99%, Sigma Aldrich), HNO_3

5. (ACS, Sigma Aldrich), NaOH (ACS, Sigma Aldrich) and deionized water.

6. The Cation Exchange Capacity (CEC) of the clays was determined according to the ammonium

7. saturation procedure proposed by Chapman (Kühnel, 1990).

8. All the metal ions concentrations in solutions were measured by Inductively Coupled Plasma -

9. Optical Emission Spectroscopy (ICP-OES) analyses using a Perkin Elmer Optima 2000DV

10. spectrometer. The measurement error is estimated to be 1%.

11. X-ray powder diffraction (XRPD) patterns of clays were recorded after each step of the recovery

12. process with a Bruker D8 Advance diffractometer using graphite monochromated Cu K_α radiation;

13. the scan step was 0.02° 2θ and the measurement time was 1 s per step. The XRPD line profile

14. analysis was performed with TOPAS P 2.1 software (Bruker AXS, Karlsruhe, Germany) using a

15. Pearson VII profile function, after background subtraction. The calculated profiles were used for the

16. determination of basal spacing (d_{001}) of the clays.

17. XPS analyses were carried out with a Thermo VG THETA PROBE ESCA spectrometer using

18. monochromatic Al K_α X-rays and an electrostatic hemispherical analyser. The spectra were

19. acquired with 300 μm X-ray spot size, 100 eV pass energy, 0.1 eV step size. The base vacuum in

20. the analysis chamber was around 10^{-9} Torr. STx and SWy powders were uniformly dispersed onto

21. an adhesive-coating carbon tape. For all the studied samples, the Binding Energy (BE) scale was

22. calibrated with respect to the aliphatic component of C1s peak (BE= 284.8 eV) of the surface

23. carbonaceous contaminants. A flood gun was used to correct for differential charging. Low-

24. resolution spectra were collected to check all the detectable elements, while high resolution ones

25. were acquired for elemental and speciation analysis. Data analysis included background subtraction

26. using the Shirley method (Shirley, 1972) and a non-linear least square fitting using a Gaussian -

27. Lorentzian product function as implemented in the Avantage software package v. 5.31.

28.

29. **2.2 Adsorption tests**

30. A weighted amount of clay was contacted with the lanthanum solution (solid/liquid ratio = 0.04

31. g/mL) at known initial concentration (C_0 = 19 mmol/L for La^{3+} and Nd^{3+}) under vigorous stirring.

32. This initial concentration was selected in a pre-industrialization perspective. In fact, the aim is to treat

33. wastewaters coming from WEEE hydrometallurgical processes. Since it was impossible, in lab scale,

After the selected contact time, the clay was separated from the liquid using a centrifuge (HETTICH 32 RotoFix). The contact time was varied in the experiments from 10 minutes to 24 hours to investigate the equilibrium adsorption time; the amount of lanthanum captured by the solid phase was determined by measuring the amount of metal in solution through ICP-OES analyses before and after the adsorption experiments.

The amount of metal ion adsorbed at time t, here termed q_t [mmol/g], was calculated from the mass balance equation (Equation 1):

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{Eq. 1}$$

where C_0 and C_t are the initial and the residual metal concentrations in the solution [mmol/L] respectively, V is the volume of solution [L] and W is the mass of clay [g]. When t is the equilibrium contact time, then $C_t = C_e$, $q_t = q_e$ and the amount of metal ion adsorbed at equilibrium q_e, is calculated using Equation 1. The uptake efficiency [%] was calculated from Equation 2:

$$Uptake\ efficiency = \frac{(C_0 - C_t)100}{C_0} \tag{Eq. 2}$$

2.3 Release tests

Release tests were performed by contacting the La-containing clays with solutions at different initial pH (1, 3, 5 and 7) under continuous stirring (magnetic stirrer, 500 rpm). The experiments were performed at room temperature, for 1.5 h, with a solid/liquid ratio of 0.026 g/mL. The amount of released ions (q_w) was calculated from Equation 3; C_w is the metal concentration in solution [mmol/L] after the release step, and it was determined by ICP-OES analyses of the liquid phase after separation.

$$q_w = \frac{(C_w)V}{W} \tag{Eq. 3}$$

V is the volume of the solution [L] and W is the mass of clay [g]. The release efficiency [%] was calculated from Equation 4:

1 $Release\ efficiency = \frac{(C_W)100}{C_e}$ (Eq. 4)

2

3   where C_e was the amount of metal ion adsorbed by the solid phase at equilibrium time.

4   Once the process was set up and the optimal conditions were found (equilibrium time of uptake and

5   pH of release) experiments were carried out also on the model neodymium and finally on the

6   solution obtained by dissolution of the NdFeB magnet. The general scheme of the procedure is

7   reported in Fig. 1.

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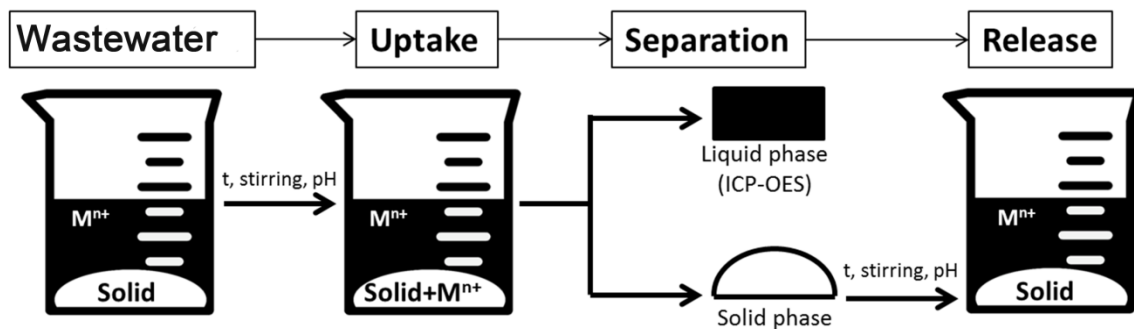
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10   **Fig. 1** - General Scheme of the UPTAKE/RELEASE process.
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12 **3. Results and discussion**

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14 **3.1 Pristine clays characterization**

15 Both STx and SWy clays have been widely characterized in the literature (Borden and Giese, 2001;

16 Chipera and Bish, 2001; Guggenheim and Van Groos, 2001); however, for sake of completeness,

17 the as-received clays were fully characterized also in our laboratories. The measured CEC is 89

18 meq/100 g for STx clay and 76.4 meq/100g for SWy; these values are in fair agreement with the

19 suppliers report. In STx clay, Ca^{2+} was mainly exchanged, while both Ca^{2+} and Na^+ were exchanged

20 in SWy. Also small amounts of Mg^{2+} ions were found to be exchanged in both clays. In XRPD

21 patterns, a well defined basal spacing d_{001} of 15.4 Å was observed in STx clay (Fig. 2 a, bottom),

22 while a very broad, low intensity basal reflection was detectable in SWy diffraction pattern (Fig. 2

23 b, bottom). The sharpness and intensity of the basal spacing are related to the degree of order of the

24 interlayers and the particle size, therefore the as-received SWy clay seems to have a particularly

25 disordered state. Anyway, line profile analysis performed on the broad reflection allowed to roughly

26 model it with two basal spacings at about 12 Å and 10 Å.

