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Treball Final de Grau

Assessment of CoNi alloys as activator substrates in a degradation process.

Avaluació dels aliatges CoNi com a substrats activadors en un procés de degradació.

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*What is a scientist after all? It is a curious man
looking through a keyhole, the keyhole of nature,
trying to know what's going on.*

Jacques Yves

I would like to thank the support received during the whole development of the project to Dra. Elvira Gómez. and Dr. Albert Serrà, they have made that project a very pleasant and formative experience. I would also like to thank my classmates and laboratory colleagues, my family and my partner for their motivation, advice, and encouragement throughout the degree.

REPORT

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1. SUMMARY

This project has been developed into two parts. The first part involves the preparation of cobalt and nickel alloys using two electrochemical techniques: cyclic voltammetry and chronoamperometry. These were synthesized in an ionic liquid (DES) and using Si/Ti/Au pieces as working electrode. We can distinguish two types of alloys according to their composition on the covered surface; cobalt-rich (84.0 Co: 16.0 Ni) and nickel-rich (83.8 Ni: 16.2 Co).

The second part is based on the study of the catalytic system and its optimization, which consists of the activation of peroxymonosulfate (PMS) by the action of the alloys previously synthesized to degrade persistent organic pollutants (POPs), in this project tetracycline (TC), by advanced oxidation processes (AOPs). TC is an antibiotic with extensive use in the intensive animal industry, as it accelerates livestock growth and therefore its production. Part of this antibiotic is not metabolized by the animal, which is excreted into the environment and represents a real problem due to its persistence and the possible development of multidrug-resistant microorganisms. Different parameters that condition the effectivity and efficiency of the catalytic process had been studied: the type of alloys used, the application of a heat treatment on the substrate, the pH conditions, the effect of the PMS concentration, the effect of visible light irradiation and the effect of the contact time with the catalyst.

Keywords: CoNi alloy, electrochemical techniques, catalyst, peroxymonosulfate (PMS), degradation, tetracycline (TC).

2. RESUM

El present treball s'ha desenvolupat en dos parts. La primera consisteix en la preparació d'aliatges de cobalt i níquel mitjançant dos tècniques electroquímiques: la voltametria cíclica i la cronoamperometria. Aquests es van sintetitzar en un líquid iònic (DES) i utilitzant com a elèctrode de treball peces de Si/Ti/Au. D'aquests aliatges en podem diferenciar dos tipus segons la seva composició a la superfície coberta; els rics en cobalt (84,0 Co: 16,0 Ni) i els rics en níquel (83,8 Ni: 16,2 Co).

La segona part es basa en l'estudi del sistema catalític i l'optimització d'aquest, el qual consisteix en l'activació del peroximonosulfat (PMS) per acció dels aliatges sintetitzats anteriorment per degradar contaminants orgànics persistents (POPs), en aquest projecte la tetraciclina (TC), mitjançant processos d'oxidació avançats (AOPs). La TC és un antibiòtic amb un us molt extens en la indústria intensiva animal, doncs accelera el creixement del bestiar i per tant la seva producció. Part d'aquest antibiòtic no és metabolitzat per l'animal, el que provoca que sigui excretat i en resulti un veritable problema degut a la seva persistència en el medi i el possible desenvolupament de microorganismes multiresistents. S'han estudiat diferents paràmetres que condicionen l'eficàcia i eficiència del procés catalític: el tipus d'aliatge emprat, l'aplicació d'un tractament tèrmic sobre el substrat, les condicions de pH, l'efecte de la concentració de PMS emprada, l'efecte de la irradiació amb llum visible i l'efecte del temps de contacte amb el catalitzador.

Paraules clau: aliatges CoNi, tècniques electroquímiques, catalitzador, peroximonosulfat (PMS), degradació, tetraciclina (TC).

