

USE OF REDUCED GRAPHENE OXIDE MEMBRANES FOR WATER TREATMENT CONTAINING Cu AND La IONS

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ABSTRACT

In recent years, the availability of drinking water, and in general of unpolluted water, has become a serious problem for many countries, and many efforts have been done to solve it. Different technological approaches have been proposed, among them liquid/solid adsorption has evidenced promising results. Several solids have been proposed as sorbent materials, however efficiency and selectivity towards metals capture are still open problems. In previous works, clays and activated carbons, pristine or modified with polyamines, have been studied. They were able to achieve interesting adsorption efficiency, but their properties were still not adequate to be applied at an industrial level. Therefore, the present work has been focused on the study of adsorption capability of reduced graphene oxide (rGO) membranes suggested in the scientific literature as promising solid sorbents for wastewater treatment. The experimental study has regarded the production of membranes of reduced GO, then their capture capability has been tested using La^{3+} and Cu^{2+} , considered representative of heavy metals pollutants. Quantification of ions uptake has been performed on both mono-ionic and bionic La and Cu solutions. Membranes before and after the capture process have been characterized by means of different techniques, such as XRD, FT-IR, Raman spectroscopy, optical and SEM microscopy.

1. INTRODUCTION

In recent years water availability issues have progressively gained prominence in view of their relationship with the three pillars of a sustainable development: i.e., economic, social and environmental. The World Water Development Report 2015, “Water for a Sustainable World” (coordinated by UNESCO’s World Water Assessment Programme (UNESCO, 2015)), clearly illustrates the complex relationships between water and critical areas of human development such as health, food (Recanati et al., 2017) and energy security (Hua et al., 2020), urbanization (Chang et al., 2020; Yuan et al., 2021), industrial growth and climate change. It is an undeniable fact that unsustainable development pathways have generated immense pressures on water resources, affecting its quality and availability and the Earth’s capacity to sustain the growing demands for freshwater is being challenged (Müller et al., 2020). Moreover, climate change will exacerbate the risks of variations in the distribution and availability of water resources (Gmitrowicz-Iwan et al., 2020). Also increasing industrial production will lead to increased water use, with potential impacts on water quality. In addition to that, competition for water between water “uses” and water “users” will lead to increasing difficulties and limits to the expansion of sectors critical to sustainable development, such as food production and energy, as for example, devoting agriculture to energy production (biofuel from food crops) (Hossain, 2020). In this competition, the need to maintain water- and ecosystem integrity in order to sustain life and economic development is of paramount importance. An ideal future where water resources are used sustainably for the benefit of all has not to be only a dream: it is therefore compulsory that the role of water has to be considered, when seeking a sustainable development. In this context, a reduced vulnerability, i.e., reduced risks and impacts of hazardous materials, is a crucial factor: water is a key