1 Since the uptake and release tests have been performed at different pHs, blank samples of clays

2 contacted at different pHs have also been prepared and characterized. The solids were suspended in

3 water solutions having pH = 1, 3, 5, 7 and 13 and stirred for 90 min while monitoring the pH.

4 Immediately after the contact, the pH of both clays suspensions reached the pH value of the

5 contacting solutions, except for a small pH increment measured in solutions with starting pH = 3

6 and 5 that set at 3.5 and 5.5 respectively.

7 After separation and desiccation, XRPD diffraction patterns were collected for both clays (Fig. 2),

8 and changes in diffraction patterns were observed.
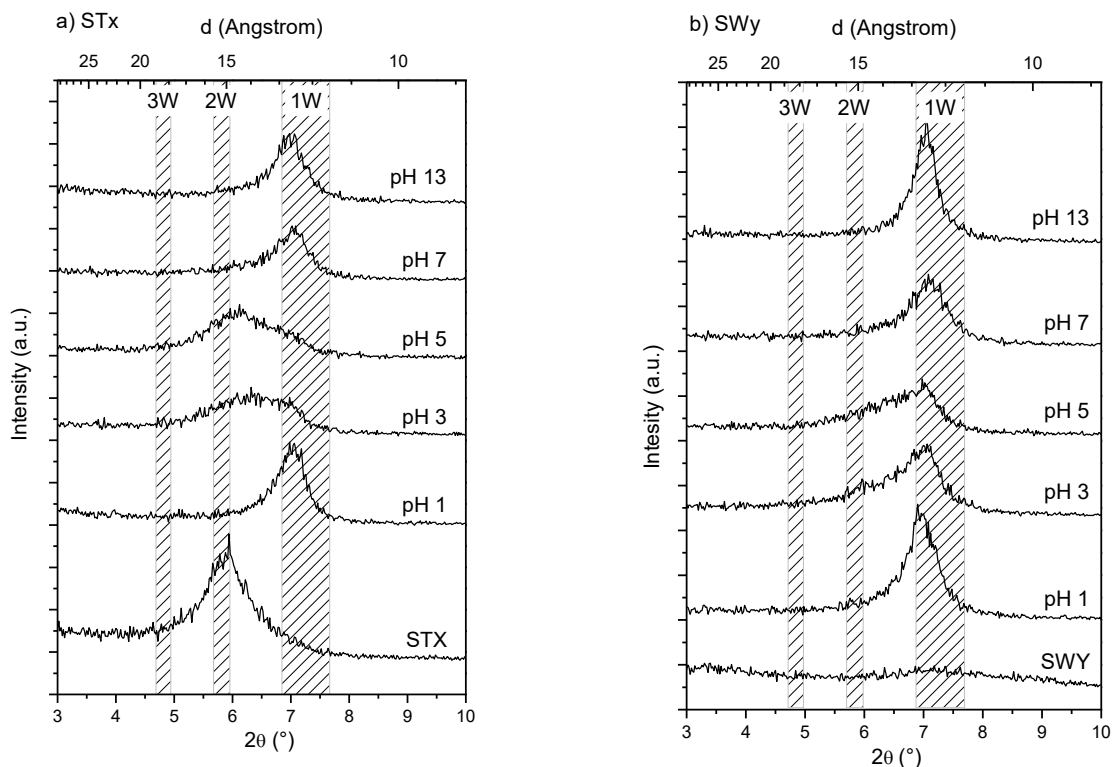
9 **Fig. 2** - XRPD spectra of a) STx, b) SWy contacted with solutions at different pH.

10

11 In STx clay (Fig. 2 a), a displacement of the basal reflection towards higher 2θ was observed when

12 the clay was suspended in solutions with pH = 1, 7, 13; this displacement corresponds to the

13 narrowing of the d_{001} spacing from the original 15.4 Å to about 12.7 Å. When the clay was

14 suspended in the solution at pH = 3 and 5 instead, the basal reflection was much broader, with a

15 distribution of d_{001} values in the range 15.4 Å - 12.7 Å. In SWy a strong ordering is obtained upon

16 contacting the solid with solutions at different pH (Fig. 2 b); a clear basal reflection at about 12.7 Å

17 develops at any pH value, but again the samples treated with the solutions at pH = 3 and 5 show a

9

much broader distribution of d_{001} towards larger interlayers. As suggested by the previous literature, the d_{001} spacing of montmorillonites can be described in terms of hydration states of the interlayers (Chalghaf et al., 2013). Unhydrated interlayers (0W) show a $d_{001} \approx 9.7 - 10.2$ Å, monohydrated ones (1W, i.e. 1 layer of water molecules) reach a value of $d_{001} \approx 11.6 - 12.9$ Å and bihydrated layers (2W) can swell to $d_{001} \approx 14.9 - 15.7$ Å. The presence of 3 layers of water molecules in the interlayer can further expand the interlayer up to $d_{001} \approx 18 - 19$ Å. The modifications of montmorillonite interlayer spacing as a function of interlayer cations and hydration states has been deeply modelled by some authors (Chalghaf et al., 2013; Ferrage et al., 2005a, 2010); such a detailed description of the interlayer distribution is out of the scope of this paper, but a few remarks can be done. The measured interlayer spacing for STx clay shows that the original clay is mainly in bihydrated state. After treatments at pH = 1, 7 and 13 the interlayer spacing shifts down to values similar to those of monohydrated montmorillonites; at intermediate pH, instead, there seem to be a combination of mono and bi-hydrated interlayers in different proportions. In SWy clay, the hydration state of the pristine clay seems to be a mixing of 0W-1W state. After treatment at any pH, the interlayer spacing value is in the range of the mono-hydration state (1W) and again at pH = 3 and 5 a blend of 1W-2W layers develops. The observed structural modifications can be accounted for the effect of protons, protonated water molecules or hydroxides on the hydration states of the interlayers. These considerations are also in keeping with the peculiar behaviour of the pH suspensions at pH = 3 and 5, where the slight increase of the values up to 3.5 and 5.5 is an indication of protons adsorption at this pH conditions.