3. INTRODUCTION

Water is one of the most abundant resources on the planet, but only a small percentage, 2.5%, is fresh water. Of this small fraction, only 0.4% is suitable for human consumption, due to the difficulty of accessing it, which makes us aware of how precious this resource is, basic to guarantee our lives and for sustainable economic, social and environmental development.

Ensuring the supply of water in sufficient quantity and quality is fundamental for the development of societies and for the fight against poverty and disease in any part of the world. Water is, therefore, an economic reality and an essential resource for the maintenance of ecosystems, but above all it is an essential right for the life and dignity of human beings.

The recognition in July 2010 by the United Nations General Assembly of basic access to water and sanitation as a human right is directly related to the condition of water as a public good, the basis of life and of the economy, and the guarantor of the common good. There is an increasing need to strike an equitable balance between all the competing commercial demands on water resources and needs for communities as the global population grows. At the human level, water cannot be seen in isolation from sanitation. Together, they are vital for reducing the global burden of disease and improving the health. However, for underdeveloped countries, the investment to acquire such infrastructure to be able to provide drinking water is unaffordable.

Fortunately, in developed countries, water purification systems allow us to access to clean water and to return it to the environment in optimal conditions. Some of the processes used can be physical: flotation, evaporation, sedimentation, absorption, degreasing, etc., chemical: coagulation, ion exchange, neutralization, redox mechanisms, etc. and biological: activated sludge, bacterial surfaces, etc.

Furthermore, there are lots of contaminants which these techniques cannot proceed, as some coming from intensive animal production. Tetracycline (TC) is one of the primarily antibiotics groups used for veterinary and agricultural purposes and for human therapy, as well as to increase feed efficiency and improve the growth rate in livestock and poultry industries. After medication, more than 70-75 % of TC antibiotics are excreted and released in active form into the environment

via urine and feces. The amounts excreted vary with the dosage level, the age, and the animal. It is estimated that daily antibiotics excreted by a single pig and cow are 18.2 and 4.24 mg, respectively. When TC antibiotics are released from animals, manure can contaminate soil and consequently being frequently found in surface water, groundwater, drinking water, wastewater, sediments, and sludge, which leads to pollution of the surrounding environment because of its persistence. One of the worst consequences is the increasing possibility of microorganism resistance because it has an adverse effect to human health by developing microbial infections with no cure. It also has an impact on human health, leading to joint disease, nephropathy, endocrine disruption, central nervous system defect, mutagenicity, and possible photosensitivity change [1, 2].

Wastewater treatment plants do not have the capacity to remove effectively persistent organic pollutants (POPs), like TC, giving such importance to investigate and develop new methods to remove those contaminants from water. We could think it's just a problem from underdeveloped countries, but in recent studies had been found that in countries like Germany, China, and USA, in rivers nearby from intensive animal production, there is present TC in their water; in lakes, rivers, seawater and drinking water.

There are several procedures for the removal of those pollutants from waters, including membrane processes, adsorption, photocatalytic degradation, and electrochemical methods. Reverse osmosis is one of the membrane processes. Some studies reveal that it is an effective method to remove pollutants as TC but if the presence of this type of agent is very high, it could cause the fouling of the membrane. In adsorption methods the pollutant is transferred from a liquid phase to a solid surface, a problem that this method presents is that the pollutant is not destroyed, there is only a transference of it from one place to another [3].

In recent studies, sulphate radicals have received great attention. Advanced oxidation processes (AOPs) could destruct efficiently persistent organic pollutants (POPs), by its final mineralization. Sulphate and hydroxyl radicals have a better performance on organic degradation, so TC could be degraded by attacking its structure. The standard reduction potential of sulphate radical (2.5-3.1 V) is very high, so it has a high grade for organic decomposition by its oxidant power. It is produced by persulfate (PS) and peroxymonosulfate (PMS) through scission of peroxy-bond, but PMS exhibits a better performance due to its shorter bond length of O-O in the removal of emerging contaminants [4, 5]. Oxone is the commercial name of potassium

peroxymonosulfate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), it is an environmentally friendly oxidant that has big importance by being a favourable source of PMS. Transition metals and metal oxides are efficient catalysts for activating PMS, among Co(II) exhibited the better activation performance compared with other metals like Ag (I), Ce (III), Fe (II), Fe (III), Ce (III), V (III) and Ni (II) [6]. Catalysts consisting of more than one metal have some advantages comparing with single metal oxides, like improved stability and activity [7]. PMS activation by transition metals own numerous benefits like ease of use under ambient conditions, higher energy efficiency, and being more economical [8].