resource for industrial and manufacturing processes (e.g., heating, cooling, cleaning, rinsing, etc.), but generated wastewater can cause environmental damages when discharged untreated. Poor water management (especially wastewater management) not only leads to the degradation of ecosystems, but also results in higher costs and energy required for water and environment remediation. The increasing awareness about water preservation has resulted in more strict limits to wastewater contaminants concentrations. Indeed, the discharge of these compounds into the aquatic environment can affect all living organisms and the viability of that ecosystem is jeopardized for years. This effect is particularly remarkable if industrial effluents are not properly treated before their re-entry in natural water environment. Pollutants in water are generally heavy metals and/or organic molecules whose removal is compulsory, indeed. However, pollutants removal requires the application of complex and expensive processes, although essential (Calugaru et al., 2018; Kumar et al., 2019). The complexity and the cost of the treatments are much more pressing in case of very low disposal limits, low concentration of the contaminants and/or contaminants hard to be removed. Because of the heavy metals' high solubility in water environment, they can be absorbed by living organisms and therefore enter the food chain. Large concentrations of heavy metals may accumulate in the human body beyond the permissible concentration limits, thus causing serious health disorders (Amin et al., 2014). Currently used processes for heavy metals removal from inorganic effluents via conventional chemical precipitation, ion exchange and electrochemical removal have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge. Recently, to decrease the amount of wastewater produced and to improve the quality of the treated effluent, numerous approaches have been explored to develop cheaper and more effective technologies. In particular, adsorption has become one of the alternative treatments; in recent years, the search for low-cost adsorbents with strong metal-binding capacities has been pursued. Also, membrane operations and electro-treatments have been proposed, however their high costs justify their use only if really worth of it (Bienati, 2016; Chen et al., 2013). The basic approach can imply the direct contact of the solid and the liquid phases, but it also can be performed in a column, a cartridge, a tube or a disk containing the adsorbent that will retain the elements or species of interest. After adsorption, sorbent and retained materials can be sent to disposal or, alternatively, retained materials can be recovered and the sorbent regenerated by properly changing the operating conditions (Bienati, 2016; Iannicelli-Zubiani et al., 2017a; Koshal, 1976). Different sorbents have been applied for the purpose, such as carbon, activated carbon, silica gel, clay minerals, activated alumina and polymeric materials. In addition to these conventional materials, some new carbon materials, including carbon nanotubes, carbon nanofibers, graphene and graphene oxide, have been proposed in the literature to improve capacity in water purification (Bienati, 2016; Koshal, 1976). Among carbon-based materials, graphene oxide (GO) has attracted great interest because: 1) in view of its self-assembling property, GO can be used as a membrane, 2) the mechanical performances of the GO membranes are higher than those of the flexible graphite foils (Han et al., 2013), 3) in view of its chemical and morphological nature, GO shows excellent water permeation and molecular sieving properties, and 4) it exhibits an extremely high surface area. Considering all these properties, GO has attracted attention for use as pollutants' sorbent in the field of wastewater treatment. GO-based membranes have some advantages, not only because of the ease of preparation, but also in view of the high uniformity of pore size in the final membrane. In addition to that, by tailoring the pore size and/or the interlayer spacing, the structure and the properties of GO membranes can be modified. Among other strategies to enhance ions capture, GO reduction is one of the most promising. Indeed, GO can be theoretically reconverted back to graphene by reduction, but the reconstituted material, reduced graphene oxide (rGO), shows different and enhanced properties than those of graphene due to residual amount of GO functional groups that have not been reconverted during the reduction process (Compton and Nguyen, 2010). To reduce the graphene oxide different processes can be applied. Among others (Thakur and Karak, 2015), processes using natural-based reducing agents such as L-ascorbic acid, saccharides, amino-acids and proteins, hormones, heparin, or urea are the most environmentally friendly. In previous works, clays and activated carbons, pristine or modified with polyamines, have been studied (Iannicelli-Zubiani et al., 2018, 2017b, 2017a; Iannicelli Zubiani et al., 2015). They were demonstrated to be able to achieve interesting adsorption efficiencies, but not enough to be applied at industrial level. Therefore, the present work is focused on the study of adsorption capability of reduced graphene oxide (rGO) membranes, as promising

solid sorbents for wastewater treatment. In the paper, the production and the characterization of the membranes are reported, as well as results on capture capability tests performed on La^{3+} and Cu^{2+} ionic solutions. Quantification of ions uptake, performed by chemical analysis, and membranes characterization before and after the uptake process by different techniques are also reported and discussed.

2. EXPERIMENTAL

The GO-based membranes were prepared by vacuum filtration of a dispersion containing GO or rGO. The rGO dispersion was prepared according to (Migliavacca et al., 2017) by diluting a commercial GO dispersion (Graphenea) at a GO final concentration of 0.4 wt. %, followed by reduction with L-ascorbic acid (L-AA) (Sigma Aldrich) (GO/L-AA = 1/10 (wt./wt.)), for 72 h; after that, the resulting membranes are named rGO-72. The rGO dispersion was poured into a Gooch funnel, sealed with a PVDF membrane (Millipore), and then vacuum (water pump) was applied up to the formation of a 4 mg self-standing membrane.

The adsorption capability of the rGO towards ionic solutions was tested by contacting: 1) 50 mL of solutions containing La^{3+} , Cu^{2+} separately and 2) 50 mL of a solution containing both La^{3+} and Cu^{2+} in a 1/1 molar ratio. Solutions were poured directly onto the membrane and the liquid separated by vacuum filtration. Ions content before and after contacting steps were analysed by ICP-OES (PerkinElmer OPTIMA 7000 DV spectrometer). Capture efficiency (%) of rGO membranes was calculated by the difference between the initial ion concentration ($C_{0,i}$) and the residual one ($C_{f,i}$) after filtration (Eq. 1)

$$\eta(\%) = \frac{C_{0,i} - C_{f,i}}{C_{0,i}} \cdot 100 \quad (1)$$

Membrane preparation process and the adsorption step are sketched in Figure 1.

