SAP^2

Sustainability Analysis of Purification with SAPonite

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1. ABSTRACT

Because of the global situation caused by the COVID-19 pandemic, aspects such as pollution and recycling have become far more severe.

The goal of our project was to develop an experimental solution to environmental pollution and to analyze the sustainability of the process.

We used a synthetic clay named Na-SAP-20, a mineral which possesses ion exchange properties which allow it to recover heavy metals and other pollutants from bodies of water.

The method we developed was tested on Co^{2+}, a material globally recognized as 'critical' due to its uses in a broad range of key industrial, sustainable and technological applications, and on Cr^{3+} which is a common polluting agent found in freshwater.

The material absorption capacities have been analyzed by spectrophotometry UV-VIS, ICP-MS and NMR relaxometry because of the paramagnetic properties of the Cr^{3+} ion; we compared the results obtained with these analytical techniques focusing on the advantages and disadvantages of each one and on the importance of conducting various types of analysis to obtain more accurate experimental data.

KEYWORDS: Sustainability, Heavy Metals, LCA, Circular Economy

2. INTRODUCTION

Water pollution is a problem which concerns the ecosystem as a whole.

Industrial development, energy plants, mining industries and environmental catastrophes are the main causes of an increase of toxic pollutants in the environment; furthermore, water demand is bound to grow bigger as the global population is expected to reach 10.8 billion people in 2100.[2]

Every day, approximately 2 million tons of industrial, sewage and agriculture waste are discharged into water worldwide, causing serious health problems and the death of approximately 14000 people every day.[3]

Particularly, heavy metal ions cannot be easily decomposed and tend to accumulate, threatening human health via the entire food chain.
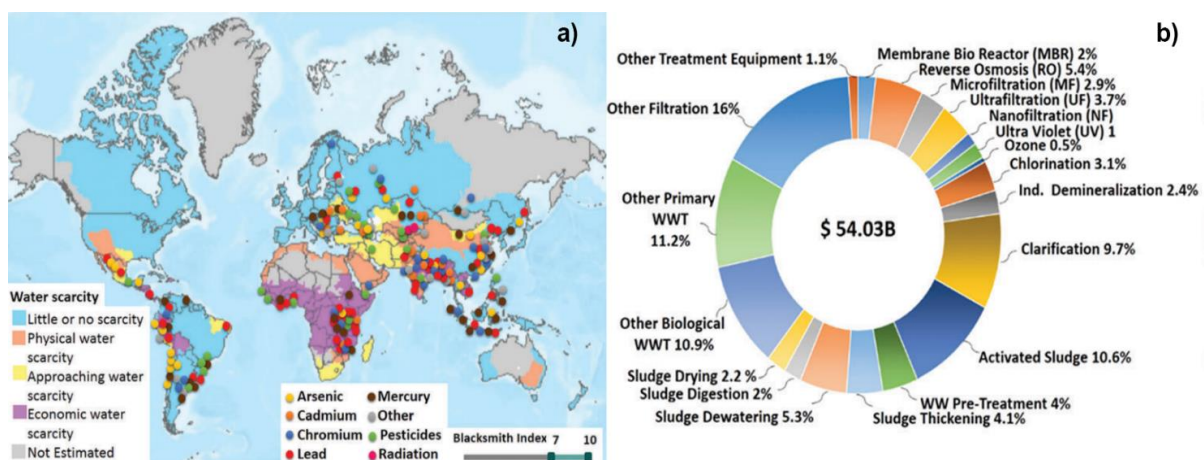

Fig. 1: *a) Geographical distribution of water scarcity and main polluting agents, b) Current technologies available for water purification in terms of global economic turnover.*[2]

Fig. 1a shows the distribution of the main sources of water pollutants, which are for the most part heavy metals such as Chromium, Arsenic or Mercury; the graph also summarizes the current global water scarcity resulting from inadequate natural water resources to supply local demand (*Physical water scarcity*) and due to poor management of the available water resources (*Economic water scarcity*).

Fig. 1b shows the current available technologies for global water purification in terms of their economic turnover contribution to the water purification market.

2.1. Water purification

Water treatment is a process which requires numerous steps; industrial water treatment units combine primary, secondary and tertiary treatment processes, so that water is treated with high efficiency against all types of pollutants (inorganic, organic and biological pollutants). Fig. 2 summarizes the main water treatment procedures.
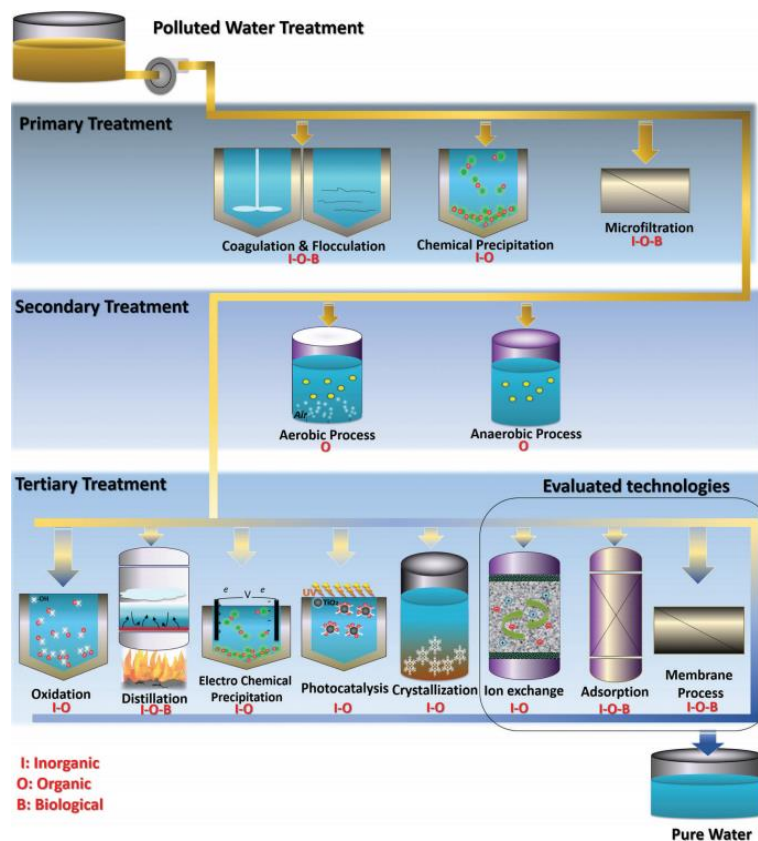
Fig. 2: *Most commonly used procedures for polluted water treatment.*[2]

Primary treatment is the preliminary water purification process before further refined treatments are applied. It can be of physical and/or chemical nature e.g. microfiltration, centrifugation, sedimentation, chemical precipitation.

Secondary water treatments rely on naturally occurring microorganisms capable of converting pollutants into simpler and safer substances. This type of treatment is commonly used in removing organic pollutants and some heavy metals.[3]

Tertiary treatments are used to remove a wide variety of pollutants.

This study will examine a tertiary water treatment which uses the ion exchange properties of a synthetic clay.

2.2. Sustainability

Sustainability is a development condition in which satisfaction of the needs of the current generation can be assured without compromising future generations. Lately, great importance has been attributed to the concept of sustainability, in particular referring to climate change, but it should be remembered that sustainability is not just an environmental issue.