PS and PMS activation by metal ions and metal oxides follows a redox reaction shown in Figure 1.

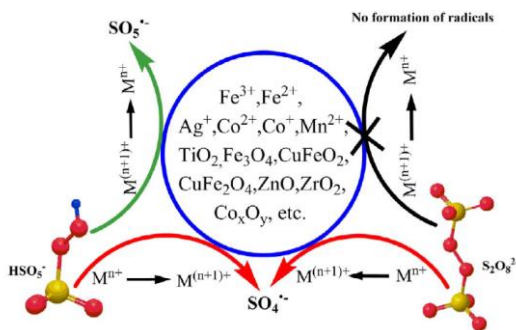


Fig 1. Activation mechanism of PMS (HSO_5^-) and PS ($\text{S}_2\text{O}_8^{2-}$) by metal ions and metal oxide. Red line represents the formation of $\text{SO}_4^{\cdot-}$, the green line the formation of $\text{SO}_5^{\cdot-}$ and the black line the no formation of radicals [9].

PMS could be also activated by ultrasound, ultraviolet, electrolysis and carbon-based catalyst.

Radicals formed due to the PMS activation degrade the pollutant by its final mineralization, thus obtaining CO_2 and H_2O as final products. It is an important fact because it prevents the formation of secondary species that could be even more harmful [10].

Catalytic activity is defined in terms of kinetics how fast a reaction is done in presence of a catalyst, which is a substance that promotes the chemical reaction by a new way without being consumed in the process. Heterogeneous catalysis has more applicability in industrial processes. The catalyst is a solid and the reactants are normally gases or liquids. Heterogeneous catalysts have achieved significant improvement in PMS system. For this work, cobalt and nickel alloys (CoNi) of different proportion of the metals are selected to study their effectivity on PMS activation. CoNi have been found to possess electronic conductivity two orders of magnitude higher than

cobalt or nickel oxides separately, making it a good candidate [11]. Usually, one of the reactants, TC, is adsorbed on the surface of the catalyst, in our case, on CoNi alloy, and over there takes place the chemical reaction.

To prepare CoNi alloys, deep eutectic solvent (DES) was prepared using choline chloride and urea as solvent for the study. This type of solvent is usually prepared by mixing a quaternary ammonium salt, that acts as hydrogen bond acceptor, and a metal salt or hydrogen bond donor [12]. They associate forming an eutectic phase characterized by its lower melting point compared by each individually.

Furthermore, DES have some different chemical properties that characterize it, as its melting point and low vapor pressure, nonflammability, high solubility, ease of preparation, toxicologically well-characterized... That is why working with DES have some advantages in economical and practical terms.

In this work, CoNi deposits of different composition were prepared by two different nickel (II) and cobalt (II) concentration solutions. Previous, an electrochemical study by cyclic voltammetry (CV) was performed, in order to establish the reduction potential range of the CoNi deposition and achieve information about the electrodeposition process [13]. CoNi were prepared chronoamperometrically and have been used as catalyst for the PMS activation.

TC degradation by PMS activation in an aqueous solution was followed using UV-Visible Spectroscopy and Total Organic Carbon (TOC).

There are many parameters that can modify its efficiency which have been studied in this project. First, the heat treatment that was performed on the CoNi alloys, one at 225°C and the other at 350°C, and its metal composition. The effect of pH was studied too, using one solution of TC at pH 6 and another at pH 8, not deviating much from the situation in which real water could be found in the environment. Another parameter was the PMS concentration used, the visible light effect and the contact time of the solution with the catalyst surface. The efficiency and reusability of the catalyst have been also studied.