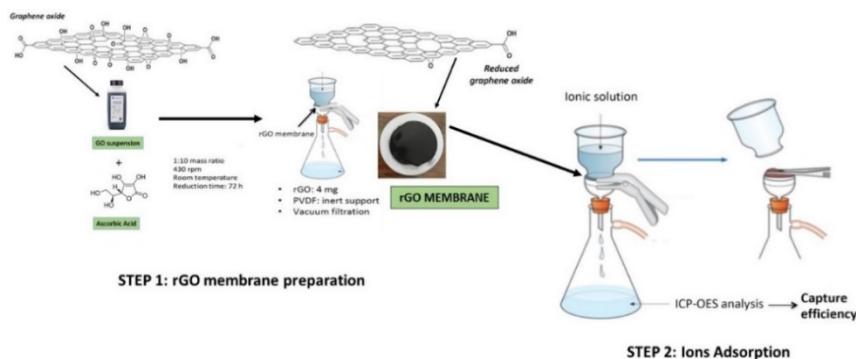


Figure 1 – rGO membranes preparation process (STEP1) and capture tests (STEP2)

Membranes before and after uptake were morphologically and structurally analysed by different techniques. X-ray diffraction (XRD) patterns were collected between 2 and $30^\circ 2\theta$ by a Bruker D8 Advanced diffractometer, in the range $2 - 30^\circ 2\theta$, using a monochromated Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$), step scan = $0.02^\circ 2\theta$, and 1 s per step.

Thermogravimetric measurements (DTA-TG) were carried out by means of the EXSTAR 6000 TG/DTA 6300 (Seiko Instruments), up to 1000°C , heating and cooling rate = $10^\circ \text{C min}^{-1}$, in flowing N_2 (55 mL min^{-1}).

FT-IR spectra were recorded by a Nicolet Nexus spectrometer, coupled with a Thermo Electron Continuum IR microscope and a diamond anvil cell (DAC) accessory fitted to the 15X reflective Cassegrain objective. Spectra were collected accumulating 128 scans with a resolution of 4 cm^{-1} .

Raman spectra were recorded by a Jobin Yvon Labram HR800 Raman spectrometer, coupled with an Olympus BX41 microscope (50X objective), at the excitation line 632.8 nm (HeNe laser, laser power $50\ \mu\text{W}$), averaging four acquisitions each one of 30 seconds.

The surface and the thickness of the rGO membranes were analysed by a Scanning Electron Microscope (SEM) Zeiss EVO 50 EP with a spectrometer OXFORD INCA energy 2000, electron high tension (EHT) voltage of about 20 kV and high vacuum (10^{-5} Torr).

3. RESULTS AND DISCUSSION

3.1 rGO membrane characterization

In Figure 2 (a-d) are reported the characterization patterns of the rGO-72 membrane before capture. All the characterization data plotted in Figure 2 pointed out a certain reduction degree of the membrane material, namely, GO reduction, and the destruction of the GO order is evidenced by the following facts.

1) XRD patterns (Figure 2a), where the disappearance of the reflection at $11^\circ 2\theta$, typical of GO structure, is detected accompanied by the appearance of a reflection at 26.7° , typical of graphite which originates from graphene formed during the reduction reaction (Moon et al., 2010). For rGO-72 an interlayer distance of about $3.3\ \text{\AA}$ was calculated, which is in accordance with the graphitic-like phase formed upon reduction.

rGO-based materials characterized by low interlayer distance are reported to possess better performances in ions capture (Chen et al., 2009; Mi, 2014). Therefore, the calculated interlayer distance ($3.3\ \text{\AA}$) makes such sample potentially good for filtration experiments.

2) TG-DTG analysis (Figure 2b) of rGO-72 evidenced in the temperature range $135 - 220\ ^\circ\text{C}$ a broader thermal phenomenon shifted to lower temperature than GO. The weight loss between $135\ ^\circ\text{C}$ and $220\ ^\circ\text{C}$ can be associated to the decomposition of labile oxygen groups like carboxylate, anhydride, or lactone groups while the slight perturbation of the curve between $220\ ^\circ\text{C}$ and $500\ ^\circ\text{C}$ can be due to the removal of more stable oxygen groups such as phenol and carbonyl (Basso Peressut et al., 2021; Huang et al., 2012). All these evidences support the reduction of GO.