3.2 Uptake/release process

*3.2.1 Uptake and release with lanthanum model solution*

Uptake - To evaluate the uptake capability of the solids, the pristine clays were contacted with a lanthanum nitrate solution (19 mmol/L, starting pH = 4.5). The effect of contact time was first explored. Uptake experiments were carried out at room temperature, with contact times ranging from 10 min to 24 hours with fixed mass of clays (2 g) and fixed initial lanthanum concentration (19 mmol/L). As shown in Fig. 3, the adsorption equilibrium was reached after 90 min for both clays. For longer contact times, the amount of adsorbed lanthanum seems to decrease decreases (in STx), but this fact cannot be achieved since the uptake values reported in Fig. 3 are the average values obtained in parallel experiments. In the case of the STx 24 h test the values are 28.8 $\pm$ 2.9

1 ~~mg/g, due to experimental errors. In this perspective, it is likely that the trends of the two clays are~~

2 ~~overlapped and no decrease in STx occurs.~~most likely due to extraction of the adsorbed lanthanum

3 from the clay. Accordingly, all the following uptake experiments were carried out with a 90 min

4 contact time, that is long enough to attain equilibration but short enough to avoid lanthanum

5 extraction at this step (Iannicelli-Zubiani et al., 2013b). The short time period required to attain

6 equilibrium suggests an excellent affinity of the clays for lanthanum.
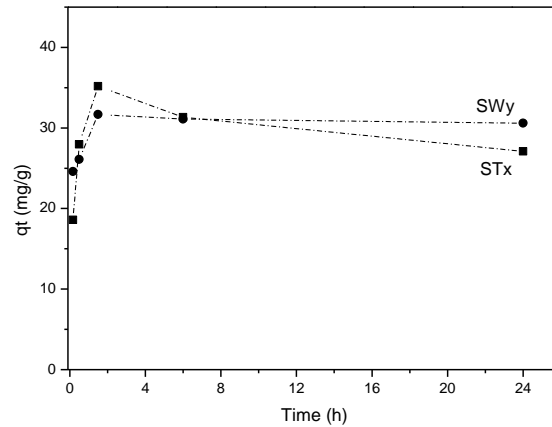
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8 **Fig. 3** - Effect of contact time on lanthanum uptake with STx and SWy.

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10 Also the pH evolution was monitored throughout the experiment (Fig. 4).
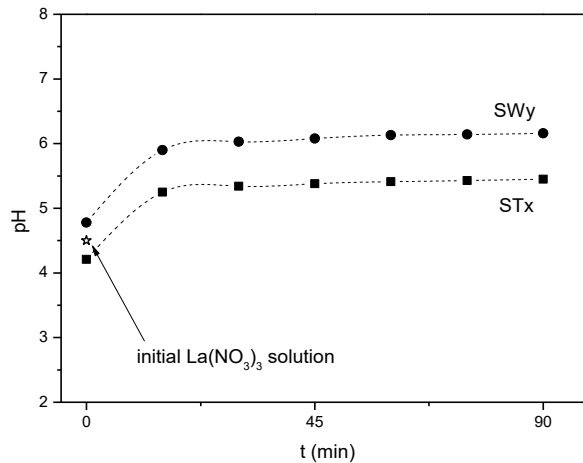
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12 **Fig. 4** - pH evolution during La uptake experiments.
13

14 Upon contacting the clay with the lanthanum solution, the pH quickly increased from 4.5 to about 5

15 for STx and to 6 for SWy, then it remained constant till the end of the experiment (90 min). In this

1   range of pH, no insoluble La species can be formed, therefore all the La^{3+} ions in solution are

2   available for adsorption and/or ion exchange with the clays.

3   The La concentration in solution was set to allow for a theoretical maximum uptake of 0.48 mmol

4   La^{3+}/g clay and the measured lanthanum uptake efficiency was 52% and 48% for STx and SWy,

5   respectively. These are close to the efficiencies reported by other authors for lanthanum adsorption

6   on clays (Table 2).

7

8   **Table 2** -Reported works on lanthanum(III) uptake using different clays.

Sorbent	Lanthanum(III) uptake (mmol/g)	Equilibrium time (h)	pH	Ref.
Ca-Montmorillonite (STx)	0.25	1.5	5	This study
Na-Montmorillonite (SWy)	0.23	1.5	6	This study
H-Montmorillonite	0.41	-	6.7	(Bruque et al., 1980)
Na-Bentonite	0.26	-	6	(Chegrouche et al., 1997)
Bentonite	0.31	-	-	(Spencer et al., 2007)
Na-bentonite (GMZ)	0.19	0.5	5	(Chen et al., 2012)
Polymers modified clays	0.43	1.5	5	(Iannicelli-Zubiani et al., 2013b)

9

10   To discriminate between adsorption and ion exchange processes (Djukić et al., 2013), the amount of

11   Ca^{2+}, Na^+ and Mg^{2+} ions in the clays interlayer was determined before and after the lanthanum

12   uptake (Table 3). In case of ion exchange, lanthanum replaces interlayer cations without modifying

13   the overall positive charge of the clay interlayer.

14   Similar results were found in the La-uptake experiment on the GMZ bentonite (Chen et al., 2012).

15

16   **Table 3** – Composition of the solid phase before and after uptake reaction.

Ions (mmol/g_clay)	STx		SWy	
	BeforeUptake	AfterUptake	BeforeUptake	AfterUptake
Ca^{2+}	0.54	0.29	0.49	0.40
Mg^{2+}	0.08	0.03	0.14	0.07
Na^+	-	-	0.50	0.09
La^{3+}	-	0.25	-	0.23
Σ charge	1.24	1.39	1.76	1.72

17

18   In the pristine STx clay, 0.54 mmol/g_clay of Ca^{2+} ions and 0.08 mmol/g_clay of Mg^{2+} are present. After

19   contacting the lanthanum solution, 0.25 mmol/g_clay of La^{3+} are captured, while only 0.29 mmol/g_clay

20   of Ca^{2+} ions and 0.03 mmol/g_clay of Mg^{2+} are still in the interlayer~~are released~~. This suggests that

21   La^{3+} uptake has occurred via a cation exchange mechanism, where La ions have displaced some

22   Ca^{2+} and Mg^{2+} ions to preserve the charge balance. This is not surprising since the size of the

23   replacing ions is comparable to that of the replaced ions (Na, Ca and La atomic radii are 1.18 Å,

1.12 Å and 1.16 Å respectively (Huheey, 1983)). However, comparing the interlayer total charge of the exchanged clay (1.39 mmol/g_{clay}) with that of the pristine clay (1.24 mmol/g_{clay}) an increase of the total charge is revealed, that suggests that also other mechanisms, like surface complexation (Tan et al., 2011), are acting.

In the SWy clay, the starting interlayer cation content is 0.49 mmol/g_{clay} of Ca^{2+}, 0.50 mmol/g_{clay} of Na^+ and 0.14 mmol/g_{clay} of Mg^{2+}. After contacting with the lanthanum solution, 0.23 mmol/g_{clay} of La^{3+} are captured, mainly by replacing Na^+ (0.41 mmol/g_{clay} of Na^+ are released, found by difference between 0.50 mmol/g_{clay} of Na^+ in the starting interlayer and 0.09 mmol/g_{clay} of Na^+ in the interlayer after uptake), while only 0.09 (0.49 - 0.40 mmol/g_{clay}) and 0.07 mmol/ g_{clay} (0.14 - 0.07 mmol/g_{clay}) of Ca^{2+} and Mg^{2+} are displaced respectively. This suggests that also in this case, the charge compensation mechanism is acting in La^{3+} uptake; in addition, the initial global charge of 1.76 mmol/ g_{clay} was preserved after La^{3+} uptake (1.72 mmol/ g_{clay}) thus indicating that the cation exchange mechanism is the only mechanism acting in SWy clay.