The surface morphology of the samples was characterised by FE-SEM (Field Emission Scanning Electron Microscopy), so the differences between the three catalysts synthesised can be observed.

4. OBJECTIVES

The main objective of this work is the preparation of CoNi alloys able to promote the PMS activation to degrade TC and the study of the best conditions for this achievement. The work is fold based:

- The first objective consists on the preparation of CoNi deposits by electrochemical techniques and their subsequent morphological characterisation.
- The second is to determine the efficiency of the PMS/CoNi catalytic system for degrading TC by absorbance and TOC measurements for subsequent application in wastewater treatment plants.
- The last is to determine the conditions and variables that favour the PMS activation and therefore the degradation rate of POPs in water. Among these parameters to be analysed there are the type of alloy synthesised, the application of a heat treatment to the alloy, the pH conditions of the solution, the PMS concentration, the irradiation with visible light and the contact time between the catalyst and the TC and PMS solution.

5. EXPERIMENTAL SECTION

5.1. REACTANTS AND MATERIAL

The deep eutectic solvent was prepared using choline chloride (ChCl) from Across Organics and urea from Merck, both reagents with analytical grade (99%). Both solids were mixed in a molar ratio of 1 ChCl: 2 urea up to a temperature of 50 °C with continuous manual stirring. It can be observed the melting of the solids and the formation of completely colourless liquid, the DES.

Prior to prepare the electrolyte solutions, the salts, cobalt (II) chloride hexahydrate from Alfa Aesar and nickel (II) chloride hexahydrate from Sigma Aldrich, of analytical grade, must be dehydrated in the stove at 120°C for 24 hours.

Two different solutions were prepared, one rich in cobalt (II) (Co solution), with a concentration of 0.03 M NiCl₂ and 0.14 M CoCl₂ and the other one rich in nickel (II) (Ni solution), with an inverse concentration, 0.14 M NiCl₂ and 0.03 M CoCl₂. Salts were dissolved in the DES under constant magnetic stirring at 70 °C to reduce its viscosity and facilitate their dissolution.

The electrochemical measurements were carried out using an AUTOLAB equipment and NOVA 2.1 software, and a cylindrical thermostatic cell with a three-electrode configuration of one single compartment. For the electrochemical study was employed:

- Working electrode: a flat silicon piece with a layer containing Ti (15 nm) and Au (100 nm), called "Si/Ti/Au", on which the deposits were prepared.
- Reference electrode: an Ag | AgCl | DES.
- Auxiliar electrode: a Pt spiral.

Before the studies are carried out, the electrodes must be treated. Si/Ti/Au area is first cleaned with ethanol and then cleaned in water and left to dry with nitrogen. Pt spiral is cleaned in concentrated nitric acid and then heated in a flame until incandescent.

In all the experiments the temperature was maintained at 70 °C in order to favour low viscosity and high conductivity and the solutions were deoxygenated by bubbling argon.

Deposits were prepared under a charge of 400 mC. This charge was chosen with a criterion to attain enough deposit on the total coverage of the substrate. To check the composition of the deposit over the entire surface of the Si/Ti/Au electrode, it was used a Fischer Scope X-Ray system XDAL and WIN-FTM software.

For the degradation kinetic studies, two solutions of TC 20 ppm from Alfa Aesar were prepared, one acidified, at pH 6 with hydrochloric acid 1 M, and another one at pH 8 adjusted with sodium hydroxide 1 M. These solutions must be stored in dark and were used for all the experiments. A 7.8 mM PMS solution was prepared daily with Oxone from Alfa Aesar, except for the PMS concentration effect experiments. Measurements were taken with a spectrophotometer UV-1800 Shimadzu UV and at a controlled temperature of 20 °C. After the absorbance measurements, the content of the cuvette solution was stored in the freezer to avoid the prolongation of the reaction. Later, TOC was measured too.

