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EFFECT OF pH IN THE SYNTHESIS OF ORGANO-CLAYS FOR RARE EARTHS REMOVAL

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Abstract

Two montmorillonitic clays were modified with N-(methoxy-polyethylene glycol) ethylene diamine and tested as sorbents for removal of Rare Earths (REs) from aqueous solutions. Lanthanum was chosen as representing element of REs family and adsorption tests were performed with the aim of selecting a system with good uptake efficiency for the pollutant abatement in wastewaters. The effects of pH were studied and the properties of the obtained final materials were evaluated with simple model systems of the final application. The modified clays were characterized before and after the intercalation, combining the results of X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR), whereas the solutions were analysed by means of Chemical Oxygen Demand to quantify the amount of intercalated polymer and by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) to quantify the metal ions concentration. The results showed that the organo-clays have been efficiently prepared while the characterization techniques showed that the intercalation mechanism was strongly dependent on the pH of the preparation procedure, affecting the protonation of the amino groups.

Key words: environmental remediation, FT-IR spectroscopy, organo-clays, rare earths removal

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1. Introduction

Adsorption has become one of the main treatments for heavy metals removal, due to its versatility, wide applicability, and economic feasibility (Ajmal et al., 2015, Ganjali et al., 2004, Jamali et al., 2007; Tsekova et al., 2015). Indeed, technical applicability and cost-effectiveness are the key factors in the selection of the treatment technology. One of the open points regarding adsorption technology is related to the kind of solid matrix used. 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 environmentally friendly themselves (Janos et al., 2016; Sheikhi et al.,

2015). In the above scenario, clays have been suggested as a green alternative (Dikmen et al., 2015; Sen Gupta and Bhattacharyya, 2014) being characterized by low cost, high mechanical intensity, good tolerance towards harsh chemical environment, convenient solid-liquid separation and excellent reusability. Furthermore, clay minerals show a well-known adsorption behaviour towards metals (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 resources exploitation. In this perspective, the study of adsorption mechanisms related to heavy metals with valuable interest and

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reutilization possibility could be worthwhile. REs correspond to these qualities: their limitation in wastewater is unregulated (Westerhoff et al., 2015) but only because insufficient data about their toxicity to human health are available (Fuad et al., 2013). Furthermore, REs are also added value elements since their demand is constantly increasing in the global market, due to the new technological applications that exploit these materials for their unique properties (Iannicelli-Zubiani et al., 2013).

The use of natural clays in treating aqueous wastes containing heavy metals and organic matter has been previously reported in other works (Sen Gupta and Bhattacharyya, 2014) and has been deeply investigated by the authors for REs recovery from aqueous wastes (Iannicelli-Zubiani et al., 2015). The obtained experimental results (Iannicelli-Zubiani et al., 2015) showed that two pristine clays, belonging to montmorillonite group, were able to capture and release La and Nd ions, by means of an ion exchange mechanism; in view of these results the use of suitably modified clays was proposed in order to enhance the recovery of REs. Smectitic clays, indeed, such as hectorite and montmorillonite are layered aluminosilicates that can be modified by intercalating agents in the interlayer through a combination of ionic and weaker forces (Malakul et al., 1998). As modifying agent, N-(methoxy-polyethylene glycol) ethylene diamine was selected, being characterized by a polyethylene-glycol chain able to intercalate in the clay interlayer (Zampori et al., 2010) and by two amino groups, already reported in the literature for the removal capability towards heavy metals (Gao et al., 2015). For all these reasons, the present work focuses on the adsorption of lanthanum, chosen as representing element of REs family, from aqueous solutions, performing adsorption tests using two suitably modified mineral clays with the aim of selecting a system with good uptake efficiency for the pollutant abatement in wastewaters.