3) In FT-IR spectrum, rGO-72 (Figure 2c) bands assigned to oxygenated groups, i.e., OH, COC, and epoxy functions are absent. Moreover, the remaining bands at 1730 cm^{-1} (C=O stretching), and at 1570 cm^{-1} and 1250 cm^{-1} (C=C stretching), suggest that during the process of reduction structurally disordered graphene moieties grow inside the rGO layers (Acik et al., 2010).

4) Raman results (Figure 2d) once more confirmed the structural changes occurring during the reduction. The Raman spectra show features similar to those of disordered graphite, namely the band near 1600 cm^{-1} , corresponding to the G band observed in graphene/graphite systems, assigned to the collective C=C stretching modes and the band near 1330 cm^{-1} similar to the D band observable for chemically and or structurally disordered graphene layers (Ferrari and Robertson, 2000) (but the same bands are observed for GO). The lower structural disorder and oxidation level observed for the rGO-72 membrane can be also quantified by calculating the average crystallites size as suggested in reference (Krishnamoorthy et al., 2013) which increase their dimensions from 15.9 nm to 19.2 nm from GO to rGO-72, respectively.

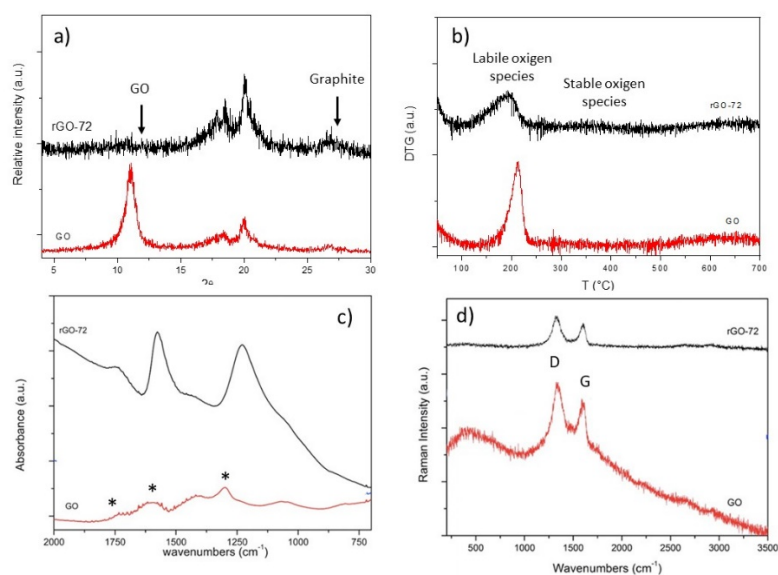


Fig. 2: Physico-chemical characterization of rGO-72 membrane: a) XRD, b) DTG, c) FT-IR and d) RAMAN (c)

Morphology of the rGO-72 membrane was analysed by SEM, images of surface (a) and cross-section (b) are reported in Figure 3. rGO-72 membrane exhibits an appreciable macroscopic roughness that can be ascribed to a decrease of surface order upon GO reduction (Migliavacca et al., 2017). Considering membrane cross-sections, the slightly corrugated membranes are characterized by a macroscopic multilayer structure, where membranes average thickness, about 3.5 μm , is the result of a continuous stacking of single layers.