Sustainability is related to compatibility between economic-productive activities and environment protection, and is based on these parameters:

- **Environmental sustainability:** aims to ensure the quality and the availability of resources.
- **Economic sustainability:** aims to guarantee efficiency and incomes for companies.
- **Social sustainability:** aims to ensure life quality, safety and citizens' services.
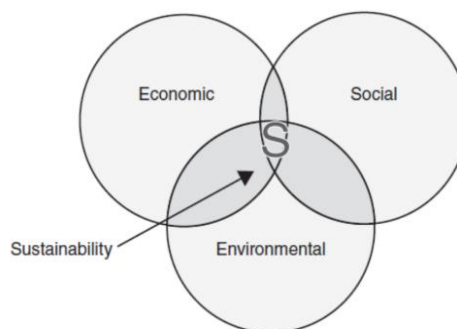

Fig. 3: *Various aspects of sustainability.*

For example, climate change has negative impacts mostly on parts of the population that already suffer other social impacts (economic, social, race, gender discriminations…), as such, climate change solutions must have social equality as the central element. These elements are present in the European *Recovery Fund.*[4]

2.2.1. Green Chemistry and Green Engineering

Hereunder are listed the main principles of *Green Chemistry* and *Green Engineering*, two approaches applied to the chemical industry and product development respectively, in order to achieve sustainable development.

GREEN CHEMISTRY	GREEN ENGINEERING
1) Prevention	1) Inherent rather than circumstantial
2) Atom economy	2) Prevention rather than treatment
3) Less hazardous chemical syntheses	3) Design for separation
4) Designing safer chemicals	4) Maximize efficiency
5) Safer solvents and auxiliaries	5) Output-pulled versus input-pushed
6) Design for energy efficiency	6) Conserve complexity
7) Use of renewable feedstocks	7) Durability rather than immortality
8) Reduce derivatives	8) Meet need, minimize excess
9) Catalysis	9) Minimize material diversity
10) Design for degradation	10) Integrate local material and energy flows
11) Real time analysis for pollution prevention	11) Design for commercial afterlife
12) Inherently safer chemistry	12) Renewable rather than depleting

The method we propose follows the principles of *Green Chemistry* for the synthesis process of the clay (with particular attention given to 1, 2, 4, 5, 6, 7, 8 and 11) and adheres to rules 4, 8, 9 and 12 of *Green Engineering*.

2.2.2. Life Cycle Assessment (LCA)

Life Cycle Assessment (LCA) is a tool that can quantify the environmental impact of a product looking at its complete life cycle, from raw material production to the disposal of the scraps, and evaluate the possibility of reusing (repurposing the product for the same function), or recycling (a new transformation made to obtain high economic performances).

The ISO14040 standards define LCA as "*the compilation and evaluation through the life cycle of incoming and outgoing flows as well as the potential environmental impacts of a product system*".[5]
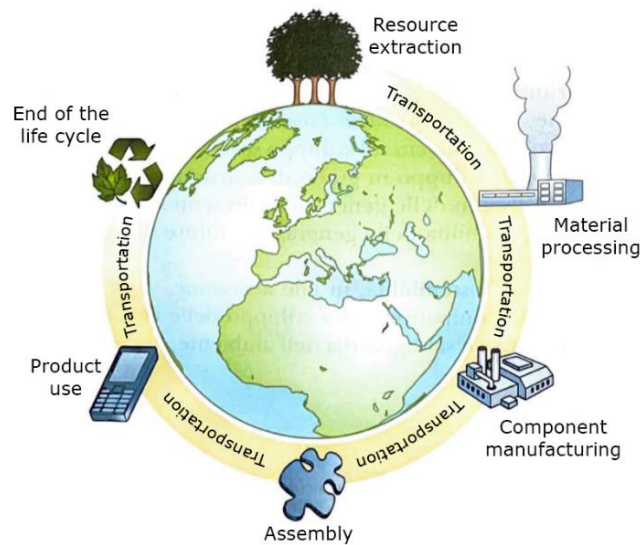
Fig. 4: *Typical life cycle of an industrial product.*[6]

The main purpose of an LCA is to identify the most suitable solutions between all the possible alternatives for a reduction of environmental loads, using as much as possible a *"cradle to grave"* approach, or even better, a *"cradle to cradle"* approach, considering even cycles that include reusing or recycling processes

The realization of an LCA is built up on 4 points:

-Defining the goal of the research.

-Realizing a lifecycle model that includes all the forms of environmental inputs and outputs (*Life Cycle Inventory*).

-Calculating the environmental impact of every input and every output (*Life Cycle Input Assessment*).

-Reading and understanding the results.

Fig. 5: *Life Cycle Assessment Framework.*

To simplify the procedure, we must identify the parts with the greatest environmental impact in the life cycle of the product, and analyze how much the different phases of the life cycle contribute to the overall ecological footprint.

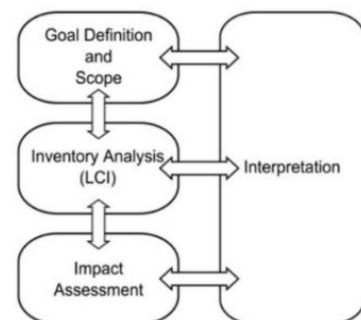Our project concerns depurations with particularly active clay materials and consequently, it limits the environmental impact (*cradle to grave*).

Our sustainability analysis is carried out on a laboratory scale.

2.2.3. Circular Economy

Circular Economy is a production/consumption model that involves sharing, lending, reusing, repairing, reconditioning and recycling existing materials and products as long as possible.[7]

It implies careful planning: to extend as much as possible the life cycle of the goods, to facilitate their repairing, their separation in components and to recover materials; products are also produced with the smallest environmental impact using renewable energy sources.

The enforcement of a circular economy can allow reaching the numerous goals fixed by the 2030 Agenda: in particular, clean water and sanitation (SDG 6) and sustainable cities and communities (SDG 11).[1] Our project allows the recovery of Cobalt as a "critical material", and the reuse of the clay.

2.3. Theoretical foundations of heavy metal chemistry

The term "*heavy metals*" is usually used to indicate a series of chemical elements that are not essential for humans including metals (Chromium, Lead, Cobalt, Mercury) and metalloids, like Arsenic, in the various forms present in nature.

Heavy metals are components of the Earth's crust and they are naturally present in the ground, in the water and in small quantities in the atmosphere. They can contaminate foods and the environment as a result of natural phenomena, human activities and some industrial processes.

These metals have a high level of long-term toxicity: their accumulation in organisms can, over time, cause important damaging effects because they interfere with the normal cellular metabolism, hindering the proper performance of vital functions.

Transition metals belong to the *d* bloc of the periodic table and therefore have common properties. They have comparable ionic radius, variable oxidation numbers and chemical behavior related to them: they generally have a basic behavior but, as the oxidation number increases, oxides formed by some of these elements can have acid behavior.

Some of the transition elements, like Nickel, Iron, Chromium and Cobalt have magnetic properties because of the presence of unpaired *d* electrons.

Every atom, on the inside, has tiny electric currents generated by the movement of electrons around the nucleus that create small magnetic fields (they don't create a total magnetic field of the material because of the random directions of the spins). By subjecting the material to an external magnetic field, a total magnetic field of the

material is created by adding to the external magnetic field, the internal one which has just been created. This particular phenomenon is called ferromagnetism and can be observed in various materials such as cobalt.

Other materials are generally divided into diamagnetic and paramagnetic, diamagnetic materials are weakly repelled by magnetic fields while paramagnetic materials are weakly attracted by them.

2.3.1. Cobalt chemistry

Cobalt is the 27th element of the periodic table. It is used for the construction of batteries, electronic devices and for making prosthesis; it's also implied in the creation of superalloys.