The above considerations are also supported by the results of XPS analyses. Upon the contacting reaction, in both clays, only the signals of C, O, Mg, Si and Al are detected in survey scans (not shown). K and Na ions signals are missing, suggesting their absence or occurrence below the detection limit (0.1-1 atom%, depending on the element) as also confirmed by the inspection of the their narrow scans, all of which resulted flat. The narrow scan of the Ca2p region (Fig. 5) showed some signals that are, however, strongly affected by the Auger $MgKL_{3,4}$ peak. Specifically, the STx lineshape can be interpreted as the convolution between the Auger $MgKL_{3,4}$ peak and the $Ca2p_{3/2, 1/2}$ doublet, whereas the latter component is negligible in the SWy spectrum.
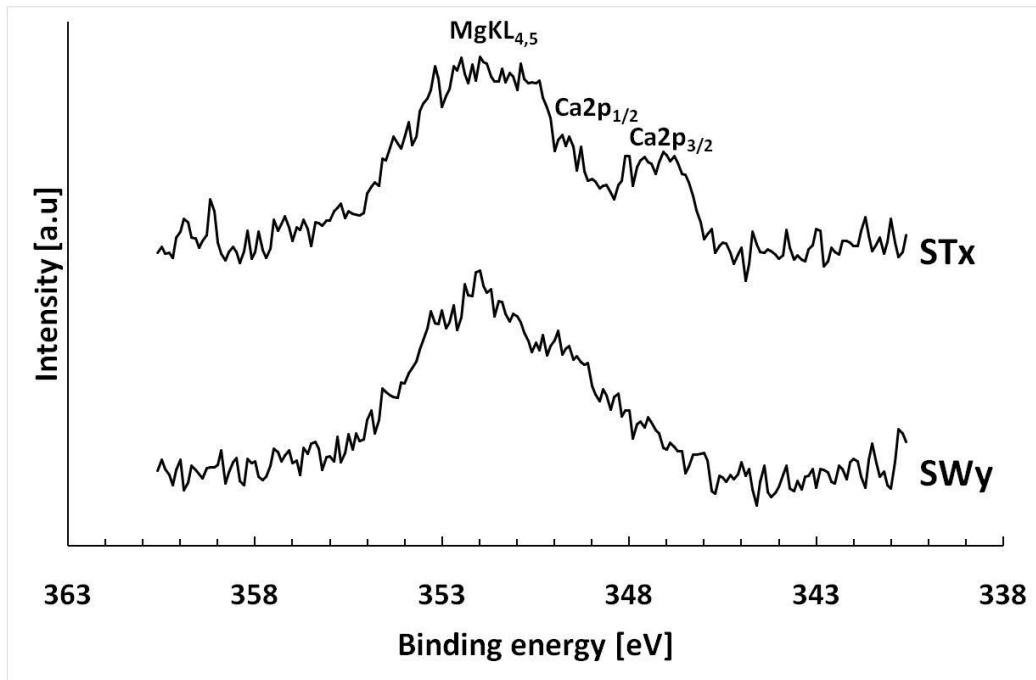
Fig. 5 - XPS spectra of the Ca2p region of La-exchanged-STx and -SWy clay.

In Fig. 6 the narrow spectra of the La3d core level in the STx and SWy clays are shown. The measured binding energy of $La3d_{5/2}$ and O1s peak are respectively 870.0 and 532.5 eV for the STx clay and 836.2 and 531.9 eV for the SWy sample and are in agreement with those reported in the literature for $La(OH)_3$ (Kumar et al., 1984).

As a consequence of screening effects in the final state (Schlapbach and Scherrer, 1982) the $La3d_{5/2, 3/2}$ peaks are split into two components (Fig.6). The magnitude of the splitting (see inset in Fig. 5) and the intensity ratio of each component are chemically diagnostic.

Compound	Δ E La3d₅/₂, ₃/₂
La-enriched STx	3.3 eV
La-enriched SWy	3.4 eV
La_2O_3	4.6 eV
$La(OH)_3$	3.9 eV
La_2CO_3	3.5 eV
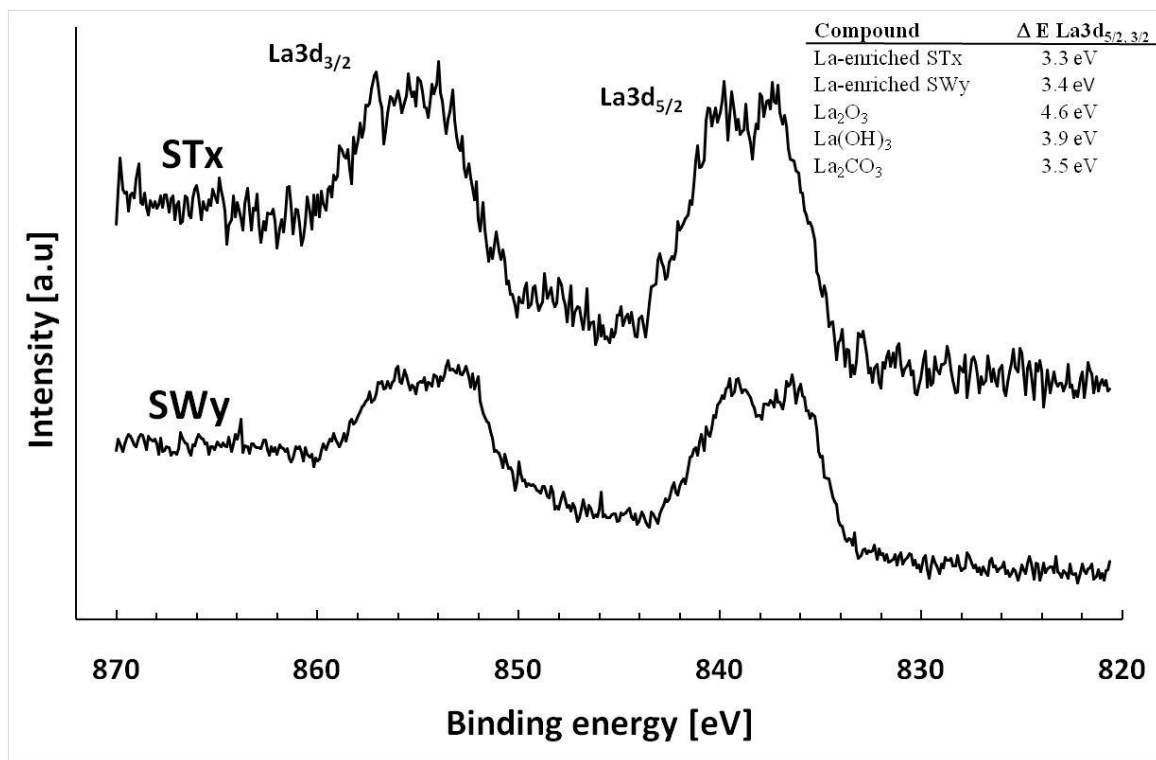
Fig.6 - XPS spectra of the La3d region of La-enriched-STx and -SWy clay. In the inset the magnitude of the split components due to screening effects of the final state are reported (see text).