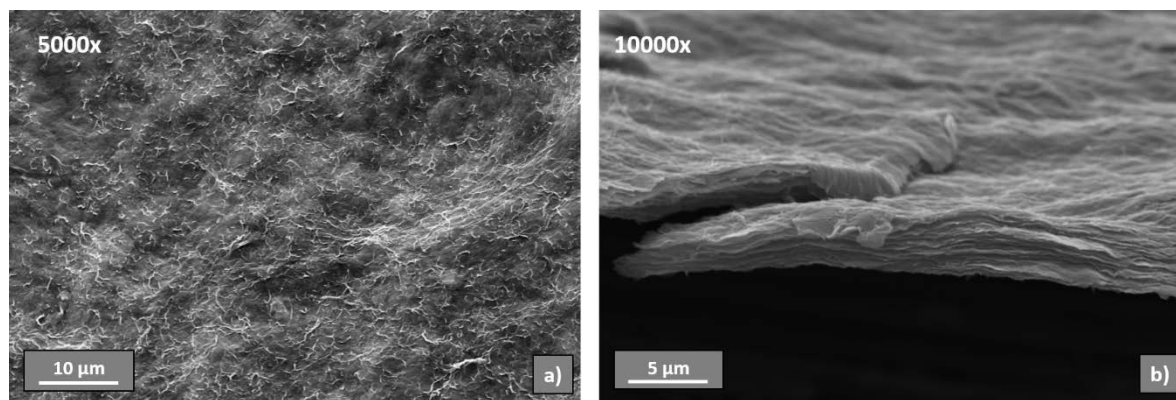


Fig. 3: SEM images of rGO: a) surface and b) cross-section

3.2 Ions capture tests on rGO-72 membrane

The rGO-72 (rGO = 4 mg) membrane was contacted with: 1) Lanthanum and Copper single ion solutions (100 mmol/L) and 2) bionic solution containing both Lanthanum and Copper (100 mmol/L, La:Cu = 1:1 mol/mol). Results in terms of capture efficiency (%) in both mono-ionic and bionic solutions are reported in Figure 4.

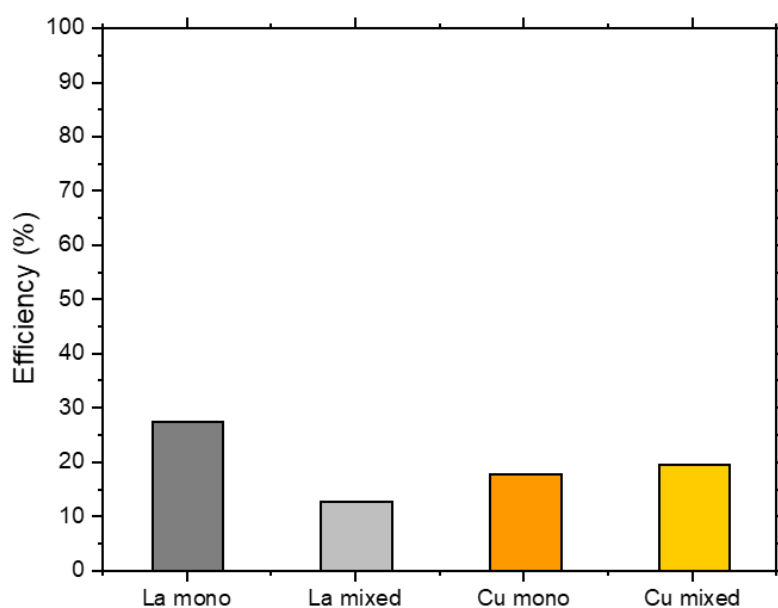


Fig. 4: Capture efficiency by rGO-72 in mono-ionic and bionic solutions of La^{3+} and Cu^{2+}

In the case of bionic solutions, a total capture of about 15% was detected, not particularly high. However, rGO is able to capture both La and Cu ions in mono-ionic solutions with interesting capture efficiency (Figure 4). These data are worth of note, because no or very low Cu capture has been reported in the literature for other sorbent materials (Iannicelli-Zubiani et al., 2018, 2017a; Iannicelli Zubiani et al., 2015).

When mono-ionic solutions are considered, La ions showed a capture efficiency around 30%; however, this value is halved in presence of Cu. Such a behaviour is in line with literature; indeed, the presence of Cu resulted in equilibria modification which limited La uptake (Iannicelli-Zubiani et al., 2018, 2017a; Iannicelli Zubiani et al., 2015). On the contrary, Cu capture in mono-ionic solution did not exceed 20%, but this value is preserved also in bionic one. Such findings pinpoint a sort of preferential interaction between rGO and Cu ions, which is hardly detected in other solids.