The most common oxidation states are +2 and +3; Cobalt takes part in the structure of B12 vitamin, which is essential for life due to the role it has on synthesis and metabolization of amino acids.

Cobalt is the 32nd most plentiful element in the world, although it isn't particularly rare it has been labeled from UE as a *Critical Raw Material* because of the role it has on the realization of sustainable products.

It's important to study solutions that allow the recovery and recycling of Cobalt in a circular economy perspective.

Geopolitics also play an important role in the critical issues of the material: the Republic of Congo, a highly unstable state, possesses more than 50% of the global Cobalt reserves.[8]

2.3.2. Chromium chemistry

Chromium is the 24th element of the periodic table. The most common oxidation states are +2, +3 and +6, of which +3 is the most stable, the dangers of chromium (III) come from the easy way it is oxidized into the hexavalent state which results really aggressive with biological systems, becoming toxic and cancerous.

In potable water the level of hexavalent chromium is usually low, but it can be found in contaminated groundwaters and can consequently be spread in the environment.

The paramagnetic properties of the Cr^{3+} ion (magnetic moment= 3.88) have been used in the NMR analysis.

2.4. Structure and properties of clays

2.4.1 Structural properties of saponite

Saponite is a phyllosilicate clay (Fig.6), which can be found both in nature and prepared synthetically, with structural formula $M^{n+}_{x/n}[Mg]_6(OH)_4[Si_{8-x}Al_x]O_{20} \cdot mH_2O$.

M is the exchanged cation with n^+ charge, X is the fraction of Aluminum present in the structure and m is the number of water's molecules. Saponite belongs to the smectite group and is particularly interesting for scientific purposes and specifically catalytic purposes due to its high specific surface, its superficial acidity and its thermal stability.

Fig. 6: Naturally formed saponite.

Its lamellar structure is T-O-T with tetrahedral and octahedral units in contact with each other and repeated alternately in the bidimensional space. In the tetrahedral layer the silicate group (SiO_4^{4+}) acts as the basic structural unit (Fig.7).
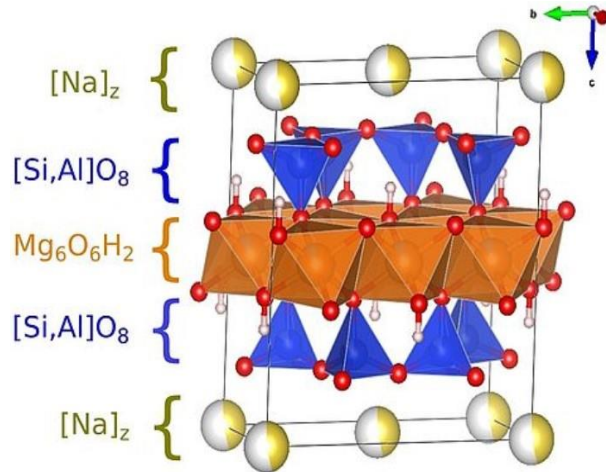

Fig. 7: *Lamellar structure of a saponite.*

The elementary chemical composition of the two layers is different: the octahedrons have Mg^{2+} or Al^{3+} as a central ion.

In the tetrahedral layers, an isomorphic substitution can occur in the silicate group between Si^{4+} and Al^{3+}.

Since the net charges are different there is a charge decompensation in the structure, which means that there is a negative charge, localized on the oxygen of the tetrahedron, which is not compensated by the presence of the metal.

A partial compensation is given by the presence of exchange cations (Na^+, K^+, Ca^{2+}) in the interlamellar space. In lamellar materials present in nature, the compensatory cations have different compositions and cause different values of the parameter connected to the repetition period that allows to better differentiate them, and to classify them.

2.4.2 Synthesis of saponite

Developing a reproducible synthesis method for saponite is of primary importance since naturally formed saponites, despite their low price and high availability, do not have controllable chemical-physical properties. In fact, while natural clays must be subjected to long purification treatments to eliminate organic and inorganic impurities, synthetic saponites present a controlled chemical composition and have well-defined morphological and textural properties.[9]

The most used methods for the synthesis of saponites are of a hydrothermal type or sol-gel microwave assisted: the latter is carried out at a low temperature (less than 100°C) and at atmospheric pressure, while the hydrothermal methods require that the synthesis gel containing Si, Al, Mg, is warmed up between 220°C and 450°C with the addition of a desired cation exchange precursor. Generally, the synthesis of a saponite depends on 3 main parameters, the composition of the synthesis gel, temperature and pressure.[10][11]

2.5. Analytical techniques

UV-VIS

UV-VIS Spectrophotometry is a technique used in analytical chemistry mainly for quantitative determinations. The sample is placed inside a spectrophotometer which produces a thin beam of monochromatic light and passes it through the sample. When a molecule is hit by radiation of wavelength between 200-400 nm (UV) or 400-800 nm (visible), electronic transitions between energetic levels occur (which means that an electron moves from a molecular orbital of a lower energetic level to a higher level one). This absorption is at the base of the Beer Lambert law: according to this law when a radiation passes through a solution, it is absorbed more or less intensely depending on the concentration.

The Beer Lambert law shows the correlation between absorbance and concentration:

$$A = \varepsilon \, [C] \, l$$

where A represents the absorbance, ε is the molar absorption coefficient which is different for every substance, C is the concentration of the sample and l is the optical path length in cm (length of the cuvette used for the absorbance measurement).

NMR Relaxometry

NMR Relaxometry is a technique based on the measurement of the longitudinal and transversal relaxation times of atomic nuclei (for example Hydrogen, H) when they are immersed in a magnetic field and irradiated by energy in the radio frequency field. Relaxation times are sensitive to different chemical-physical factors, and particularly to the dynamic and the structure of the nucleus of the materials they are part of.

ICP-MS

The inductively coupled plasma mass spectrophotometry (ICP-MS) is an analytical technique used to determine the concentration of numerous chemical elements which are present even in traces (in the order of ng/L) in different types of matrices (sea water, fresh water, sediments, rocks).

ICP-MS uses plasma, an ionized gas rich of ions and electrons, which, unlike a normal gas, presents long-range atomic forces, which make it neutral. Plasma is formed in a quartz tube called torch, and through the ionization process generated by an electric discharge and an electromagnetic field, ions and electrons are formed. The sample to analyze must be nebulized before being introduced in the injector tube of the torch. Through a system of lenses and ionic mirrors, only the positive ions of the ion beam are selected to be conveyed to the mass spectrometer where they are separated and identified according to their mass/charge ratio through a static or oscillating magnetic field.