Although the preparation procedure here proposed is quite easy, at least from the experimental point of view, of course the knowledge of the effect of any operative parameters, such as pH, is fundamental to handle the properties of the final material, thus its performance. Therefore, the effects of pH were studied and the properties of the final materials thus obtained were evaluated with simple model systems of the final application. The modified clays were characterized before and after the intercalation, combining the results of X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR), whereas the solutions were analysed by means of Chemical Oxygen Demand to quantify the amount of intercalated polymer and by

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) to quantify the metal ions concentration.
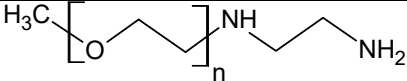
2. Experimental

2.1. Materials

Two natural smectite samples were used, 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 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). The Cation Exchange Capacity (CEC) of the clays was determined according to the ammonium saturation procedure proposed by Chapman at pH 7, resulting 120 meq/100 g for STx clay and 240 meq/100g for SWy (Kühnel, 1990). The main differences between the two used clays are the CEC values and the interlayer cations: STx is a calcium montmorillonite while SWy is a sodium montmorillonite. In this way it should be possible to observe potential different behaviours having interlayer cations with different: oxidation states, charges, dimensions.

A N-(methoxy-polyethylene glycol) ethylene diamine (AM in the following, supplied by Bozzetto Group) was used as modifying agent, whose formula and properties are reported in Table 1. AM is a yellow viscous liquid material at room temperature, soluble in water. Together with clays and polymer, the reactants used in this study were lanthanum nitrate (La(NO$_3$)·5H$_2$O 99.99%, Sigma Aldrich), HNO$_3$ (ACS, Sigma Aldrich), and deionized water.

2.2. Hybrid-clay materials preparation

Organo-clays (Finocchio et al., 2011, Zampori et al., 2012) were obtained according to literature(Iannicelli-Zubiani et al., 2017), via an intercalation reaction. In a typical experiment, 2.5 g of clay were mixed, in a jacketed reactor under vigorous stirring, with 50 mL of aqueous polymer solution for a fixed time of 90 min (Zampori et al., 2010). The initial polymer concentration was fixed at 30 mM (initial polymer/clay ratio = 0.7 g/g), considered enough to potentially remove all the lanthanum ions put in solution, being the amino group number three times higher than the contacted lanthanum. All the experiments were carried out at the controlled temperature of 30°C.

Table 1. Main properties of polymer AM

Label	Formula	Structure	MW	pH
AM	H$_3$C(OCH$_2$CH$_2$)$_n$NH(CH$_2$)$_2$NH$_2$ n = 25		1174	11

The pH of the solution was measured before and after the reaction using a Mettler Toledo FE20/EL20 digital pH-meter. The initial pH of the polymer solution was about 11. In order to evaluate the effect of the contacting pH on the intercalation reaction, this parameter was varied from 11 to 1 by stepwise addition of nitric acid to the initial polymer solution, and it was monitored throughout the preparation. At the end of the reaction, the solid phase was separated by the aqueous one using a centrifuge (HETTICH 32 RotoFix, 3500 rpm for 15 min). The amount of the reacted polymer was found as the difference of the polymer concentration, determined by COD (Chemical Oxygen Demand) analysis, in the aqueous solution before and after the intercalation experiment. The solid, upon drying (one day at room temperature), was ground in a mortar and fully characterized as reported in the following.

2.3. Adsorption tests on model solution: lanthanum ions uptake

2 g of the synthesized organo-clays (in the following STx-AM, SWy-AM) were contacted with 50 mL of an aqueous solution of $La(NO_3)_3$ at known concentration, vigorously stirred at room temperature and separated from the aqueous using a centrifuge.

2.4. Characterizations

The Chemical Oxygen Demand (COD) analyses were carried out using a Spectrodirect Lovibond instrument. In a standard instrumental procedure the unknown sample was oxidized by heating for 120 min at 150 °C (ASTM, 2006).

All the metal ions concentrations in solutions were measured by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analyses using a Perkin Elmer Optima 2000DV spectrometer. The measurement error is estimated to be 1%.

X-ray powder diffraction (XRPD) patterns of clays were recorded after each step of the recovery process with a Bruker D8 Advance diffractometer using graphite monochromated Cu K_α radiation; the scan step was 0.02° 2θ and the measurement time was 1 s per step. The XRPD line profile analysis was performed with TOPAS P 2.1 software (Bruker AXS, Karlsruhe, Germany) using a Pearson VII profile function, after background subtraction. The calculated profiles were used for the determination of basal spacing (d_{001}) of the clays. FT-IR analyses (mid-IR region) were performed on the powders with a FT-IR Thermo Nicolet 380 Avatar using the KBr pressed disk technique.