5.2. EXPERIMENTAL METHODS

5.2.1. Electrochemical techniques

Two electrochemical methods have been used: cyclic voltammetry, which is an electrochemical technique that allows the gathering of information on electrodic processes occurring on an electrode surface. In this work it was used to gain information about the general behaviour of the deposition process. Experiments were mainly carried out at 50 mV·s⁻¹, scanning at first to negative potentials, and cycling one run in each voltametric experiment. Also, chronoamperometric experiments were performed to prepare the CoNi deposits using Si/Ti/Au. In this electrochemical technique, a constant potential is applied to the working electrode and current versus time is monitored.

5.2.2. Catalytic experiments

TC degradation has been studied by measuring absorbance as a function of time with a spectrophotometer and with TOC measurement, allowing us to evaluate its mineralization grade. For the study, a quartz cuvette was filled with 2.5 mL 20 ppm TC solution, basic or acidic, and left with the sample for 30 minutes to allow its adsorption. This process was followed for all the

experiments. After this time, 0.1 mL PMS 7.8 mM was introduced, therefore the final concentration of PMS in the cuvette is 0.3 mM.

For the determination of the optimal conditions for the TC degradation, different parameters have been studied, one of them is the kind of alloy synthesised. For each alloy composition three kinds of deposits were analysed, deposits as prepared and deposits with two different heat treatment: treated at 225°C for two hours in the stove and treated at 350 °C for two hours in the oven. The protocol for them is described in Figure 2.

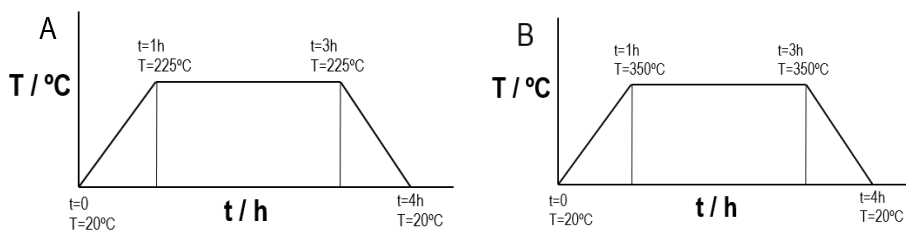


Fig. 2. Heat treatment applied for the samples A) 225°C in the stove B) 350°C in the oven.

At the same time, pH conditions were analysed for both TC solutions. The effect of PMS concentration used was another parameter studied. For this purpose, three solutions were prepared with different PMS concentrations: 7.8 mM, 5.2 mM, and 2.6 mM. In the cuvette, 2.5 mL of TC was added and carried out with both samples, cobalt-rich alloy (Co sample) and nickel-rich alloy (Ni sample) and left for 30 minutes to allow its adsorption. After this time, 0.1 mL of the PMS solutions was added, so finally, the concentration in the cuvette is 0.3, 0.2, and 0.1 mM, respectively. Experiments to study the visible light effect were performed using 2.5 mL of TC and 0.1 mL of 7.8 mM PMS. For this, the substrate was left in the TC solution for 30 minutes to allow its adsorption. After that, 0.1 mL of PMS was added and at this time the absorbance measurements started but irradiating the dissolution with visible light. The contact time of the sample with the TC and PMS solution have also been analysed. Once the PMS was added to the cuvette, after 3.5, 7.5, 15 and 30 minutes, the alloy was removed.

Catalytic degradation in ten consecutive cycles was also performed to verify the stability and reusability of the substrates for the TC degradation. In these experiments, 2.5 mL of TC, 0.1 mL of 7.8 mM PMS and the same pieces of Co and Ni samples were used.

5.3. CHARACTERIZATION

Surface morphology of the samples were observed by FE-SEM (JSM-7100F Analytical Microscopy). With this technique, images of the substrates are obtained by scanning the surface with a focused beam of electrons, where these electrons interact with the sample atoms producing various signals that give information about de surface morphology.

