

Recovery of Rare Earths and Precious Metals from Waste Electrical and Electronic Equipment by Acid Leaching and Immobilized Chelating Agents

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1. Introduction

Rare Earth (REs) demand is constantly increasing in the Global Market, since new technological applications such as optical, electronics, ceramics and nuclear (Iannicelli Zubiani et al., 2013) exploit these materials for their unique properties. Since natural resources are located just in focused areas (mainly China) (Massari and Ruberti, 2013), European Commission highlighted REs as critical raw materials (EU, 2010) and promoted processes for their recovery, separation and substitution (ERECON, 2014).

Currently each EU citizen produces about 17 kg of WEEE per year. These wastes are rich in precious and strategic metals (Egedy et al., 2013) and, in many cases, are characterized by higher metal contents than those of natural minerals. Accordingly, recycling can be considered a valuable opportunity: this perspective is known as "urban mining" (Di Maria et al., 2013). For these reasons, the study of a targeted and efficient REs recovery from WEEE can only lead to undeniable both socio-economic and environmental benefits.

From a technological point of view recycling of end-of-life WEEE and recovering of metals therein contained can be divided into three major steps: disassembly, upgrading and refining (Cui and Forssberg, 2003). Regarding the last unit operation of refining, different methods have been proposed. Among the others, hydrometallurgical method has been reported to be one of the most interesting being: 1) generally applicable to very different compositions; and 2) allowing the same processing steps as those for extraction of metals from primary ores (Cui and Forssberg, 2003). On the other hand, some disadvantages of this process are: 1) the need of many process steps, 2) the consumption of large amounts of chemicals (Birloaga et al., 2014) and

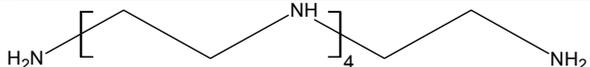
3) the generation of large amounts of waste water (Iannicelli Zubiani et al., 2013). Some of the reported disadvantages are related to the step of metal ions removal from aqueous solution. Recently, the use of solid sorbents is obtaining more and more attention (Balintova et al., 2014) because of its advantages of high recovery, short extraction time, high enrichment factor, low cost and low consumption of organic solvents over liquid-liquid extraction. In particular, clays as solid-phase are characterized by some outstanding advantages, such as low cost, good mechanical properties, good acid tolerance, convenient solid-liquid separation and excellent reusability. Moreover, clay minerals show an adsorption behaviour towards metals (Cantuarria et al., 2014) even though they do not show an equally release towards these elements. For all these reasons, this work, performed under the project “E-WASTE - Il ciclo intelligente” (ID 40511448, financed by Lombardia Region), proposes the use of solid sorbents based on clays and properly modified for the recovery of Rare Earths Metals from WEEE, namely magnetic components, mobile phones and Printed Circuits Boards (PCBs). Anyway, the involved systems are very complex (e.g. in a magnet from a hard-disk there are 16 different ions and the amount of REs is very low) thus a preliminary study has been conducted on model systems in order to validate the experimental idea.

Accordingly the aim of the work was to study the possibility of REs recovery from WEEE by using selective chelating agents immobilized on clays: in particular a natural smectite mineral clay (STx-1b) was modified with different concentrations of the chelating agent polyamine Pentaethylenehexamine (PEHA) and studied for Lanthanum (chosen as representing element of REs family) adsorption and release. The obtained results will be part of the basis for the implementation of a pilot plant by September 2015 where the solid sorbents could work both as recovering, both as finishing purifying materials.

2. Materials and methods

STx-1b, STx in the following, is a standard smectite mineral clay, in particular a Ca-montmorillonite (supplied by the Clay Mineral Society). The polymer used as intercalating agent is a Pentaethylenehexamine (PEHA in the following), whose formula and properties are reported in Table 1. It was supplied by Sigma-Aldrich. Lanthanum(III) nitrate pentahydrate and nitric acid ACS reagent, both of them from Sigma-Aldrich, were the other reactants used in this study. Deionised water was also used as solvent throughout the whole study.

Table 1: Structure and properties of Pentaethylenehexamine (PEHA)

Name	Structure	Molecular Weight (g/mol)	pH	Density at 25 °C (g/mL)
PEHA		232	11	0.96

2.1 Hybrid clay materials preparation: intercalation of polymer

The first procedure consists in converting pristine STx in an organophilic system, with the intercalation of a pre-determined amount of PEHA inside the clay. Both the procedure and the operating conditions have been already examined in previous works (Zampori et al., 2010) and therefore the same pattern is followed in this study. Initial amine concentration is imposed to be 35 mM, 90 mM, 180 mM and 270 mM and the organic phase is diluted with 50 mL of deionised water, with no variation in the pH, always 11. Then a fixed amount of clay, 2.5 g, is contacted with the liquid phase inside a jacketed reactor: reaction time is 90 min and temperature is kept constant to 30 °C through a thermostat. Water is the heating fluid that is employed for this operation. Moreover, the solution is continuously stirred at a rate of 500 rpm, in order to guarantee uniform conditions for what concerns both the temperature and the material exchange. A centrifuge (Hettich ROTOFIX 32) separates the liquid from the solid; centrifugation is carried out for 15 min at 3,500 rpm. The wet organo-clay is dried for about 12 h in environmental conditions, then is milled, analysed by XRD and ready to be used for the next procedure. The solutions are further analysed by COD and ICP-OES.