3. Results and discussion

3.1. Organo-clays preparation

Different organo-clay samples were prepared contacting the clay with a polymer solution at constant initial polymer concentration (30 mM, corresponding to a polymer amount of 0.6 mmol/g) but different pH, namely 1, 5, 8, and 11. In the following these samples will be identified by a label indicating the type of clay and the initial pH of the polymer solution: e.g. STx-AM1 is the organo-clay synthesized using STx and a polymer aqueous solution at pH 1.

The amount of the reacted polymer as a function of initial pH is reported in Fig. 1. During the contacting reaction, the presence of the clay did not influence the pH value of the mixture: the actual pH of the suspensions rapidly reached the pH value of the polymer solutions and kept constant throughout the experiments. However, the reaction pH influenced the total amount of the intercalated polymer, and this effect was exerted in different extent depending on the clay nature: indeed, at acid pH, larger amount of polymer interacting with the clay was found (70% of the initial one in case of SWy, to be compared with 35% measured for STx). Anyway, when the reaction was performed at pH ≥ 8 for STx and at pH ≥ 5 for SWy a marked decrease in adsorption capacity of polymer was found. This difference could be related to the CEC of clays and to the superficial charge of particles. The difference between the two systems became smaller on increasing pH, until reaching very close contents of polymer (about 30 and 25% for SWy and STx, respectively) when the intercalation is performed at pH 11.
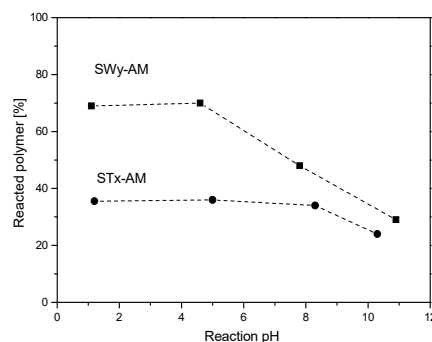

Fig. 1. Intercalated polymer as a function of the reaction pH

Accordingly, the same intercalation mechanism can be supposed for both the clays and the intercalation efficiency can be correlated specifically with pH, with a particular effect of the basic environment. Considering that the amino groups of the polymer are possibly more stable in the amine form at basic pH, the observed behaviour could be related preferentially to the nature of the polymer than to the nature of the clay. The effect of pH could be explained if the polymer speciation at the different pH is taken into account together with the polymer-clay interaction mechanism. It is well known that amino groups are largely influenced by pH: depending on their pK_a, they could be present in

solution both as amine or protonated amino groups. The interaction of the polymer with the clay interlayer can occur via two possible mechanisms: i.e. intercalation by ionic exchange and intercalation by other bonds not involving cations exchange, such as, for instance, H-bonding with water in the hydration shells, ion-dipole interactions, coordination between the oxygen atoms of the PEG segments of the polymer and the interlayer exchangeable cations (Deng et al., 2006). The ionic exchange mechanism implies the presence of a charged organic molecule partially or totally replacing the interlayer cations via a charge compensation mechanism. Otherwise, the intercalation occurs via weaker interactions between some functional groups of the uncharged polymer and the interlayer environment (e.g. cations, water molecules). Hence, no permanent charges are involved (Chiu et al., 2013). Of course, both ion exchange intercalation and intercalation not involving ion exchange could be co-present in view of the nature of the intercalating molecule. Accordingly, the presence of protonated amino groups on the polymer should drive the reaction preferably towards the ion exchange mechanism, while the weaker interaction becomes active in the absence of charged species. Therefore, according to our results, at very low pH values, where the polymer amino groups are mainly present as ammonium ions, the ion exchange reaction will be preferred; while in basic environment, where only the neutral amine is available for the reaction, the intercalation based on weak bonds will be the main process. In between, where the polymer could be partially protonated, both the mechanisms could account for the intercalated polymer, thus mixed and quite complex interactions will result from the contacting reaction.