3. EXPERIMENTAL PART

3.1. Synthesis of saponite materials

3.1.1 Reagents

- Fumed / amorphous silica ($SiO_{2(s)}$, purity: 99.8% M.M.: 60.09 g/mol)
- Sodium Hydroxide ($NaOH_{(s)}$, purity: $\geq$ 97.0 %, M.M.: 39.997 g/mol)

- Ultrapure water Milli-Q® ($H_2O_{(l)}$, M.M.: 18.01528 g/mol)

- Magnesium Acetate Tetrahydrate ($Mg(CH_3COO)_2 \cdot 4H_2O_{(s)}$, purity: 99 %, M.M.: 142.39 g/mol)

- Aluminum Isopropoxide ($Al[OCH(CH_3)_2]_{3(s)}$, purity: $\geq$ 98 %, M.M.: 204.25 g/mol)

- Sodium chloride ($NaCl_{(s)}$, purity: $\geq$ 99 %, M.M.: 58.44 g/mol)

- Silver nitrate ($AgNO_{3(s)}$, purity: $\geq$ 99.0 %, M.M.: 169.87 g/mol)

- Hexaminocobalt (III) chloride ($[Co(NH_3)_6]Cl_3$ (s), purity: 99.0%, M.M.: 267.48 g / mol)

SAP-20 was prepared starting from an initial gel with stoichiometry:

[SiO_2:MgO:Al_2O_3:Na_2O:H_2O] 1:0.835:0.056:0.056:20

Chemical composition of the gel:$(Na)_{0.81}Mg_6(OH)_4(Si_{7.19}Al_{0.81})O_{20} \cdot nH_2O$], with $H_2O/Si = 20$

3.1.2   SAP-20 synthesis procedure:

Inside a 400 ml becker, disband 12.01 g of fumed silica in the solutions previously prepared by dissolving 0.98 g of NaOH in 59.0 g of ultrapure water. Shake the gel at RT for 1 hour with 'manual shaking' and 'automatic shaking'. Check that all the silica is solubilized and add 37.78 g of $Mg(CH_3COO)_2 \cdot 4H_2O$, 4.71 g of $Al[OCH(CH_3)_2]_3$ and 16.36 g of ultrapure H_2O. Let it shake it at RT (manual or automatic) for 2 hours. Submit the gel (pH=8-9) to the hydrothermal treatment in autoclave (Anton Paar 4748) at 240 °C for 72 hours. Following the hydrothermal process, the pH was reduced to 4-5.

After a filtration with Büchner, dry the solid, named SAP-20, inside a stove for ~ 24 h, grind it and recover it. The solid appears in the form of a white powder.
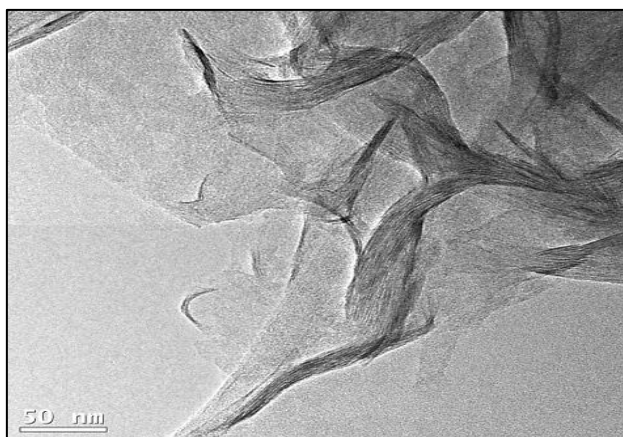

Fig. 8: *Saponite structure at the end of the synthesis process.*

3.1.3   Ionic exchange of SAP-20 with Na$^+$ ions (Na-SAP-20)

The previously described hydrothermal synthesis leads to a final saponite where there are different cations in the interlamellar space besides Na (*i.e.*, Al^{3+}, Mg^{2+}, H^+), which is the main ion to balance the negative charge of the lamellae: because of this, in order to obtain a saponite which contains only sodium, an ion exchange with a saturated solution of NaCl is carried out.

In a 400 ml becker dissipate 1.0 g of SAP-20 in a saturated solution of NaCl (note that 1 g of SAP x 100 ml of solution), previously prepared by dissolving 32 g of NaCl in 100 ml of ultrapure H_2O. Shake the dispersion at

RT for 36 h with magnetic agitation. Filter the obtained material under vacuum with a Büchner filter and wash with warm ultrapure H_2O until complete disappearance of chlorides in the washing water, verified using $AgNO_3$ that causes the precipitation of the remaining chlorine anions in the form of AgCl. Dry the solid, named <u>Na-SAP-20</u>, inside the stove for ~ 24 h, grind it and recover it. The solid shows up as a white powder.

3.2   UV-VIS analysis

Measurements using the UV-VIS technique required the preparation of a stock solution of the Co^{2+} ion and the Cr^{3+} ion, the subsequent preparation of the samples and the relative spectrophotometric analysis.
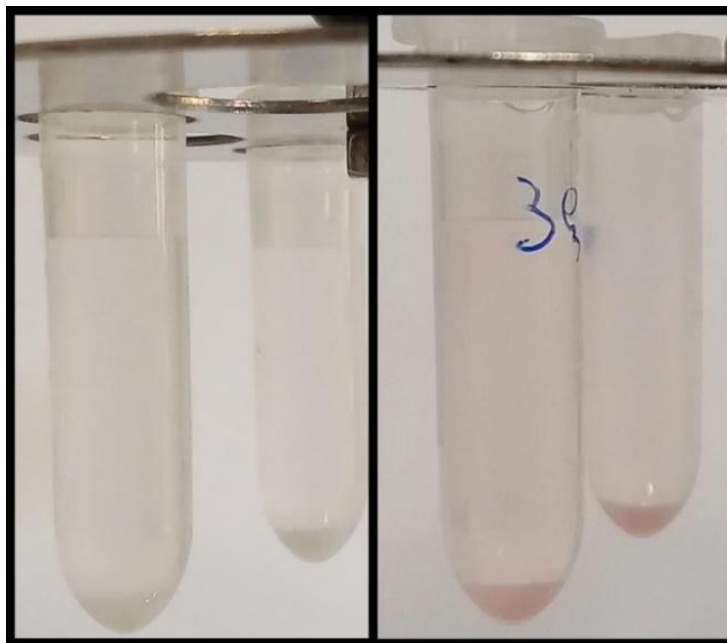

Fig. 9: *Na-SAP-20 sample before and after Co²⁺ capture test.*

3.2.1   Preparation of Co^{2+}/Cr^{3+} stock solution and relative standard solutions

- Prepare a 10 mM stock solution of cobalt (II) chloride / chromium (III) sulfate monohydrate in a 100 mL flask
- Prepare standard solutions (Std) 0.1-0.5-1-2-4-8-10 mM from stock solution 10 mM via dilution
- The 10 mM stock solution will be used for Co^{2+} / Cr^{3+} capture tests

3.2.2   Preparation of samples for Co^{2+} and Cr^{3+} contact/capture tests:

- Weigh 20 mg of clay (Na-SAP-20) in a 1.5 mL eppendorf
- Prepare 7 samples (three times) at 25 ° C as many as the contact tests to be carried out (5 min, 15 min, 30 min, 1 h, 3 h, 5 h, 24 h)
  - Carry out the tests both with the Co^{2+} solution and with the Cr^{3+} solution
- Add 1 mL of 10 mM stock solution in each container
- After the designated time, separate the supernatant from the solid (via centrifugation or, carefully, with a glass / plastic pasteur)

3.2.3   Spectrophotometric analysis UV-Vis-NIR:

- Measurement parameters:
  - 800-190 nm, 150 nm/min
  - quartz cuvette, standard optical path (1 cm)
- Background with ultrapure / deionized water (the same used to prepare the standards)
- Measure the Absorbance (A) of the standards → maximum absorbance at λ_{MAX}=518 nm (Co^{2+})/417 nm (Cr^{3+})
- Graph Absorbance (A) vs. Concentration [C] → perform linear regression (calibration line), obtaining the equation $Y = m\,X$ ($q = 0$) equivalent to the "*Beer Lambert law*":

$$A = \varepsilon \cdot b \cdot [C]$$

$$(A = Y, m = \varepsilon\,b, X = [C])$$

  ε = molar extinction coefficient of the analyte [M-1 · cm-1]

  b = optical path of the cuvette [cm; 1 cm]

  [C] = molar concentration [M = mol / L; mM = mmol / L]

- Measure the supernatant for each contact test
- Measure the absorbance value for each contact test (measurement of the amount of Co^{2+} or Cr^{3+} ion left in solution, not captured by the clay), and insert in the equation of the calibration line above (*) obtaining the concentration left in solution. By knowing the initial concentration (of the solution at 10 mM), it is possible to obtain by difference the quantity captured, in Molarity (M or mM) and in mass (mg of captured ion / g of weighted clay, for each contact test)

$$(*)\ X = Y / m$$

Y = A, parameter measured on the UV-Vis spectrophotometer

(equivalent to: $[C] = A / \varepsilon \cdot b$)

3.3. ICP-MS

20 mg of Na-SAP-20 + 1 ml of Co^{2+}-chloride 10 mM solution were inserted in a 1.5 ml Eppendorf (pH=6.5). The samples prepared were kept at 25 °C in a thermostated sand bath, in static conditions (not under agitation) and at different times from 30 min to 24 h. The surnatant of each test was separated by filtration from the solid and recovered for analysis. The concentration of Co^{2+} ion left in solution was quantified via ICP-MS Spectrophotometry.