6. RESULTS AND DISCUSSION

6.1. ELECTROCHEMICAL STUDIES ON Si/Ti/Au

6.1.1. Electrochemical window

The electrochemical window of the substrate and the DES solution have been established by the CV technique.

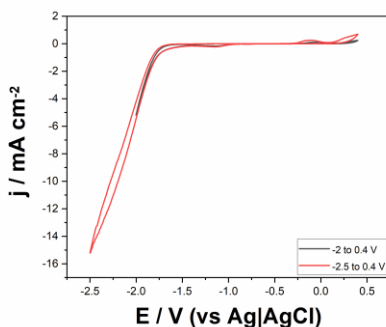


Fig 3. Cyclic voltammograms in the DES solvent with different electrochemical windows using as working electrode Si/Ti/Au, $v=50 \text{ mV}\cdot\text{s}^{-1}$.

Figure 3 shows the profile of the voltammograms recorded at two different negative potentials; -2.0 and -2.5 V maintaining the positive limit at 0.4 V. When negative potentials were applied, the *initio* of the DES reduction process appeared around -1.75 V. Scanning towards positive potentials, it can be observed the beginning of the oxidation of gold from the Si/Ti/Au electrode. As the manner the electrochemical window was established in the potential range between -1.75 V and 0.3 V.

6.1.2. Cyclic voltammograms of CoNi

A previous electrochemical study was carried out using the CV technique on the two electrolyte solutions, Co solution and Ni solution. This will allow to analyze the behavior of these solutions according to the applied potential.

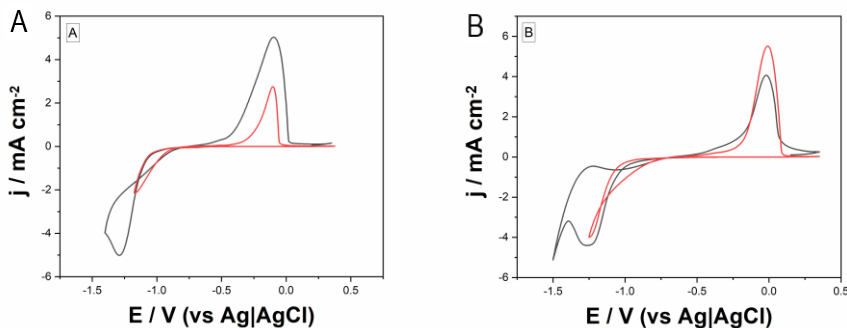


Fig 4. Cyclic voltammograms on Si/Ti/Au electrode with different electrochemical window, $v=50 \text{ mV} \cdot \text{s}^{-1}$.

A) Co solution, B) Ni solution.

The voltammograms have been recorded scanning at first towards negative potentials. In Figure 4 it can be observed for both samples the appearance of the reduction peak at negative potentials. In a previous work it was demonstrate that these peaks are sensitive to the stirring of the solution as corresponds to a mass-controlled process [14]. One of the most identifiable features is the formation of the nucleation loop (red curve in Figure 4.A) when the scan was reversed current begins to appear indicating that a nucleation process takes place, as corresponds to a nucleation and a three-dimensional growth.

Scanning to positive potentials a single peak is recorded for both solutions. It seems that they have relatively similar standard reduction potentials, -0.25 V for Co(II)/Co and -0.28 V for Ni(II)/Ni , which facilitates the formation of a solid solution alloy.

Elonging the negative potential it can be observed that the DES reduction is advanced respect to the observed to the free substrate, evidencing the electrocatalytic process of the CoNi deposit over DES reduction. This fact leads a pernicious effect on the deposit that is evidenced in the diminution of the recorded oxidation charge, fact that limits the suitable working potential range.

Comparing the potentials at which current starts was evidenced that in the cobalt-rich solution the process is slightly favored.