The extent of the intercalation reaction can be quantified on the bases of the reacted polymer via COD analysis, but this technique, accounting for all the polymer inside the clay, is unable to discriminate between the intercalation via exchange mechanism or not.

The exchange reaction, instead, can be directly evaluated analysing the ionic composition of the solutions after the contacting experiments. In presence of an ion exchange reaction, part or total of the interlayer cations should be found in the solution after the contacting reaction, having been replaced by the interacting molecules. Therefore, ICP-OES analyses were performed on the solutions after the contacting reaction at different pH, their results are summarized in Fig. 2.

First of all, ICP analyses were consistent with the interlayer composition of the pristine clays since, in the case of STx, calcium and magnesium were found, while for SWy large amounts of sodium were primarily present. Moreover, the pH of the reacting polymer solution had a marked effect on the release of the interlayer ions: not surprisingly, the lower the pH the larger the amount of the exchanged cations. Therefore, it can be assumed that the interlayer cations have been replaced by the charged polymer.
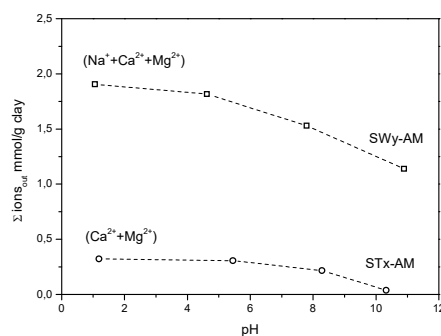

Fig. 2. ICP-OES analyses of the solutions after the intercalation reaction at different pH

Comparing Fig. 1 and 2 it is evident the strong correlation between the intercalated polymer and the replaced cations: in the case of SWy, the amount of intercalated polymer is higher compared to STx and this fact is confirmed to be linked to the higher amount of exchangeable ions in the interlayer (CEC of SWy 2.45 mmol/g of charge compared to 1.24 mmol/g of charge for STx). In both the clays, increasing the pH, the amount of cations in the solution after intercalation progressively decreased. In the case of STx, this amount goes down to near zero (at about pH 11), confirming that no exchange has occurred at alkaline pH (Fig. 2). The close similarity of the two clays at high pH (see Fig. 2) can be related once more to the nature of the amino groups. Indeed, at high pH, where the polymer is primarily intercalated without ion exchange, the similar amounts of polymer that were intercalated were just depending on the interlayer expansion capability of the clay.

For both the clays it can be concluded that at low pH the intercalation via ion exchange mechanism is predominant, while at high pH intercalation without exchange is the main reaction.

So, the following picture can be drawn. At alkaline pH, where the amine is not protonated, the intercalation based on weaker bonds is the prevailing mechanism, while on decreasing pH, the amino groups are progressively protonated and the exchange reaction becomes the most likely. At intermediate pH it is difficult to find out a priori the predominance of one on the other owing to the complexity of the system. In any case, the condition of ion exchange, even partial, is not good for the intended application. As already pointed out, the protonated amine is expected to be less effective for metal ions uptake purposes since the amino groups, i.e. the coordinating functions, are involved in bonds or interactions with the interlayer environment, thus the coordinating effect is lost.

Also the study of the solid phase is of considerable importance. The XRD results are shown in Figs. 3a and b. For both clays a shift towards lower angles (thus larger interlayer dimensions) of the basal reflection position (d_{001}) was evident. This effect was much more manifest in the case of STx, where the

position of the basal reflection can be clearly identified.