3.4. NMR relaxometry

20 mg of sample were inserted inside an NMR tube with a diameter of 10mm. Slowly, 1 ml of water solution of Cr^{3+}(10 mM) was added. Finally, the sample was inserted inside the instrument and analysed in static over time at the temperature of 25°C. At different times, the relaxation rate of the water protons interacting with the paramagnetic metal at 10 MHz was measured. From the longitudinal relaxation rate values (R1), knowing the

relaxivity (r1) of the aqueous-Cr^{3+} complex (5.98 mM-1s-1) it was possible to extrapolate the concentration of Cr^{3+} remaining in the aqueous solution. The equation used to determine the concentration is the following:

$$r_1 = (R_1\text{-}0.38) / [Cr^{3+}]$$

4. RESULTS AND DISCUSSION

4.1. Structure of the synthetic clay

The synthesized saponite was analyzed using X-RAY powder diffraction (Fig.10). The diffractogram obtained shows the diffraction intensities typical of saponites.[12] To analyze the amount of cations exchangeable in the interlayer space (CEC: *Cation Exchange Capacity*), the Na^+ ions are exchanged with Co^{3+} ions via cation exchange in a 0.02M solution of hexaminocobalt chloride (III) which is a diamagnetic compound of Co^{3+}. The Na-SAP-20 CEC was calculated by measuring the amount of hexaminocobalt chloride (III) left in solution after the exchange process via UV-Vis-NIR.
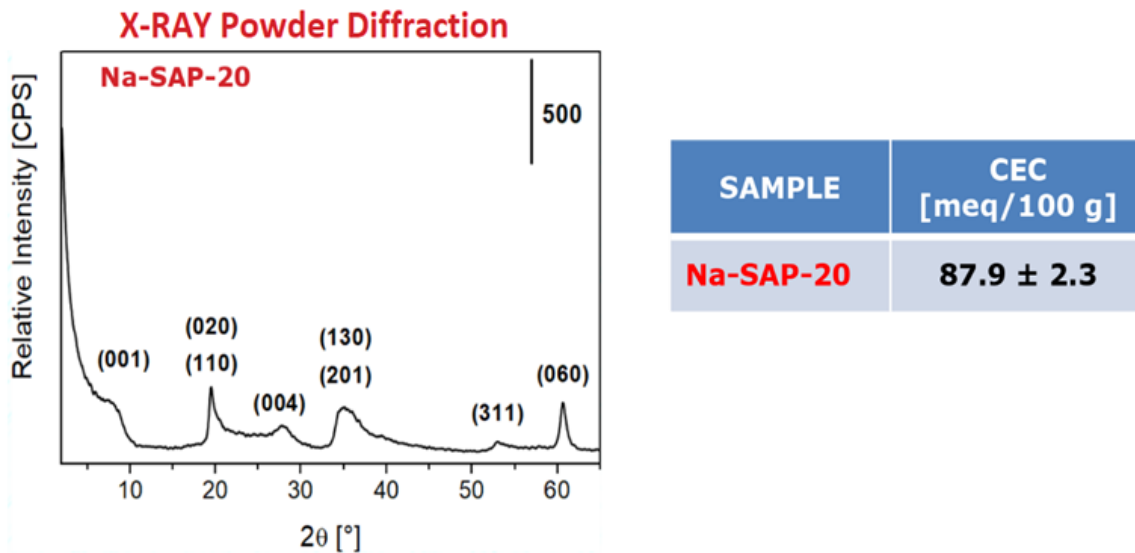

SAMPLE	CEC [meq/100 g]
Na-SAP-20	87.9 ± 2.3

Fig. 10: *Na-SAP-20 X-RAY Powder Diffraction and Cation Exchange Capacity determined via UV-Vis*

4.2. UV-VIS

The absorption spectrums of the stock solutions were analyzed and the maximum absorbance peaks were determined: The peak of the Co^{2+} solution was at a wavelength of 518 nm while the peak of the Cr^{3+} solution was at a wavelength of 417 nm.
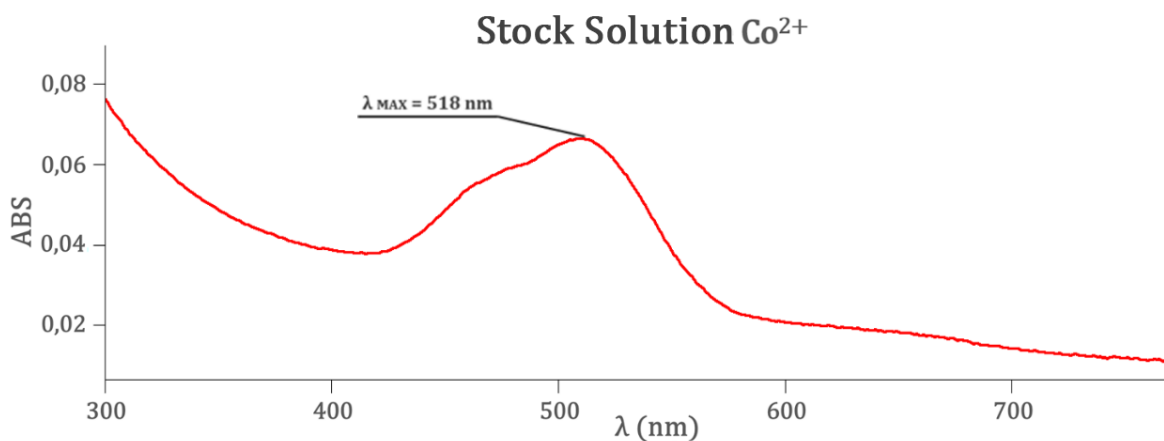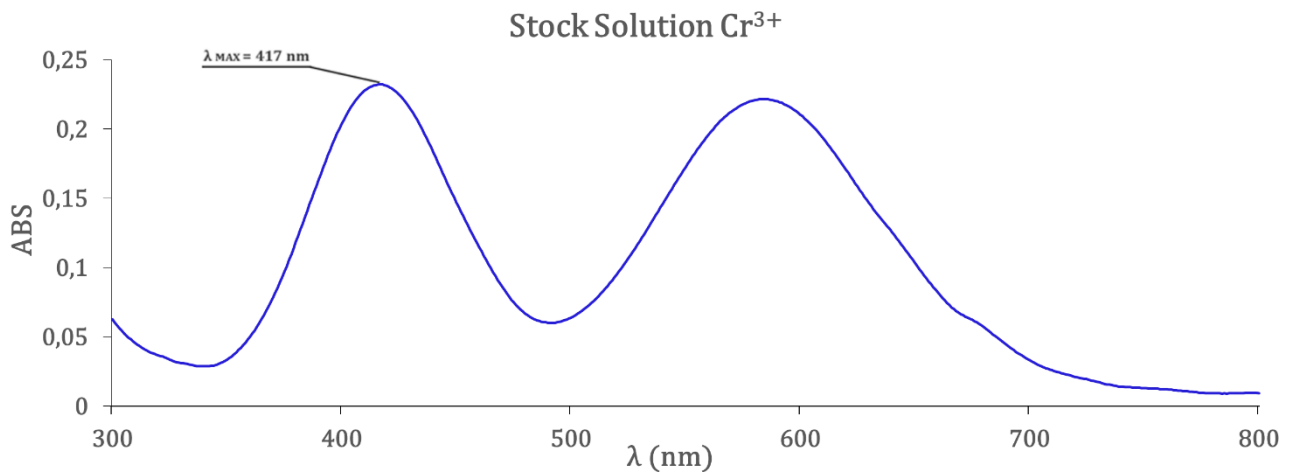
Fig. 11: *Absorption spectrum of the Co²⁺ and Cr³⁺ stock solutions.*