From these voltammetric results was possible to select for each solution the adequate working range potentials.

6.1.3. Chronoamperometric preparation of the catalytic substrate

In this work, two kinds of samples were prepared; CoNi deposits cobalt-rich (Co sample) and CoNi deposits nickel-rich (Ni sample) in order to evaluate the effect of the sample composition on the PMS catalytic process over TC degradation. CoNi deposits have been prepared by means potentiostatic technique. Due to the deposition process depends on mass transport, it is necessary stirring the solution during the deposition process in order to attain a homogeneous composition in the prepared deposits.

Jointly to the previous voltammetric study, it was observed that for the Ni solution the potential to be applied is -0.95 V by generating the Ni samples and for the Co solution the potential of -1.05 V by synthesizing the Co samples [14] in order to have the inverse proportions as seen in Table 1.

Figure 5 shows that the cobalt deposition process takes place quicker in comparison with nickel at the selected potentials. In all the experiments under stirring conditions the current remains in stationary. Deposits were prepared under a charge of 400 mC.

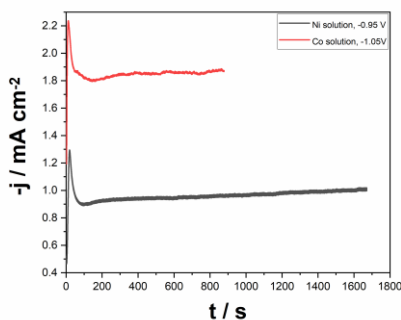


Fig 5. j - t transients on Si/Ti/Au under stirring and bubbling with argon. Ni deposition $E_{\text{applied}} = -0.95$ V, Co deposition $E_{\text{applied}} = -1.05$ V.

The metallic composition for all the synthesised samples is shown in Table 1, confirming that the selected conditions allow us to obtain the desired compositions.

Sample	E / V	Co / at %	Ni / at %
Co sample	-1,05	84.0	16.0
Ni sample	-0.95	16.2	83.8

Table 1. Metallic proportion of the alloys synthesized.

6.2. DEPOSITS CHARACTERIZATION

In Figure 6 it is observed that all the deposits prepared have a compact and homogeneous structure. All the surface has been covered by thin platelets with randomly distributed sharper edges, oriented vertically to the surface. The principal difference between Co samples and Ni samples is the dimension of the structures formed.

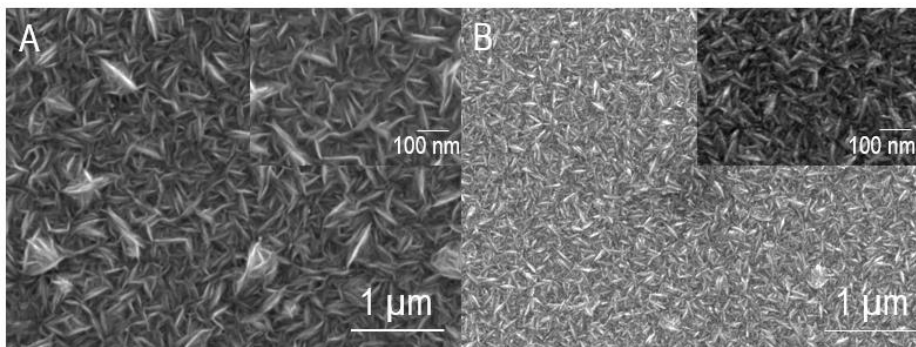


Fig. 6. SEM picture at different magnifications of CoNi deposits as prepared over Si/Ti/Au substrate. A) Co sample, B) Ni sample.

Some of the samples were subjected to heat treatment in order to form different oxides in a controlled way. Some of the samples were treated at 225°C for 2 hours in the stove and others at 350°C for 2 hours in the oven, both according to the sequence explained in the Experimental methods section Figure 2. By FE-SEM technique (Figure 7) the surface morphology of the deposits was analyzed and compared. As can be seen on the Co sample, the thin platelets observed in the as prepared developed to spheric morphology under heat treatment. It is also seen that a higher temperature the feature dimensions of both samples increases.