The splitting of the La3d$_{5/2,3/2}$ components for the studied clays (3.3 and 3.4 eV for STx and SWy, respectively) is close to ΔE values, i.e. 3.9 eV and 3.5 eV found for lanthanum hydroxide and carbonate (Levan et al., 1993). However, in this case, the attribution of the signal is not straightforward by only considering the extent of the splitting. The deconvolution of the O1s signal shows the occurrence of a minor H_2O component, whereas the curve fit of the C1s peak (representative of carbonates species) is consistent with the occurrence of compounds with C/La about 1:1. These results indicate that La ions occur partially as carbonated and partially as hydrated species, in agreement with the above ICP data.

Fig. 7 shows the XRPD patterns of the lanthanum containing samples, compared with those of the pristine clays and those of the blank samples at pH = 5 (i.e. clay contacted with a solution at the same pH of the uptake reaction) for both STx (a) and SWy (b) clays. As mentioned above (Section 3.1) the structural changes occurring when contacting the clay with the blank solution are not straightforward: mixed 1W-2W interlayers develop in different proportions in STx and SWy clays, (See Fig. 7 a, STx-pH 5 and Fig 7b, SWy-pH 5); this is likely due to the complex interaction between protons, hydroxyl ions and the interlayer cations with water in the interlayers (Ferrage et al., 2005b).

15

1 Yet, La^{3+} adsorption clearly affects the clay interlayers structure in both clays. In STx the d_{001}

2 reflection is sharper and shifts towards lower 2θ respect to the blank sample; the insertion of La^{3+}

3 ions seems to favour the formation of bi-hydrated interlayers (Fig. 7 a).

4 A similar behaviour was observed also in SWy: a sharp basal reflection shows up after lanthanum

5 adsorption, at 2θ values corresponding to bi-hydrated layers formation (2W), much different from

6 the broad basal reflection obtained after contacting with the blank solution (Fig. 7 b).
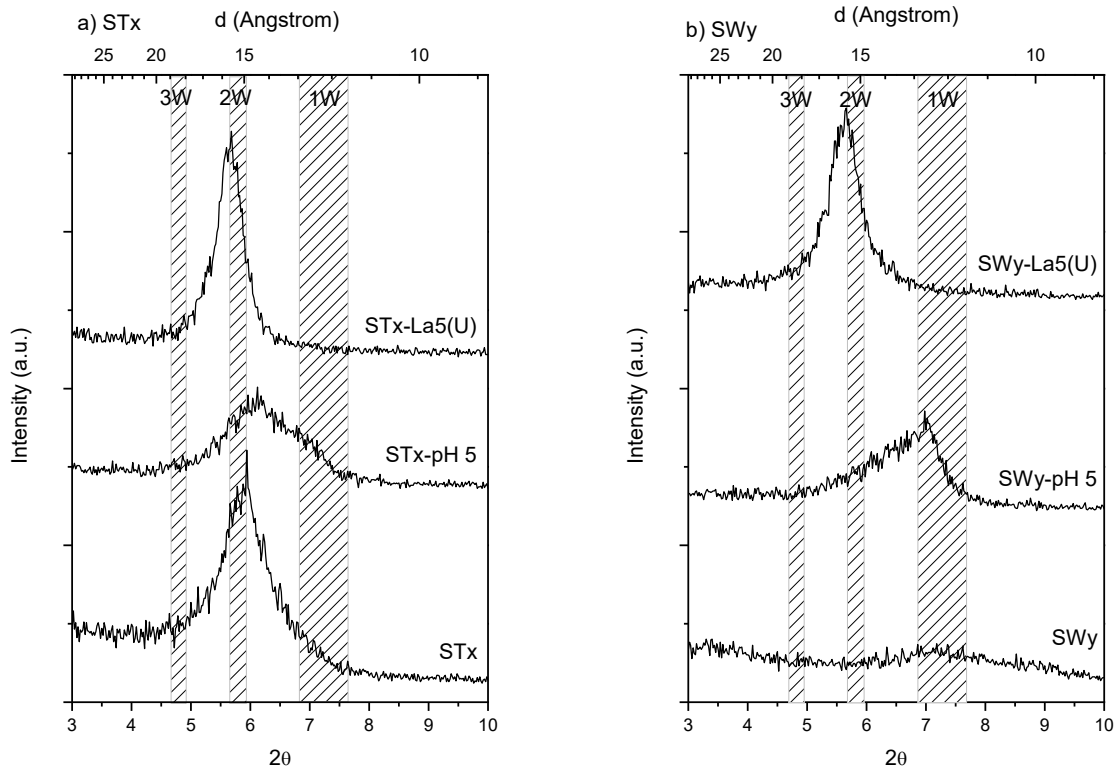
7
8 **Fig. 7** - XRPD spectra of a) STx, b) SWy contacted with solutions at pH = 5 with and without La
9   ions.
10

11 Possibly, such behaviour could be explained by the different water coordination environment

12 promoted by the interaction of different ions with the interlayer water and the clay surface;

13 however, further investigation is needed to clarify this point.

14

15 _Release_ - As discussed above, the capture of La^{3+} ions by the clays is mainly an ionic exchange

16 reaction involving the interlayer cations, with only STx presenting also phenomena due to surface

17 complexation. Furthermore, this reaction is pH-dependent, being the cationic composition and

18 hydration state of the interlayers modified by this parameter (Ferrage et al., 2005b). Hence, also the

19 results of the release experiments are expected to depend on pH. On these bases, the release tests

16

1 were performed contacting the lanthanum enriched clays with solutions at different initial pH

2 values, namely 1, 3, 5, and 7 and the reaction pH was monitored during the whole release

3 experiments. In this experiments, when the La-enriched clay were contacted with an initial solution

4 at pH = 3, a pH increase was observed, that resulted more remarkable in case of SWy (reaching a

5 pH = 7-8) than for STx (final pH = 4)
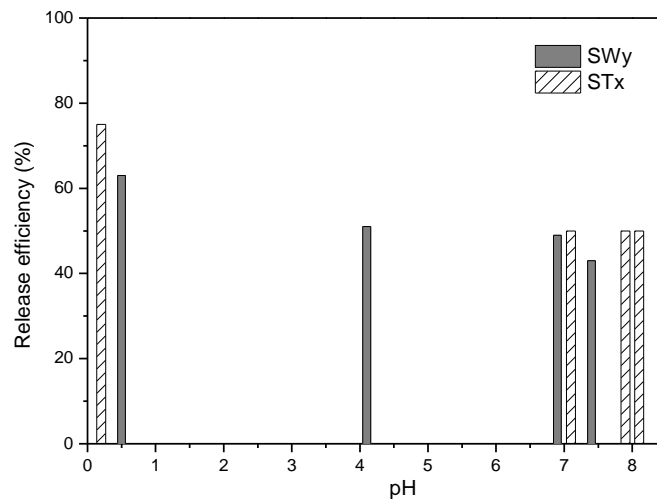
6

7 **Fig. 8** - Lanthanum release efficiency at different pH.