This point is better evidenced by comparing uptake efficiency of different sorbents from previous studies (Iannicelli-Zubiani et al., 2017a; Iannicelli Zubiani et al., 2015). In Figure 5, La and Cu capture in mono- and bi-ionic (equimolar) solutions using rGO-72 are compared with those obtained for: 1) a clay, pristine (STx) and modified with a polyamine (STx-AmL6) and 2) an active carbon, pristine (AC) and modified with the same polyamine (AC-Am-L6). The preferential rGO-72 interaction with Cu is clearly evident. Indeed, Cu is always captured by rGO-72, but it is not captured by STx and STx-Am-L6 when in mono-ionic solutions and in case of pristine STx Cu is never captured.

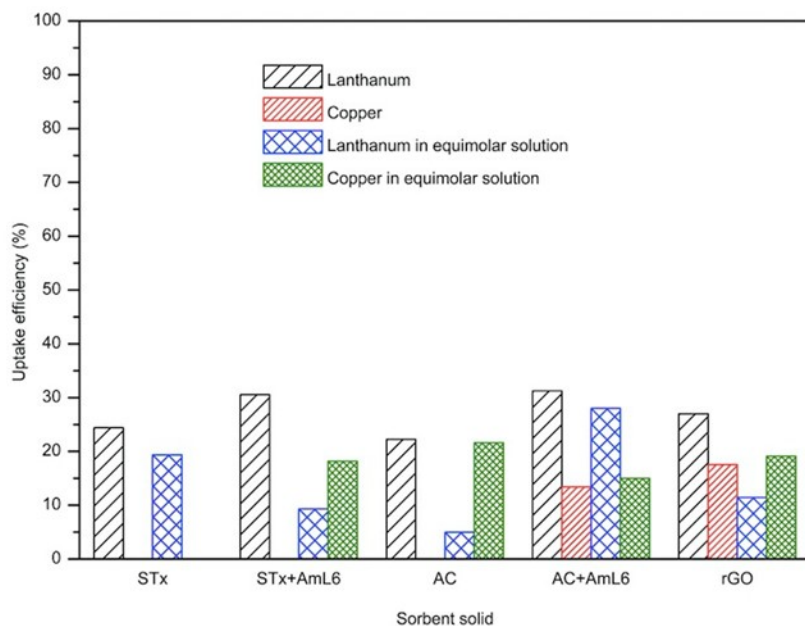


Fig. 5: Uptake efficiency of different sorbent materials towards mono and bi-ionic solutions of La^{3+} and Cu^{2+}

3.3 rGO-72 membrane characterization after capture tests

To get information on membrane-ions interaction and capture mechanism, rGO-72 membranes were fully characterized after the contacting step with lanthanum, copper and lanthanum-copper mixed solutions. In Figure 6a, images taken with the optical microscope coupled with Raman spectrophotometer of rGO-72 membrane contacted with a La mono-ionic solution are reported. A complex surface situation was observed, with zones characterized by clusters (arrows in the figure) of different shape, size and colours, which were never present in the pristine membrane.

To investigate the nature of these agglomerates, they were irradiated with the exciting light $\lambda = 632$ nm and Raman spectra were collected. Clusters consist of different composition; in particular, the largest one (spectrum not reported in the Figure) was formed of organic phases, probably the residues of the L-ascorbic acid used for the reduction of graphene oxide. For the other smaller agglomerates, the spectrum recorded was dominated by a strong signal of fluorescence, where D and G bands float on the fluorescent signal as very low features (Figure 6b). However, the positions of D and G bands remains constant at about 1333 cm^{-1} and 1608 cm^{-1} , thus confirming that the contacting process did not modify the graphitic structure of the rGO-72 membrane.

The origin of this fluorescence has to be ascribed to the presence of new chemical species on the surface of the rGO-72 membrane. In particular, the band at about 1050 cm^{-1} visible in the spectrum corresponds to the main Raman band of lanthanum nitrate (Figure 6b).