SWy is characterized by a very broad, low intensity basal reflection, not clearly detectable in Fig. 3. The sharpness and intensity of the basal spacing are related to the degree of order of the interlayers and the particle size, therefore the as-received SWy clay seems to have a particularly disordered state. Anyway, line profile analysis performed on the broad reflection allowed to roughly model it with two basal spacings at about 12 Å and 10 Å (Iannicelli-Zubiani et al., 2015). So, also in the case of SWy the same enlargement of interlayer dimension could be hypothesized if the poorly evident spectrum modulation centred around 7 (2θ) is considered as d_{001} in the pristine clay.
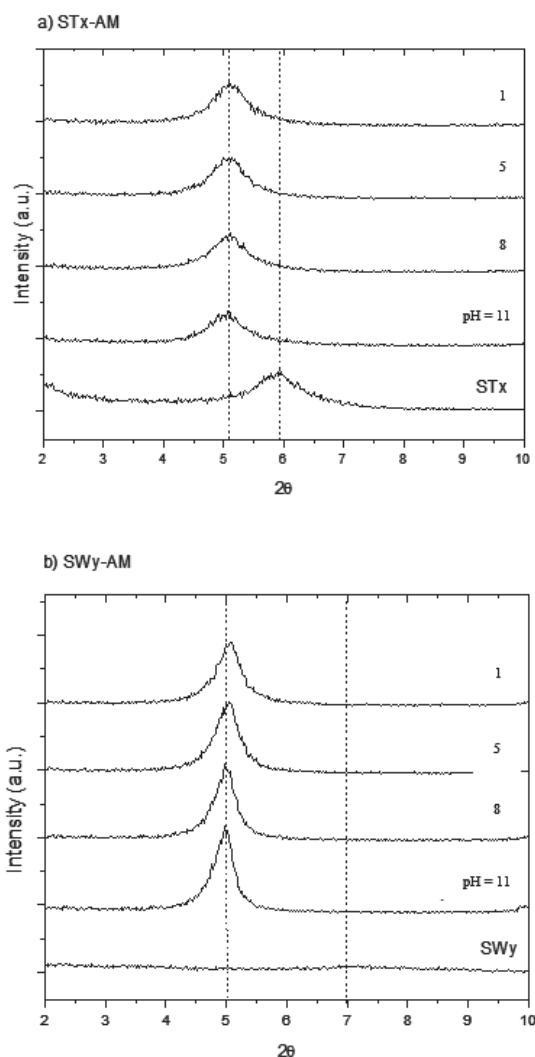

a) STx-AM

b) SWy-AM

Fig. 3. XRD analyses of organo-clays obtained at different pH values: a) STx-AM and b) SWy-AM (pristine STx and SWy here reported for comparison).

In the STx-based system (Fig. 3a), in addition to the reported displacement of the d_{001} from 15.4 Å to 17.6 Å, no other remarkable effects were seen. The d_{001} enlargement arises just from the allocation of the polymer inside the interlayer (Finocchio et al., 2014, Zampori et al., 2010), but it does not depend on the

pH environment as evidenced by the constancy of the d_{001}. Conventional XRD was not helpful for the evaluation of the polymer nature inside the clay possibly due to the fact that from the dimension point of view, no appreciable differences are present between an intercalated exchanged or not-exchanged polymer. Moreover, no particular ordering effects were observed in the STx-AM system: large and slightly asymmetric reflections were present at any pH values. It is reported in the literature (Brown and Brindley, 1980) that the sharpness and intensity of the basal spacing are related to the degree of order of the interlayers and the particle size. The absence of an ordering effect suggests that the polymer filled the interlayer in a quite random way without any preferential allocation site. The observed reflections asymmetry is also an indication of a random filling of the interlayers. Indeed, a random filling of the interlayers could result in a random d_{001} distribution, thus in the asymmetry of the corresponding XRD reflection.

A similar behaviour was found in the case of the SWy-based system, where no particular effect of the pH was present (Fig. 3 b), thus a constancy in d_{001} was detected also in these samples. On the contrary, the polymer amount allocated in SWy was strongly dependent on pH and higher than STx (up to 70% of the initial polymer contacted with the clay, as reported in Fig. 1). An ordering effect of pH is instead found in SWy-AM samples: upon the contacting reaction the XRD spectra showed the presence of sharp and quite symmetric d_{001} reflections at any pH value. The progressive ordering of the interlayers in presence of acid or basic environment was already observed and reported in the literature (Bieseki et al., 2013, Chalghaf et al., 2013) and by the authors (Iannicelli-Zubiani et al., 2015) for pristine SWy. Depending on the considered pH, the partial or total replacement of cations in the clay interlayer with protonated water molecules or basic species was considered responsible for the d_{001} sharpening (Iannicelli-Zubiani et al., 2015).