In the following the samples will be labelled as follows: the clay STx, the polymer PEHA, and the initial polymer concentration: e.g. STx-PEHA-35.

2.2 Uptake and release

The uptake is the operation of capturing, selectively or not, some ions by using a solid sorbent. For what concerns this work, the purpose was collecting Lanthanum from liquid solutions. Lanthanum nitrate has been dissolved in deionised water: concentration is fixed to 19 mM per 50 mL of solution, with a pH around 5. Molarity was determined in previous works and was evaluated as similar to the amount of Rare Earth that

could be found in some leached scraps, in particular in NdFeB magnets from hard-disks (Donelli and Girolimetto, 2014). A constant amount of organo-clay, 2 g, is then mixed with the solution prepared: the system is kept in continuous agitation for 90 minutes by means of a stir bar immersed in it. The adsorption contact time was fixed at 90 min since in a previous work (Iannicelli Zubiani et al., 2013) it was found as the equilibrium time: slow enough to be sure of the equilibration between solid and solution and fast enough to avoid Lanthanum extraction at this step. All the systems, during the uptake step, reached a pH around the values of 6 or 7. A centrifuge was used for solid-liquid separation.

The further step is the release of the captured Lanthanum, in order to evaluate the recovery capability of the process. A previous work (Donelli and Girolimetto, 2014) studied the effect of pH onto the release mechanism and found out that acid conditions correspond to the best operative ones. So a fixed amount of clay, 1.3 g, has been added in a solution of 50 mL which is brought at a pH of about 1 through the addition of 3.15 g of HNO₃. The solution is continuously stirred for 90 minutes at room temperature and then the liquid is separated from the solid through centrifugation. Powders are then analysed by XRD techniques, while the liquid is characterized by ICP-OES procedure

2.3 Characterization techniques

X-ray diffraction measurements were carried out on powder samples with a Bruker D8 Advance diffractometer using graphite monochromated Cu-K α radiation; the scan step was 0.02° 2 θ and the measurement time 1 s per step. The XRD line profile analysis was performed with TOPAS P software using a Pearson VII profile function after background correction. The calculated profiles were used for the determination of basal spacing d_{001} .

Quantitative analysis of intercalated polymer was determined by COD analysis (Spectrodirect Lovibond) according to the ASTM D1252-06 standard method. Samples have been oxidized with pure air at 150 °C for 120 min.

The metal-ion concentrations were measured by an Optima 2000DV inductively plasma optical emission spectrometer (Perkin Elmer).

3. Results and discussion

3.1 Interaction mechanism between clay and polymer

The XRD spectra of all the organo-clays are reported in Figure 1, STx is also reported for comparison.

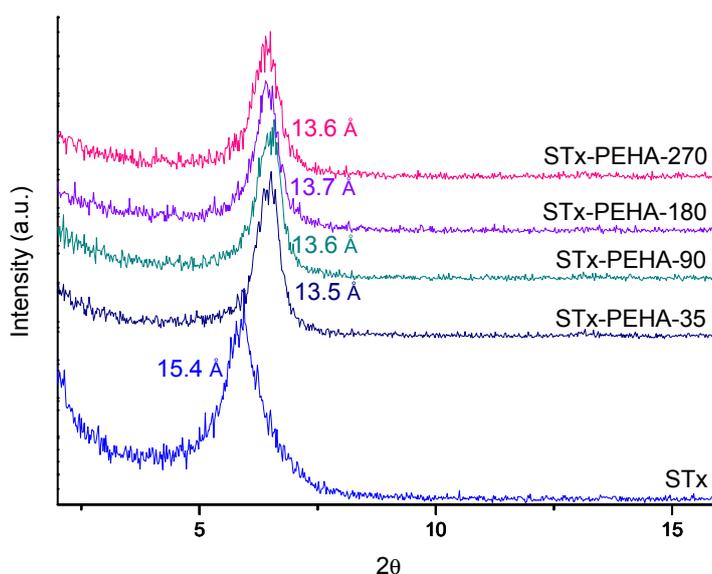


Figure 1: XRD analyses of the organo-clays prepared at different initial PEHA concentrations: 35 mM, 90 mM, 180 mM, 270 mM

A displacement of the basal reflection of STx towards higher angles, corresponding to a shrinkage of the interlayer, is observed. This effect can be due to a strong clay-polymer interaction in view of the number of amino-groups of the chain. Anyway, no variation in the d_{001} values was found while increasing the polymer content in the clay.