8

9 Fig. 8 reports the release efficiency as a function of pH: lanthanum release is obtained at any

10 considered pH value, even if it is evident that the lower is the pH, the higher is the amount of

11 recovered lanthanum; besides, the nature of the clay does not (or to a minor extent) affect the

12 process. As also reported elsewhere, the better results are found contacting the solid with very acid

13 solutions, at pH lower than 3, best at pH = 1 (Iannicelli-Zubiani et al., 2013a). Moreover, some

14 information on the release mechanism can be drawn if the ratio between the released and the

15 captured La amount (La_R/La_U) is plotted as function of pH (Fig. 9). Irrespective of the clay nature,

16 all the data lay roughly on a line. Accordingly, these data confirm that the release reaction occurs

17 involving similar ionic species in similar chemical environments, thus mainly proceeding through
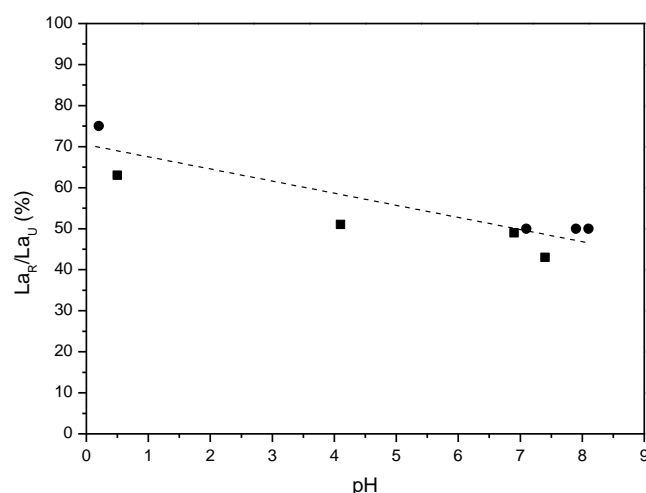
18 the same ionic exchange mechanism.

Fig. 9 - Efficiency of the release process as function of pH (■ STx, ● SWy).

Fig. 10 reports the XRPD patterns of the samples; only the samples that underwent the release at pH = 1 are shown, although the characterization was performed on all the samples. However, the release at pH = 1 is fully representative of the release at any other tested pH.

As expected, the lanthanum release, modifying the interlayer composition, altered the interlayer structure. A displacement of the d_{001} reflection towards higher angles, corresponding to an interlayer shrinkage, is revealed. This is not surprising, since the release is performed in a HNO_3water solution, where only protons are available for the ionic exchange reaction. During the release, protons are able to replace La ions in the interlayer; as a consequence, the interlayer shrinkage occurs, as already observed when pure clays were contacted with acid or basic solutions (See Section 3.1, Fig. 2). To support this conclusion, the spectra of the La-clays upon release are compared with those of the pristine clay upon treatment at the corresponding pH. A pretty good resemblance is found: the d_{001} reflections of the samples after release are almost overlapped with those of the pure clays at the corresponding pH (Fig. 10). The slight differences observed in the reflections can be explained by considering that the release is non-quantitative (i.e. some La ions are retained by the clay), and by the effect of the double contacting with acid solutions (i.e. uptake and release) of the leached samples.
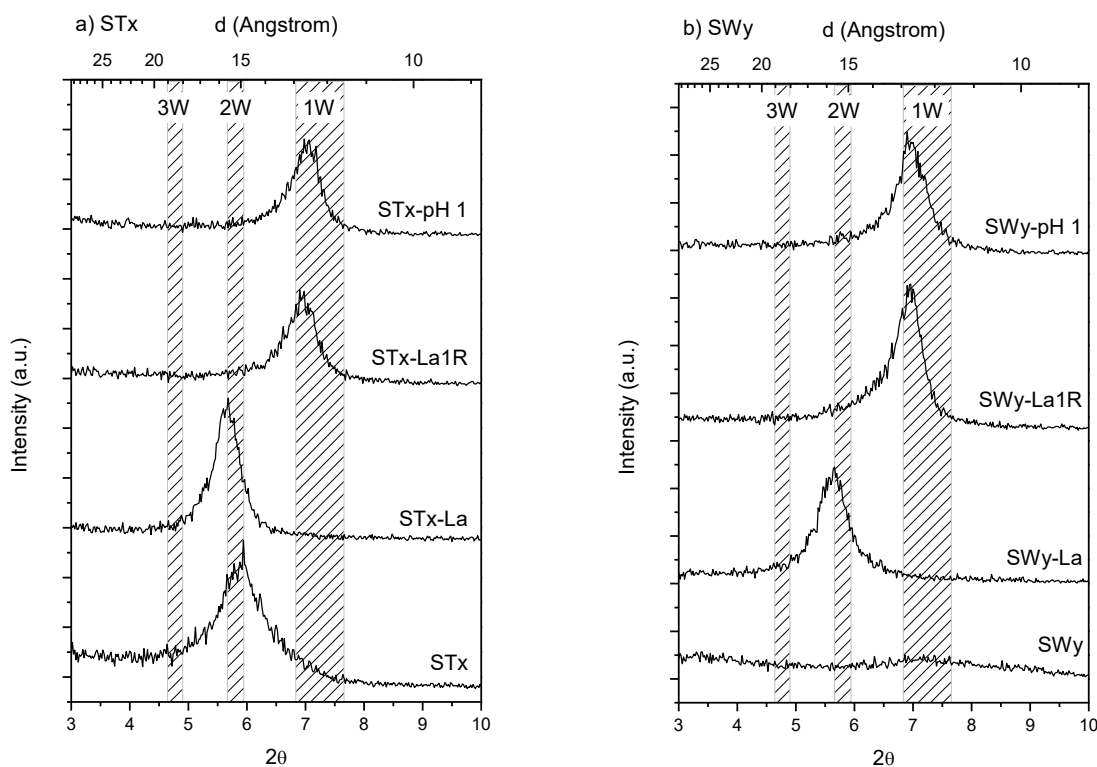
Fig. 10 - XRPD spectra of a) STx and b) SWy before and after release at controlled pH.

At pH = 1 lanthanum release efficiencies are around 60-70%, corresponding to a global efficiency of the process (uptake + release) of 30-35% (w/w).