In further studies it could be useful to relate this sharpening of the d_{001} reflection to the amount of intercalated polymer and to the homogeneity of the polymer orientation in the clay gallery. Similar effects can be put forward to explain the observed behaviour in the presence of the polymer. This is not surprising in the case of STx, where almost a constant amount of polymer was allocated in the structure (Fig. 1). On the contrary, it is hardly understandable in the case of SWy, where the intercalated amount of polymer at low pH was found more than double with respect to high pH. The constancy of d_{001} values in SWy-based samples could be explained either with a planar configuration (Chiu et al., 2013, Deng et al., 2006) of the polymeric chains inside the interlayer or with the presence of some polymer interacting with the external surface of the clay.

Accordingly, the observed enlargement (about 17.5 Å) could account only for the maximum amount

of polymer allocable inside the interlayer. A priori this hypothesis cannot be discarded either in case of the STx-based system.

An attempt to understand which polymer form, ammonium or amine, was interacting with the clay, FT-IR spectra were recorded on the solids. Results are reported in Fig. 4 for the STx-AM and SWy-AM samples prepared at pH 1 and pH 11. The overall IR spectra of both STx and SWy based materials show bands due to the clay matrix together with bands due to the organic component. In the high frequency region, the band at 3625 cm^{-1} detected in all the samples is assigned to stretching vibrational mode of inner OH groups, characterizing montmorillonite clay (Madejová, 2003). The spectra of organo-clays also show another weak shoulder at 3675 cm^{-1}, whose assignation is still doubtful, possibly due to hydroxyl groups of the clay matrix modified by the preparation procedure itself. In the samples prepared at pH 11 the NH stretching mode of the amine groups appears as a weak and broad band at 3260 cm^{-1}, overlapped with the band of H-bound hydroxyl groups. Moreover, in this spectral region, both STx and SWy based hybrid materials

show bands typical of the polymer alkylic chain: a complex absorption centred at 2885 cm^{-1} with a shoulder at 2950 cm^{-1}, both components to be assigned to the CH stretching modes of the CH$_2$ units. In the low frequency region, beside the main and complex absorption below 1200 cm^{-1} due to Si-O and OH deformation/stretching modes of the clay matrix, several weak bands can be assigned to the AM chain. In particular, bands at 1470, 1455 (asymmetric CH$_2$ deformation modes), 1355 and 1250 cm^{-1} (CH$_2$ wagging and twisting modes), as well as bands at 950 and 845 cm^{-1} (CH$_2$ rocking modes) are due to the PEG-type chain (Finocchio et al., 2011). As for the amine group, at pH 11 the NH deformation mode can be detected at 1620 cm^{-1}, although strongly overlapped with the band due to the adsorbed molecular water. Bands at 896 and 823 cm^{-1} are also characterizing the amine moieties. Decreasing pH down to 1 results in the detection of a new weak IR band at 1530 cm^{-1}, which could be due to the protonated form of the amine (symmetric –NH$_3^+$ deformation mode), whose corresponding asymmetric deformation mode is expected at 1630 ca. (Fig. 5), thus masked by molecular water absorption.
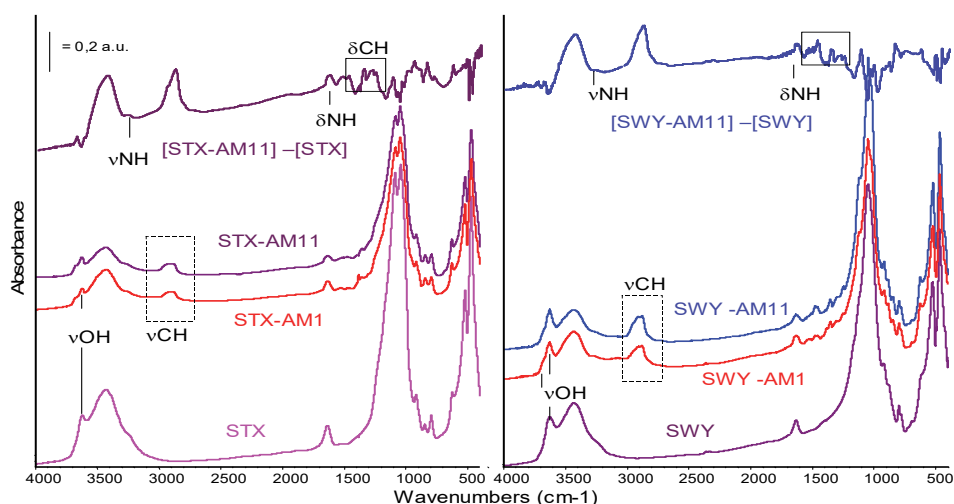