The amounts of intercalated polymer as a function of the initial polymer concentration are reported in Figure 2. A linear correlation is found, evidencing that the amount of intercalated polymer can be increased just increasing the initial molar concentration. Moreover, no asymptotic value has been achieved yet, suggesting that the 270 mM concentration is not enough to saturate the clay intercalation capability. Thus, the amine concentration could further be increased, if required.

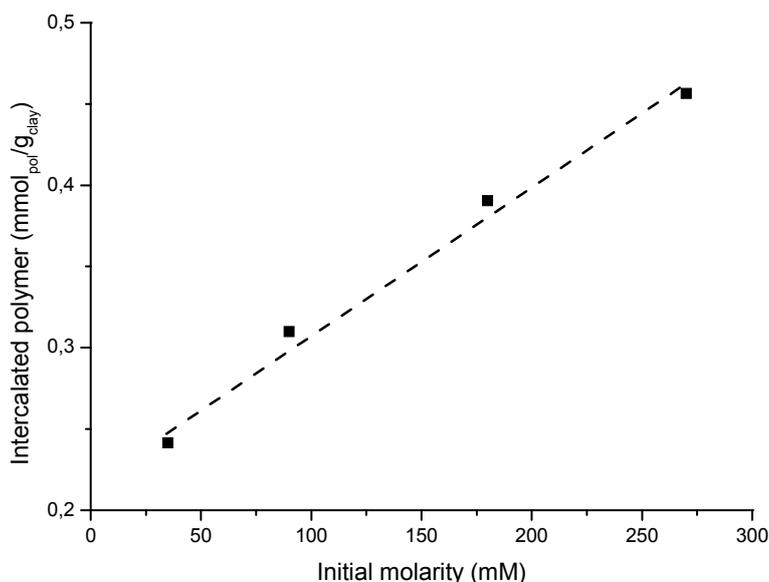


Figure 2: Intercalated polymer as a function of the initial PEHA concentration

The mechanism of interaction between the clay and the amine has also been analysed. According to ICP analyses, no evidence of Ca and Mg ions (interlayer cations of STx) was found in the solution after the intercalation reaction and, in view of the contacting pH of 11, no ions exchange occurred. Thus the polymer interacts with the interlayer environment in its neutral form: this form is that of selection for the final application.

3.2 Lanthanum uptake, release and global process

The organo-clays prepared with the four initial concentrations were contacted with a 19 mM Lanthanum model solution and then, for each sample, Lanthanum release was performed. All the efficiency values are plotted in Figure 3.

The Lanthanum uptake achieves values of 99 % that, compared to the uptake efficiencies of about 50 % obtained with pristine clays (Iannicelli Zubiani et al., 2013), results in a huge improvement.

The higher is the amine content in the organo-clay, the larger is the amount of captured Lanthanum. In particular, the amount of captured Lanthanum increases with a non-linear trend on increasing the intercalated amine until reaching a plateau value. However, in this case, it is evident that the chosen Lanthanum nitrate initial concentration could not be principally enough for saturating the organo-clay adsorption capability.

The release process has also been evaluated and results are always reported in Figure 3, together with those calculated for the global process. The release process shows a linear behaviour characterized by constant values of efficiency: the release trend can much be due to the low pH of the release solution (pH 1) rather than some effects of the organo-clay composition. However, 70 - 90 % of the Lanthanum is recovered and also in this step a strong improvement is obtained, considering the values of release efficiency of 30 % obtained with natural clays (Iannicelli Zubiani et al., 2013). As expected, the efficiencies of the global process just reflect the behaviour of the other two processes: the global efficiency increases with the intercalated amine content even

though a linear trend can only be evidenced in the first part of the curve. Nevertheless, the plateau value is clearly due to the total uptake of the contacted Lanthanum ions and apparently not to a saturation effect. Regarding the application of interest, the global efficiency of all the studied samples evidenced that a polymer content lower than $0.4 \text{ mmol}_{\text{polymer}}/\text{g}_{\text{clay}}$ is not enough for the total recovery process of a 19 mM Lanthanum containing solution.