3.2.2 *Uptake and release with neodymium model solution*

To verify the effectiveness of the process on other REs, and thus to evaluate its general feasibility, a similar approach was applied to neodymium solutions. STx clay was selected as the sorbent, and it was contacted with Nd solution for 90 min at the natural pH of the Nd solution (i.e. pH = 5). The subsequent recovery of the captured ions was performed by contacting the Nd-enriched clay with a nitric solution at pH = 1. This value is expected to reach the best results in the release step as was the case of lanthanum. Also in these experiments, the liquid phases before and after the contacting reaction were analysed by ICP-OES to determine their composition. In Fig. 11 the uptake, the release and the global efficiency of Nd uptake/release process are reported and compared with those of lanthanum.
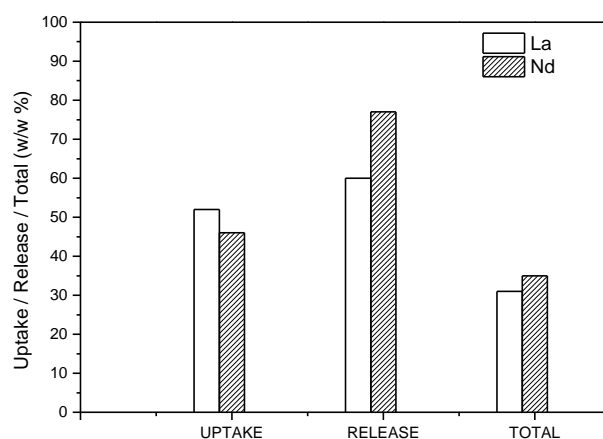
Fig. 11 - Uptake, release and total efficiency of the process measured for Nd using STx as sorbent (lanthanum is reported for comparison).

It is noticeable that the STx clay is able to capture and release the Nd ions. In each step of the process, the efficiencies are similar to those of lanthanum; however, the STx clay has a slightly lower affinity for neodymium with respect to lanthanum: the adsorption efficiency was lower, while the release one was much higher (up to about 80 % of the captured ions are released) respect to lanthanum. This difference in affinity led to a slightly higher global efficiency of the process for Nd ions.

In Fig. 12 the XRPD patterns of the clay after uptake and release of Nd ions, compared with those of La, are reported.
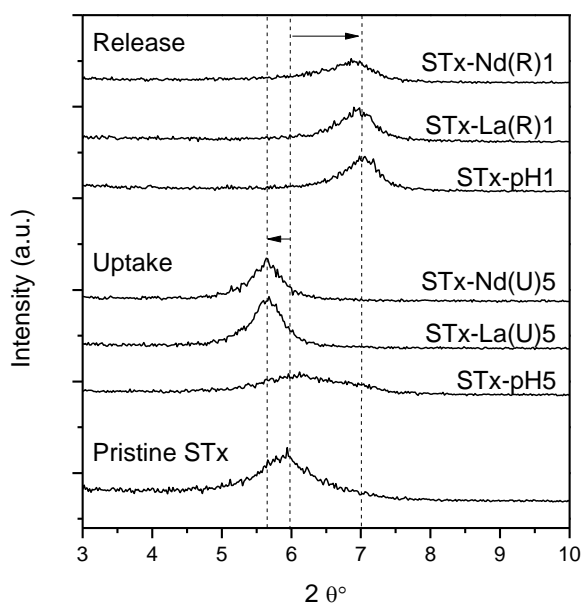
Fig. 12 - XRPD spectra of STx after uptake and release of La and Nd ions.

A displacement of the d_{001} reflection towards lower angles was observed also in the case of Nd-containing clays, suggesting that Nd ions, as La ones, are captured in the clay interlayer. Therefore, it is likely that the Nd uptake process occurs via the same ions exchange mechanism already discussed for La. Regarding the release step, when the STx-Nd sample was treated with the nitric solution at pH = 1, the d_{001} reflection was displaced towards higher angles, reaching the spacing values of the blank sample (i.e. the pristine STx treated at pH = 1). In addition, by comparing the XRPD patterns of Nd-based and La-based samples it can be presumed that the clay swelling behaviour is insensitive of the captured ion, while the reaction pH is the main responsible of the d_{001} displacement. This is a further proof that the whole process is related to ions exchange reactions: ions with similar charge originate similar effects. Such a conclusion is further clarified in Fig. 13 where the d_{001} of the different samples are compared.
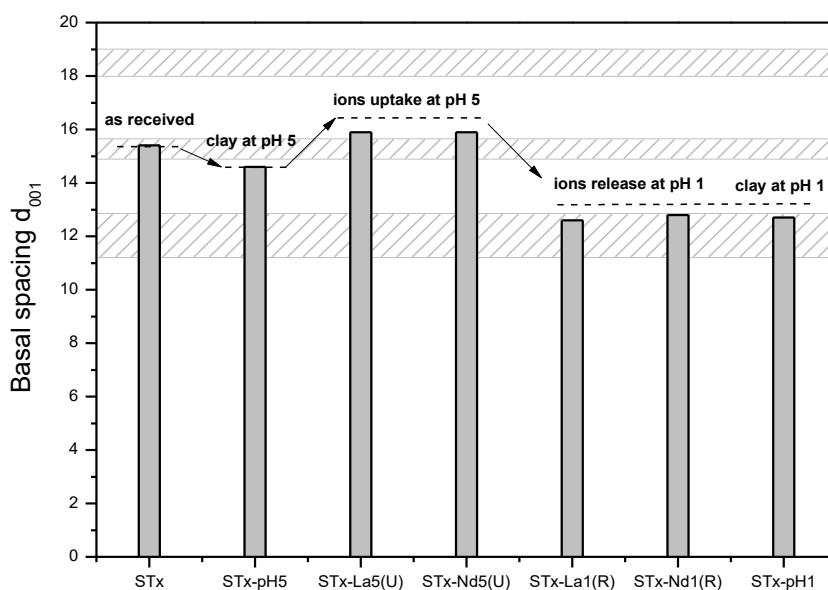
Fig. 13 - Evolution of the basal spacing of STx clay as a function of the reaction pH.

In detail, the d_{001} always decreases when the clay is contacted with solutions at medium/low pH. This finding is in line with an interlayer restriction upon partial replacement of the interlayer cations (Ca, Mg) with protons: the lower the pH, the less the interlayer space. The d_{001} = 15.4 Å of the pristine clay drops down to 14.2 Å and 12.5 Å respectively upon treatment at pH = 5 and pH = 1. When the clay is contacted with the ions solutions at pH = 5 an expansion of the basal spacing occurs due to the replacement of Ca and Mg with La or Nd at the interlayer. The d_{001} expansion does not depend on the specific RE ion: an increase up to 16.8 Å is found for both La and Nd ions. No shrinkage was observed even though the RE solutions were contacted at pH = 5; in this case the ions exchange mechanism prevails on the simple pH effect. When the release reaction is performed at pH = 1, the exchanged La and Nd ions are removed but only protons can replace them, thus a d_{001} close to STx treated at pH = 1 is observed, (i.e. d_{001} of about 12.5 Å are observed in any case). Finally, such a reaction allows for the release of nearly the total captured ions, resulting in d_{001} reaching the original value of the pristine clay (12.5 Å). Thus, pH is a simple parameter that can be used to handle the process.

22

3.2.3 Uptake and Release with real wastewater

A NdFeB magnet was taken from a dismantled hard disk memory and completely dissolved through a hydrometallurgical treatment: it was leached in a HNO_3 solution (50% V) at 60 °C for 2 days under vigorous stirring.