Fig. 4. FT-IR skeletal spectra of the STx and SWy series samples. Insets: subtraction spectra
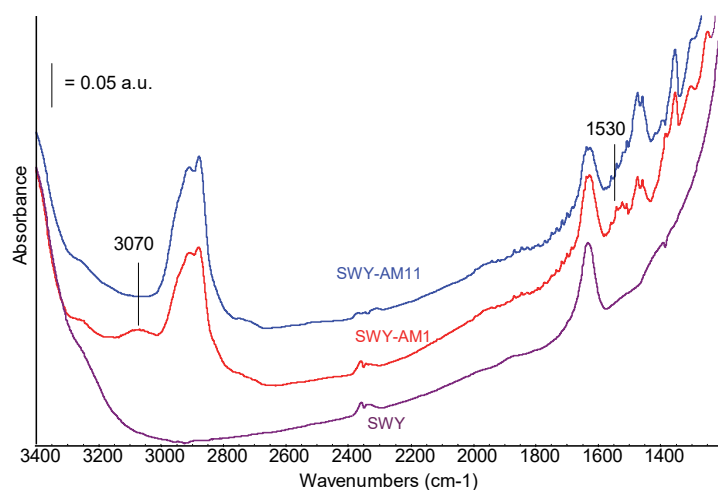

Fig. 5. FT-IR skeletal spectra of the SWy series samples. Insets: subtraction spectra

Correspondingly, another component is appearing at 3070 cm^{-1}, which can be assigned to the $-NH_3^+$ stretching mode (Colthup, 2012). On the other side, even at such a low pH, we have still some evidence of free NH/NH_2 groups (for instance, the broad absorption at 3250 cm^{-1} and the band at 1620 cm^{-1}). These data should confirm the protonation of at least a fraction of AM polymer, in agreement with the proposed interaction mechanism. Moreover, it is worth noticing that the spectra features assigned to the protonated AM are slightly more evident in the spectrum of SWy-AM1 sample, than in the spectrum of STx-AM1 sample.

3.2. Uptake capability towards a La ions model solution

In order to evaluate the effectiveness of the prepared organo-clays towards REs recovery, the new materials were tested by contacting with a La-based model solution and their capability of uptake towards these ions was evaluated. Starting from 19 mM La model solutions (corresponding to 0.48 mmol/g$_{clay}$), the amounts of adsorbed lanthanum ions are reported in Table 2. It is evident that all the organo-clays are effective in La^{3+} uptake, but with different uptake efficiencies. Such efficiencies are much more related to the nature of the intercalated amine than to its total amount. It is indeed evident in Fig. 6, that STx-AM1 and SWy-AM1, i.e. prepared at pH 1, presented quite a low uptake (both about 0.15

mmol/g), despite the large polymer content (0.43 and 0.78 mmol/g for STx-AM1 and SWy-AM1, respectively). This behaviour is even more stressed when considering the SWy-based system, where twice the polymer content did not correspond to a double La uptake.