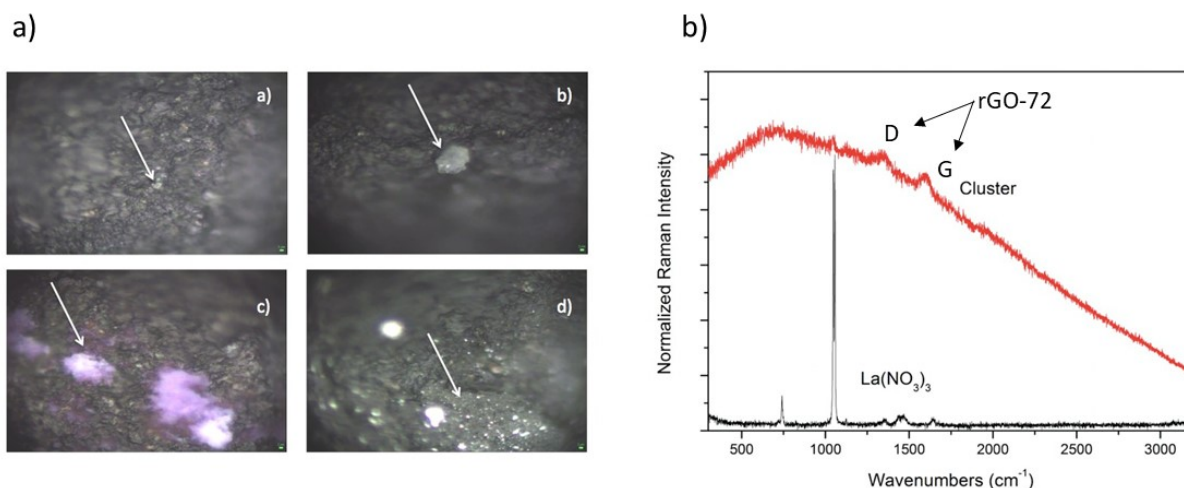


Fig. 6: a) Optical images (acquired through the Raman microscope) of rGO-72 membrane after contact with La solution and b) Raman spectra of the white cluster pointed out by the arrow in (a) and of lanthanum nitrate for reference.

Accordingly, Lanthanum capture, seems to occur via Lanthanum nitrate precipitation and re-aggregation onto rGO-72 surface.

To get an insight of this process, and to verify if a similar mechanism occurs in presence of Cu and in bionic solutions, FT-IR analyses were also performed. Spectra are reported in Figure 7 a, b.

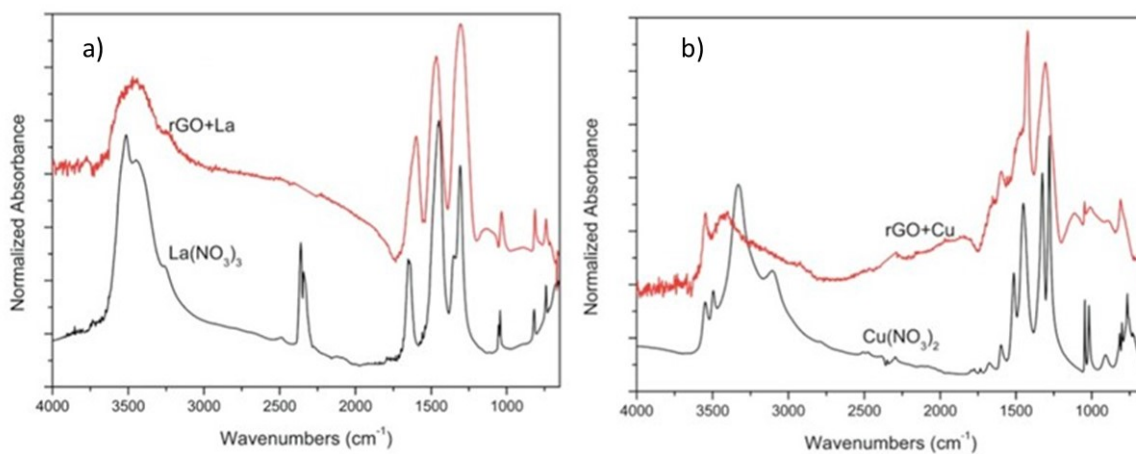


Fig. 7: FT-IR spectra of a) lanthanum on rGO-72 membrane and lanthanum nitrate; b) copper on rGO-72 and copper nitrate.