Fig. 12 shows the calibration curves obtained by measuring the absorbance of Co^{2+} and Cr^{3+} solutions at increasing concentrations from 0.1 up to 10 mM.
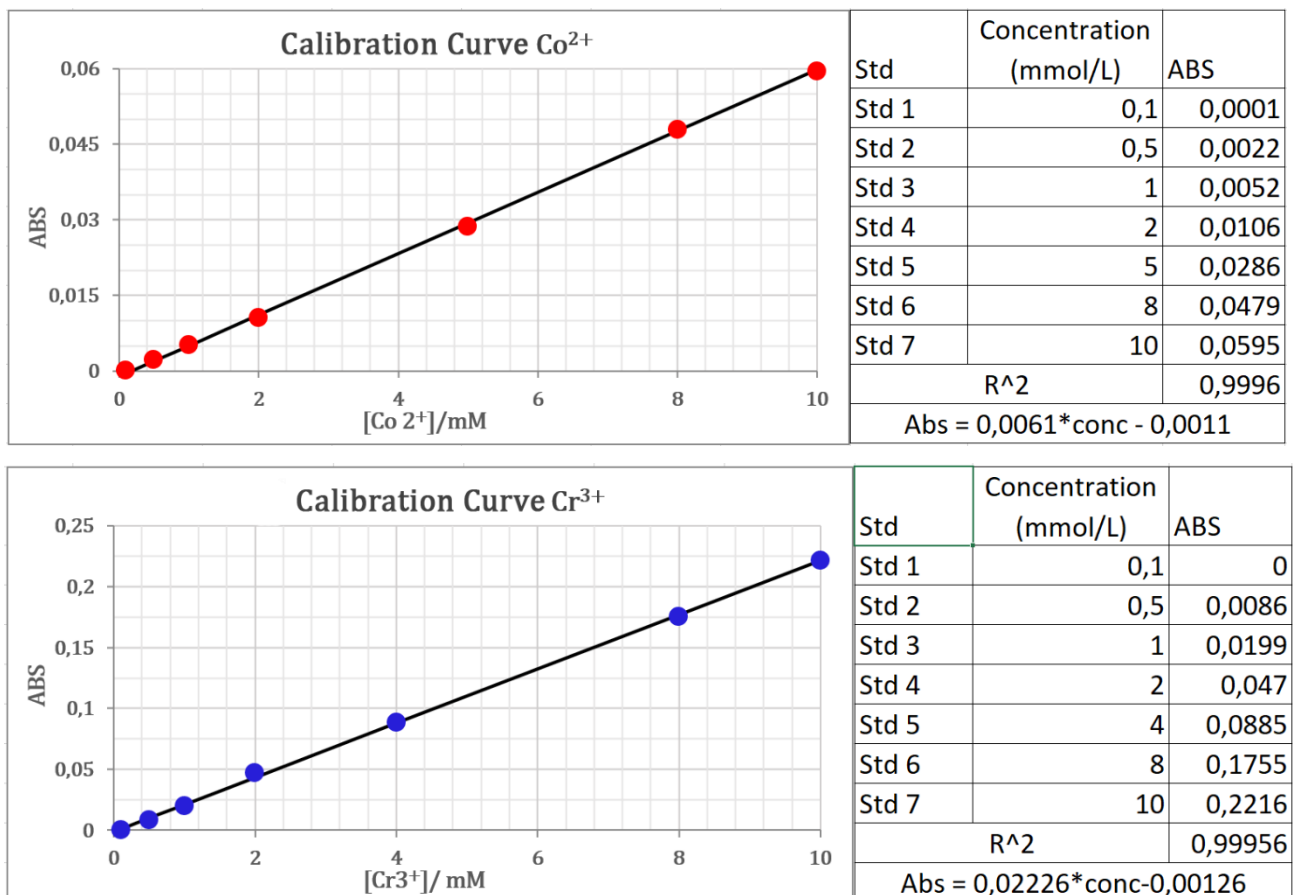

Std	Concentration (mmol/L)	ABS
Std 1	0,1	0,0001
Std 2	0,5	0,0022
Std 3	1	0,0052
Std 4	2	0,0106
Std 5	5	0,0286
Std 6	8	0,0479
Std 7	10	0,0595
R^2		0,9996
Abs = 0,0061*conc - 0,0011		

Std	Concentration (mmol/L)	ABS
Std 1	0,1	0
Std 2	0,5	0,0086
Std 3	1	0,0199
Std 4	2	0,047
Std 5	4	0,0885
Std 6	8	0,1755
Std 7	10	0,2216
R^2		0,99956
Abs = 0,02226*conc-0,00126		

Fig. 12: *Absorbance of Co²⁺ and Cr³⁺ solutions at known concentrations and calibration curves.*