These results have to be compared with those obtained for the organo-clays prepared in basic environment (STx-AM11 and SWy-AM11) where, although they contain at least the half of the polymer of the samples prepared in acid conditions, could account for, more or less, twice the lanthanum ions uptake.
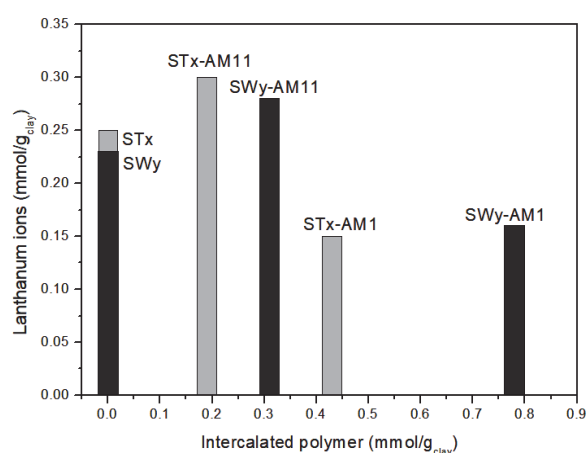

Fig. 6. Lanthanum uptake as a function of polymer content and pH

Table 2. Lanthanum uptake efficiencies

Sample	pH	Uptake (mmol/g)	Uptake (%)
STx-AM1	1	0.15	31
STx-AM5	5	0.15	31
STx-AM8	8	0.17	35
STx-AM11	11	0.30	62
SWy-AM1	1	0.16	33
SWy-AM5	5	0.17	35
SWy-AM8	8	0.19	39
SWy-AM11	11	0.28	58

Table 3. Lanthanum uptake efficiencies

Sorbent	Measured adsorption capacity (mmol/g)	References
Organo-clay STx-AM11	0.30	This study
Montmorillonite STx	0.25	(Iannicelli-Zubiani et al., 2015)
Montmorillonite SWy	0.23	(Iannicelli-Zubiani et al., 2015)
Bentonite	0.26	(Chegrouche et al., 1997)
Na-bentonite named GMZ bentonite	0.19	(Chen et al., 2012)
Sargassum biomass	0.52	(Palmieri et al., 2002)
Sargassum polycystum Ca-loaded biomass	0.90	(Diniz and Volesky, 2005)
Leaves powder of Platanus orientalis	0.19	(Sert et al., 2008)
Iron oxide loaded calcium alginate beads	0.89	(Wu et al., 2010)
2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester-grafted magnetic silica nanocomposites	0.40	(Wu et al., 2013)
Micro algal cells	0.72	(Birungi and Chirwa, 2014)
Granular hydrogel composite	2.40	(Zhu et al., 2014)
Lewatit TP 214 Resin	0.28	(Ferrah et al., 2014)
Polydopamine (PDA) membrane	0.43	(Hong et al., 2014)

These results can be explained on the basis of the polymer nature inside the organo-clays. In the materials prepared at low pH the amino groups are highly protonated, as demonstrated in the characterization section. Accordingly, the amino groups, that are supposed to exert the coordinating function towards the REs ions, are partially or at least totally deactivated by protons.Thus they are not available for the capture of positive charged ions as lanthanum ones. In conclusion, the nature of the intercalating polymer plays a major role than its amount and it is the parameter of interest to boost the process.

In Table 3 the obtained results were compared to the ones reported in literature for lanthanum adsorption, resulting interesting if compared with other clays or with other sorbent materials: only high specific and ad hoc synthesized composites as granular hydrogels are characterized by a strongly higher adsorption capacity but they are not natural materials and are characterized by high costs and syntheses issues.

4. Conclusions

Two families of organo-clay materials have been efficiently prepared, based on montmorillonite structure intercalated with N-(methoxy-polyethylene glycol) ethylene diamine.

The experimental procedure was proved to be appropriate to intercalate the polymer in the clay and the characterization techniques show that the intercalation mechanism is strongly dependent on the pH of the preparation procedure, affecting the protonation of the amino groups. Indeed, at alkaline pH the interaction is mainly based on weak bonds between the free amino groups of the organic moiety and the clay matrix and this is the required condition for the application of these materials in ions uptake. In this condition of pH 11 the obtained organo-clays were effective in lanthanum uptake (0.30 mmol/g and efficiency up to 60%), suggesting the possibility to use these innovative materials as finishing purifying materials for waste water treatment.

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

Acknowledgements

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