For both contacted rGO membranes, different spectral features appear in the fingerprint region 1750 – 1000 cm⁻¹. These new bands have to be assigned to the presence of lanthanum or copper chemical species adsorbed into the rGO-72 membrane. Moreover, considering the contribution of –OH groups, the corresponding band at around 3500 cm⁻¹ greatly increases in case of La. A less evident increase is observed for the case of copper contacting. Interestingly, the band at 1750 cm⁻¹ characteristic of the residual C=O groups of the reduced GO decreases in the

contacted samples, suggesting that carbonyl groups are, in some way, involved in the adsorption mechanism. To identify the new chemical species adsorbed by the rGO-72 membranes, we recorded the spectra of lanthanum and copper nitrate salt solutions. When lanthanum and copper were adsorbed on the rGO-72 membrane, they might reform the starting salts. The spectra of the rGO-72 membrane contacted with lanthanum and the reference lanthanum nitrate are very similar (Figure 7a), thus supporting the idea that lanthanum adsorbed on the rGO membrane re-forms the nitrate salt. In the case of the copper salt, the two spectra (Figure 7b) are not so similar, all the features are broad and some coincide with the sharp absorption of the copper nitrate. Probably, also in this case the nitrate is forming but with a disordered structure and probably in different hydration states. From FT-IR spectra, we can conclude that lanthanum and copper salts are homogeneously distributed in the rGO-72 membranes without altering the graphitic structure.

Finally, FT-IR analysis of rGO-72 membrane contacted with bionic solution was performed. Preliminary results are reported in Figure 8 and compared with those of mono-ionic solutions.

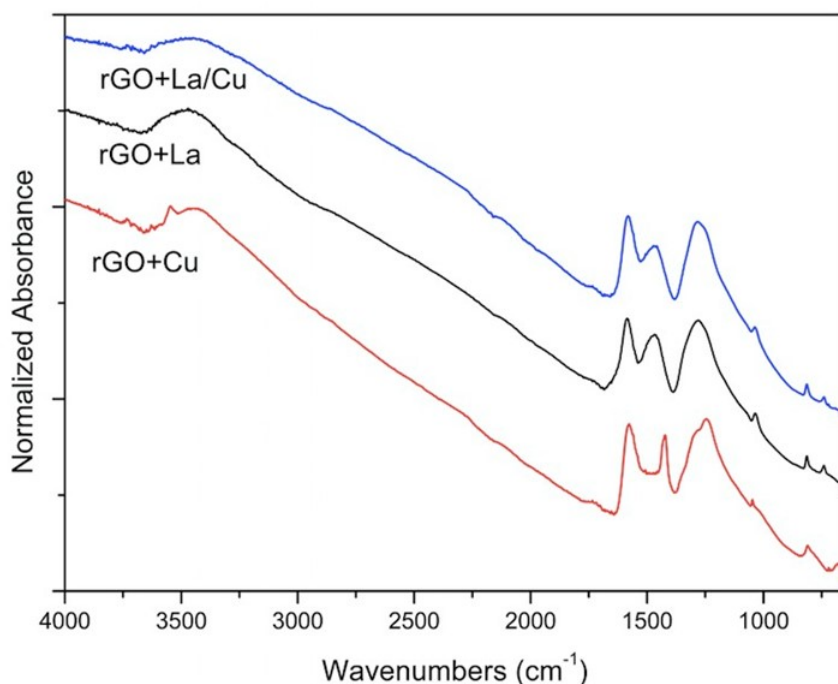


Fig. 8: FT-IR spectra of rGO-72 membranes contacted with mono and bi-ionic solutions of La^{3+} and Cu^{2+} .

The spectrum of the rGO-72 membrane contacted with the mixed solution evidences a minimum contribution of Cu, while the spectrum is dominated by the La-containing species. These evidences appear in line with the surface picture already discussed, where Lanthanum nitrate accounted for Lanthanum uptake, while Cu nitrate, although present, is possibly more dispersed or present with distorted structure. Cu behaviour could suggest the presence of a stronger interaction between Cu and the membrane surface, thus accounting for its preferential capture discussed above. However, this point deserves further experimental evidences to be confirmed.

4. CONCLUSIONS

1) rGO-72 showed interesting performances in ions capture upon reduction; this property arises from the interlayers distance in rGO structure, which is able to trap ions.

- 2) Adsorbed ions do not modify the graphitic structure of the carbon-based material. On the other side, a perturbation of residual rGO functional groups suggests that the ions-sorbent interaction occurs involving these groups.
- 3) Cu ions are preferentially captured in bionic solutions, suggesting the presence of stronger interaction between Cu and the membrane surface.
- 4) Preliminary results seem to point out a capture mechanism that implies lanthanum and copper salts recrystallization.

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