The obtained solution had a strongly acid pH (less than 1) and was analysed via ICP-OES and the results are reported in Table 4. Then it was contacted with the STx clay, to verify the efficiency and the selectivity of the proposed approach on a *"real sample"*.

Table 4 - Composition of the NdFeB magnet solution ~~dissolved NdFeB magnet~~ determined by ICP analyses.

Element	mg/L ~~% w/w~~
Fe	37000 ~~88.5~~
Nd	3440 ~~8.2~~
Ni	900 ~~2.2~~
B	145 ~~0.3~~
Co	130 ~~0.3~~
Mn	110 ~~0.3~~
Others	52 ~~0.2~~

The uptake and release experiments were carried out under the ~~same~~ following conditions: ~~as used for lanthanum and neodymium~~ for uptake solid/liquid ratio = 0.04 g/mL, vigorous stirring, 90 min of time, room temperature, and pH of the solution = 1; for release solid/liquid ratio of 0.026 g/mL, continuous stirring, 90 min of time, room temperature, and pH = 1.

Results are plotted in Fig. 14 where the yield (a) and the selectivity (b) of the single steps and of the global process are reported. With the term "selectivity" towards an A ion in a system with more ions, it is meant the ratio between the amount of adsorbed A ion (in moles or ppm) with respect to the amount of all the adsorbed ions.
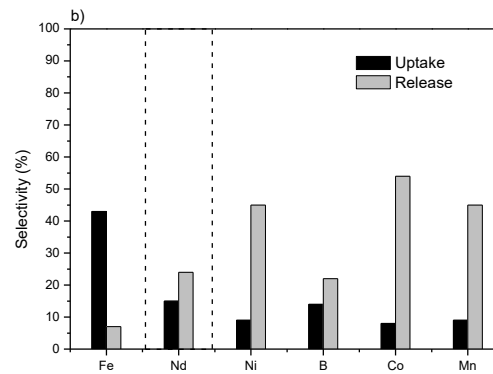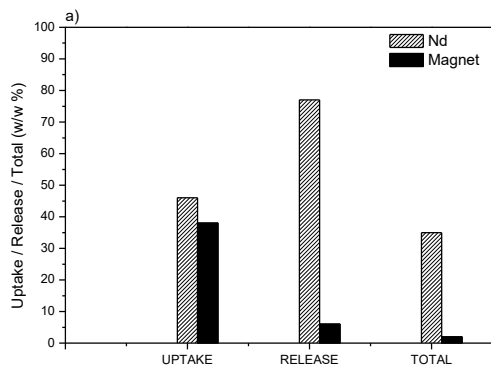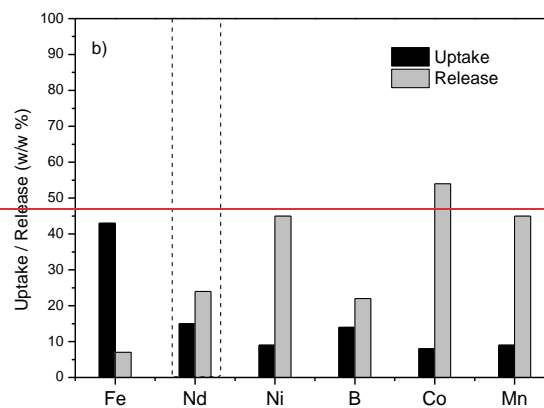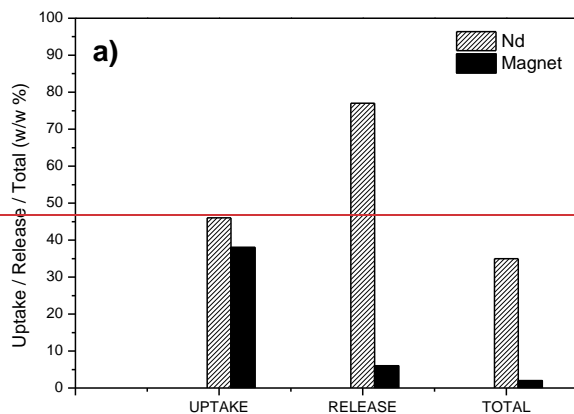
Fig. 14 - Yield (a) and selectivity (b) of the single steps and the global process towards Nd model and real solutions.

Although preliminary, some interesting indications can be drawn from such experiments. The total uptake efficiency was around 40% (Fig. 14 a), slightly lower than the uptake efficiency obtained when only Nd was in the solution. STx clay preserved a good uptake efficiency even when the complexity of the system was greatly increased, achieving 40% of metal ions removed by the solution. On the contrary, the efficiency of the release step strongly decreased when shifting from a mono-ion system to a real system (from 80 to 5%). Nevertheless, this behaviour can be ascribed to a pH effect. Indeed, the NdFeB magnet was dissolved into a nitric acid solution already having a strongly acid pH, so no variation in the pH conditions were really obtained during the release step. Concerning selectivity (Fig. 14 b), a significant matrix effect was found when Nd is in the complex solution: in this case the matrix composition affected both the uptake and release, lowering the efficiency of the Nd global process (4% in the complex matrix, respect to 35% in the single ion solution). Phenomena of competitive capture (likely with Fe ions) can be responsible for the worse results.

On these bases, the use of clays for the removal of heavy metals can be considered promising (efficiency is about 40% in a single step, possibly improvable by increasing the number of cycles); by the way, no particular selectivity was found towards REs. Indeed, the release step is still unsatisfactory when applied to real systems; in this perspective, the use of suitably modified clays could enhance the recovery of REs from a complex matrix.

4. CONCLUSIONS

The present study shows that adsorption of REs onto natural montmorillonite samples followed by release has a potential both for the valorisation of natural resources (clay minerals) and the recovery of REs in terms of efficiency. The following main conclusions can be drawn:

1) Both the employed clays are able to capture and release La and Nd ions. The optimised parameters are pH = 5 and contact time = 90 minutes for the uptake process, and pH =1 for the release step. The ions are captured at the clay interlayer, mainly via an ions exchange mechanism that implies the replacement of the interlayer cations with the REs ones.

2) At pH = 1 the release efficiencies are about 60-80%, depending on the clay.

3) Neodymium has a slightly lower affinity for the clay with respect to lanthanum: its adsorption is lower than La, whereas, in turn, its release is highly efficient (up to about 80% of the captured ions are released).

4) In complex solutions, the uptake was around 40%, slightly lower than the uptake efficiency obtained with only one ion in solution. On the contrary, release efficiency strongly decreased passing from a mono-ion system to a real system (from 80 to 5%).

5) Nd suffers from a strong matrix effect when in a complex solution. The matrix affects both uptake and release processes and lowers the global efficiency (4% in the complex matrix, to be compared with 35% in a single ion solution).

7) The use of clays for the removal of heavy metals is promising (efficiency around 40% in one step, possibly increasable with more cycles of treatment) whereas the recovery can be further improved.

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