Fig.13 shows the concentration of Co^{2+} and Cr^{3+} after contact with the saponite; this concentration decreases with time, showing the absorption capacities of the clay.
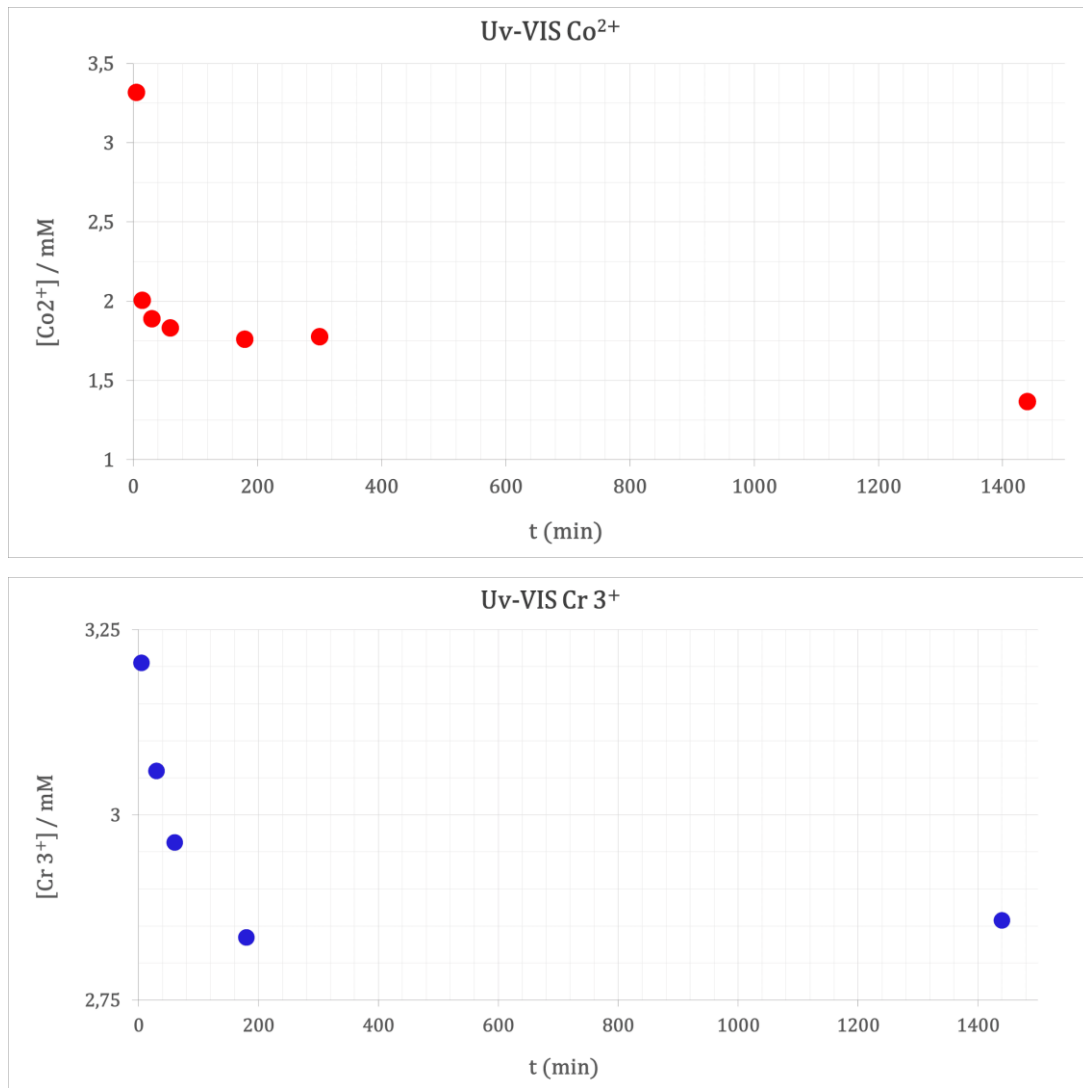
Fig. 13: *Concentration of Co²⁺ and Cr³⁺ in samples analyzed via UV-Vis.*

4.3. ICP-MS

The ICP-MS analysis carried out on the Co^{2+} samples confirms that the clay possesses absorption capacities, the chart in Fig.14 shows a remarkable decline in the concentration of Co^{2+} ions.
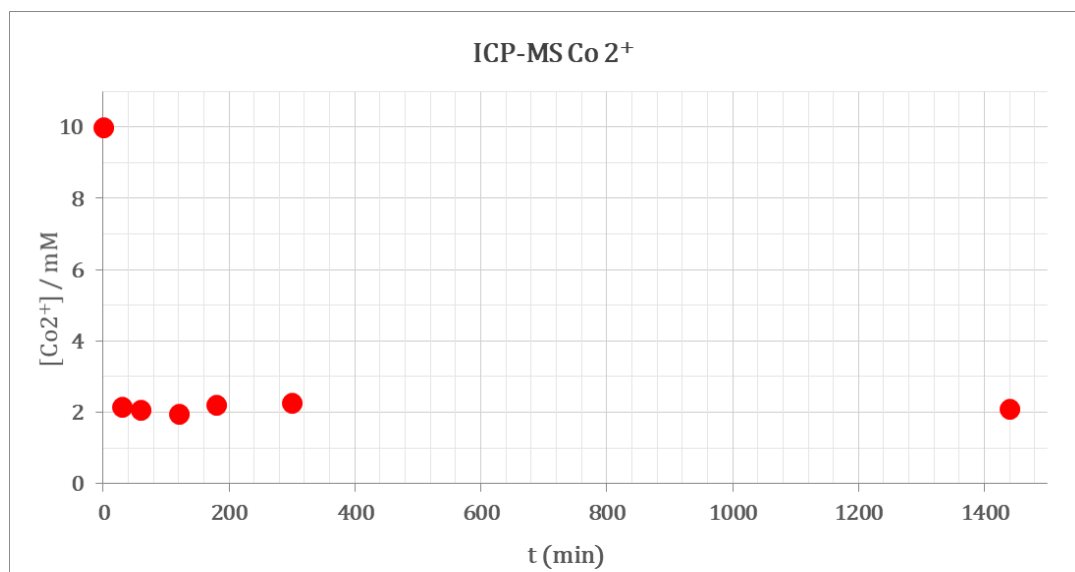

Fig. 14: *Concentration of Co²⁺ in samples analyzed via ICP-MS.*

4.4. NMR relaxometry

A Cr^{3+} sample has been analyzed using NMR relaxometry, the results obtained are comparable to those of the UV-VIS analysis.

The sample shows a reduction of the concentration of Cr^{3+} ions from 7.58mM to 4.68 mM.
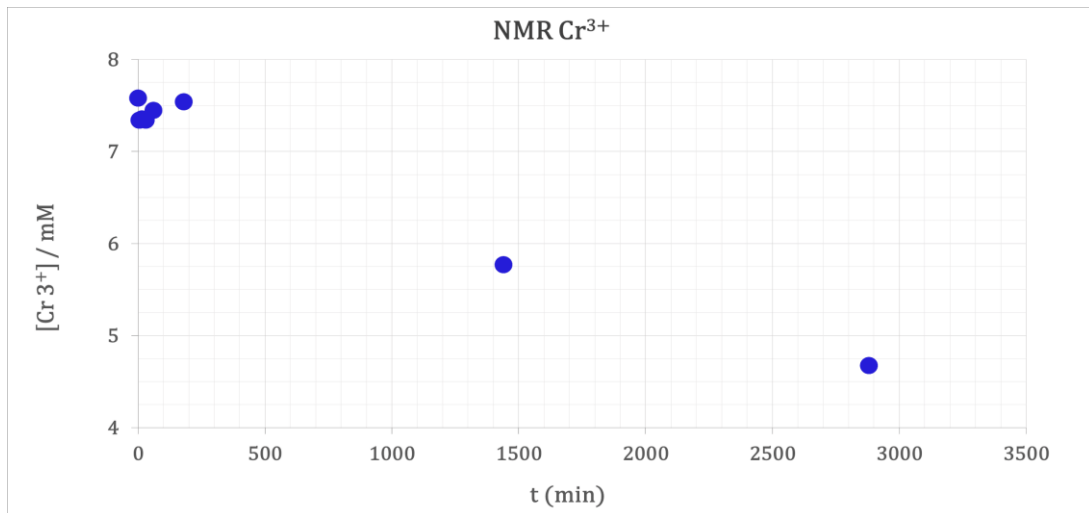

Fig. 15: *Concentration of Cr³⁺ in samples analyzed via NMR relaxometry.*

4.5. Uptake tests (Co^{2+} and Cr^{3+})

The data obtained by the analyses was used to evaluate the kinetic model relative to the absorption reaction of Co^{2+} and Cr^{3+} ions.