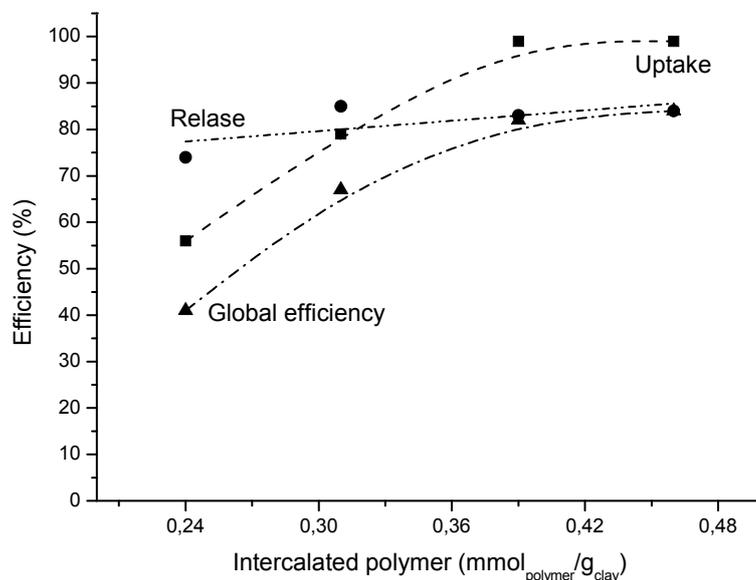


Figure 3: Uptake, release and global efficiencies as function of the intercalated polymer at the different initial concentrations: 35 mM, 90 mM, 180 mM and 270 mM

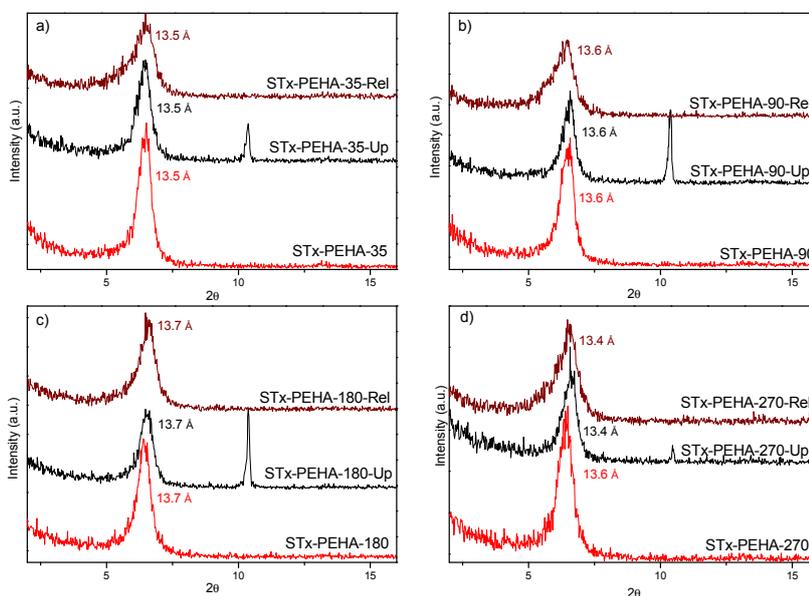


Figure 4: XRD analysis after uptake/release of Lanthanum ions for: a) STx-PEHA-35 b) STx-PEHA-90, c) STx-PEHA-180 d) STx-PEHA-270

Moreover, XRD analyses have been performed before and after both uptake (label Up) and release processes (label Rel): data are compared in Figure 4. No effects of the presence of Lanthanum were found. The

positions of the basal reflection before and after uptake and release steps are unchanged. Some differences can be pointed out regarding the asymmetry developed by the reflection, mainly after the release process. Nevertheless, these modifications could be explained by different hydration levels of the material, as already observed in pristine clays (Donelli and Girolimetto, 2014). Another peak for 2θ values of 10, in addition to the basal reflection of the clay, is detected in every case after Lanthanum uptake and it is due to the presence of precipitated Lanthanum Carbonate.

4. Conclusions

The following conclusions can be drawn:

- new materials were synthesized starting from a solid matrix and a liquid chelating polymer: the experimental procedure was proved to be appropriate to intercalate the polymer PEHA in the clay and the mechanism of interaction was supposed to not involve ion exchange;
- the amount of intercalated polymer could be enhanced increasing the initial molar concentration and no asymptotic value was achieved: thus, the amine concentration resulted to be further increasable;
- the obtained organo-clays were effective in both uptake (efficiencies up to 99 %) and release processes (efficiencies around 80 %); the high efficiencies in the uptake step suggest the possibility to use these innovative materials as finishing purifying materials for waste water treatment;
- the modified clay having a minimum content of $0.4 \text{ mmol}_{\text{polymer}}/\text{g}_{\text{clay}}$ ensured a global process efficiency of more than 80 %, meaning more than 80 % of Lanthanum recovery.

So, the studied clay-polymer system seems promising for the proposed application.

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