The kinetic model for the Co^{2+} exchange reaction was obtained using data from the spectrophotometry UV-VIS analysis; the reaction follows a parabolic model. [13]
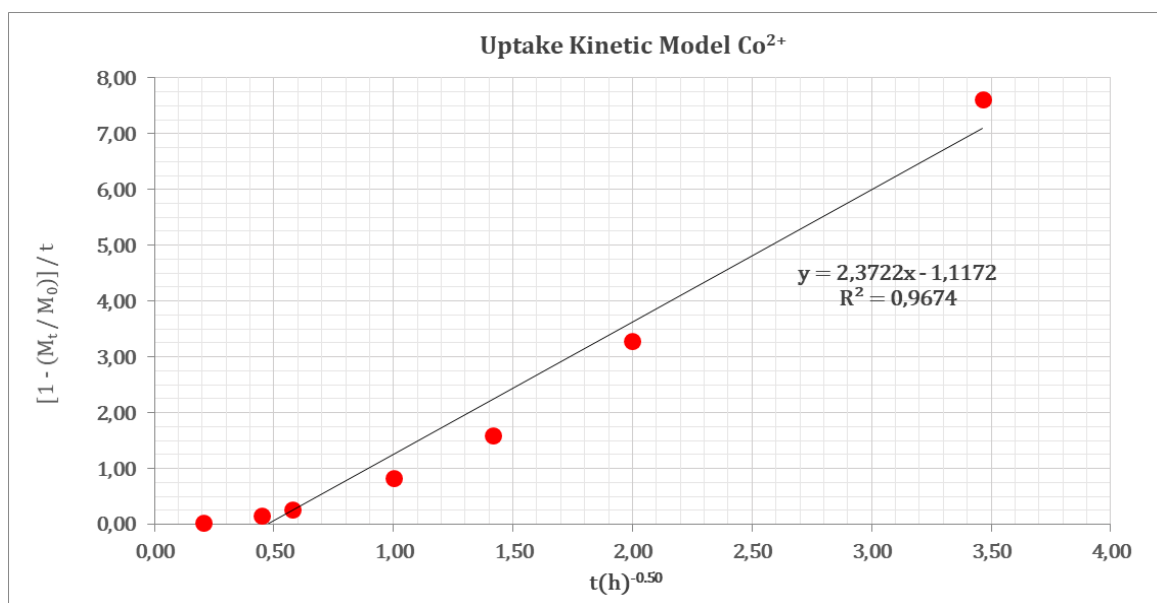

Fig. 16: *Uptake kinetic model of Co²⁺ ions.*

The kinetic model for the Cr^{3+} exchange reaction was obtained using data from the NMR relaxometry analysis; the reaction follows a first order equation; the reaction speed is directly proportional to the concentration of Cr^{3+} ions.

For reactions which follow a first order equation, the variation of concentration relative to the time follows an exponential trend.[13] The chart in Fig. 17 shows on the y axis the natural logarithm of the concentration of ions at a set time divided by the initial concentration; this chart can be approximated by the linear equation y= -0.0002x.
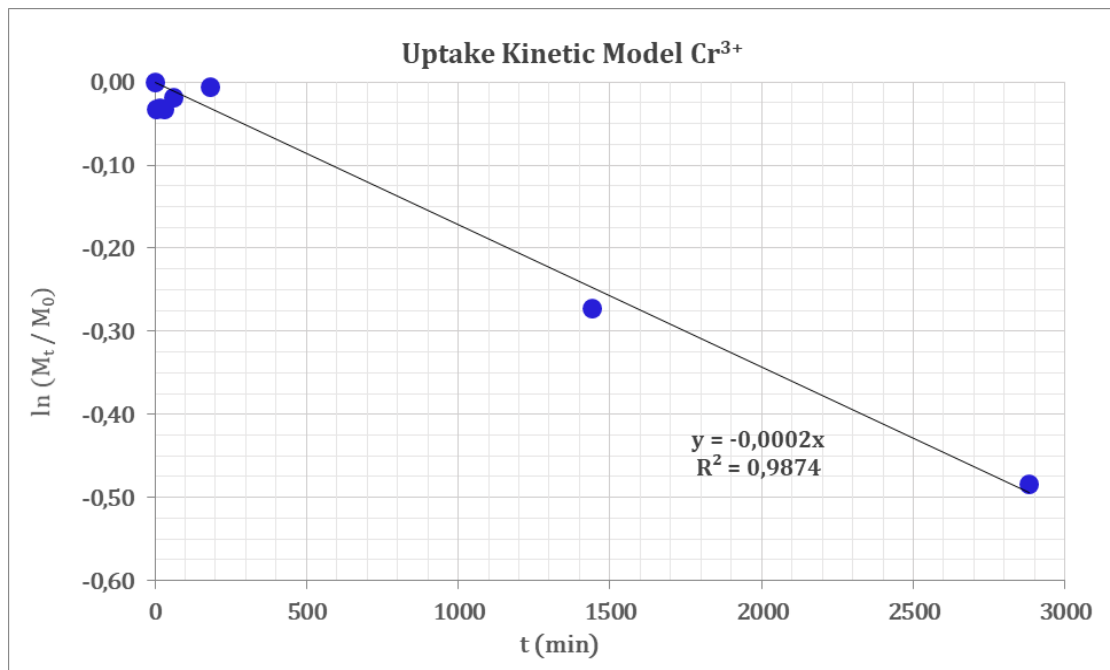

Fig. 17: *Uptake kinetic model of Cr^{3+} ions*

4.6 Saponite (Na-SAP-20) laboratory costs

The costs of the production process were determined on a laboratory scale:

1. **FUMED SILICA:** 99.00 € x 0.500 Kg → used 11.91 g → 2.35818 €
2. **NaOH:** 65.50 € x 0.500 Kg → used 0.93 g → 0.12183 €
3. **MAGNESIUM TETRAHYDRATE ACETATE:** 83.40 x 0.500 Kg → used 37.78 g → 6.301704 €
4. **ALUMINUM ISOPROPOXIDE:** 47.30 € x 1 Kg → used 16.36 g → 0.773828 €

   TOTAL: 9.555542 € for about 18 g of material → ca. 0.530863444 €/g [14]

5. CONCLUSIONS

5.1. Synthesis of SAP-20

The analyses carried out demonstrate the excellent absorption capacity of the synthesized saponite, which thanks to its lamellar structure is much more effective than the commercial products currently used for the purification of water from Cr^{3+} and Co^{2+} ions.

5.2. ICP-MS vs UV-VIS

The use of the ICP-MS technique for the determination of ions present in a sample is extremely useful and advantageous. This technique can identify the presence of many metals, even in very small concentrations (in the order of ng/L). Besides, the analysis will reveal the presence of all the elements simultaneously, without having to be repeated multiple times, as would be necessary when using a different technique such as UV-VIS spectrophotometry.

The only disadvantages of ICP-MS are the high costs and the interferences (isobaric, molecular ecc.) that can occur during the analysis.

In this regard, however, the interferences are more determinable compared to other techniques, such as UV-VIS spectrophotometry, which, although simpler and less expensive, provides less accurate results.

5.3. NMR relaxometry vs UV-VIS

NMR Relaxometry finds vast use in analyzing paramagnetic heavy metals due to some of its attributes: first of all, it can analyze small quantities of material and it makes it possible to follow concentration variations in samples in real time.

Furthermore, multiple measurements can be performed on a single sample at different time intervals, resulting in a faster analysis process.

There are however some disadvantages: the technique is only usable on paramagnetic ions and samples with a rather high ion concentration are needed to achieve accurate results.

As such, it's important to use various analytical techniques to measure more accurately the amount of metal ions absorbed by the synthesized clay and similar materials.

5.4. Sustainability

Each part of the experimental process we used follows Green Chemistry's main principles.

By analyzing the procedure costs, we concluded that the experimental method used is sustainable and low cost. In our analysis we didn't account for costs required by electricity, use of analytical instruments and labour.

There isn't enough data to conduct an LCA analysis, which would require an evaluation of the entire production process.

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