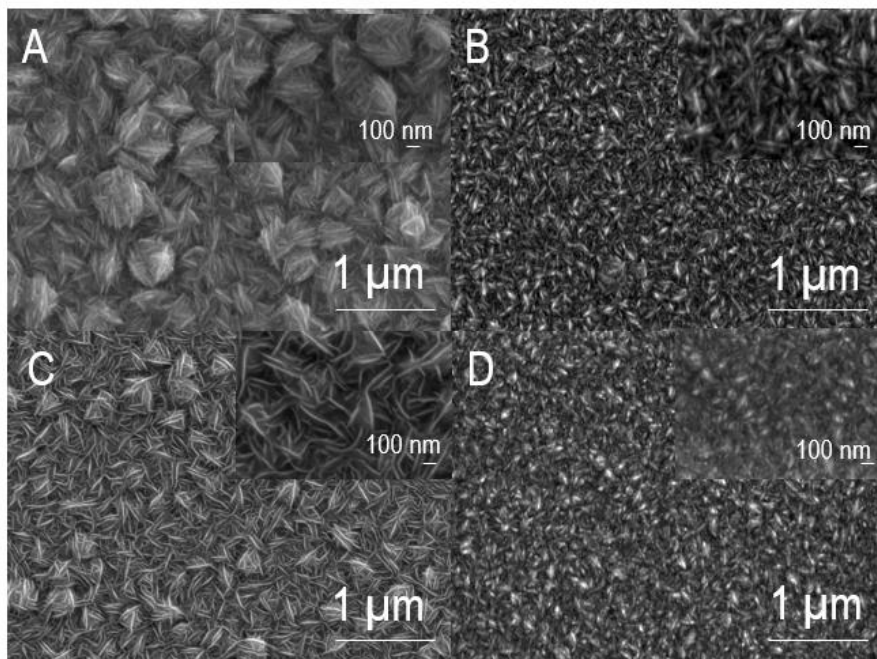


Fig. 7. SEM pictures at different magnifications of Co (A, C) and Ni (B, D) samples with a thermic treatment at 225°C (A, B) and at 350°C (C, D).

Co sample presents sharper edge oriented vertically to the surface, generating open space and more active sites for PMS activation. Such architecture ensures the fast electron transfer between PMS and active cobalt and nickel transition metals atoms.

The atom ratio of Co(II)/Co(III) could be higher in 350°C heat treated Co samples. Consequently, these substrates could have a higher oxygen vacancy density. This higher density improves the electron transfer between the catalyst and PMS, which gives this substrate the best catalytic performance. This success also contributes to the generation of $O_2^{\cdot-}$ radicals, so it has more degrading power [15].

6.3. CoNi DEPOSITS AS CATALYSTS FOR TETRACYCLINE DEGRADATION

6.3.1. Tetracycline stability

Since the study of TC degradation is performed by absorbance measurements, the wavelength of maximum absorption had to be determined. pH is an important factor for TC, as its charge varies accordingly and its interaction with the catalyst surface will vary according with it. Figure 8 shows the variation of its protonation state as a function of pH. pKa values are $pK_{a1}=3.30$, $pK_{a2}=7.68$ and $pK_{a3}=9.69$ [16]. Thus, in the basic solution, TC will be negatively charged and in the acidic solution it will be neutral.

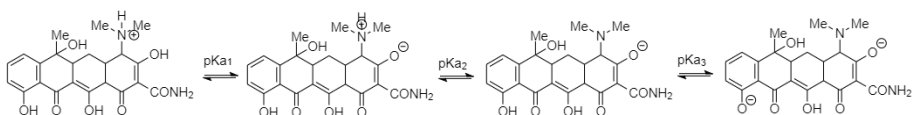


Fig 8. TC dissociation as a function of solution pH.

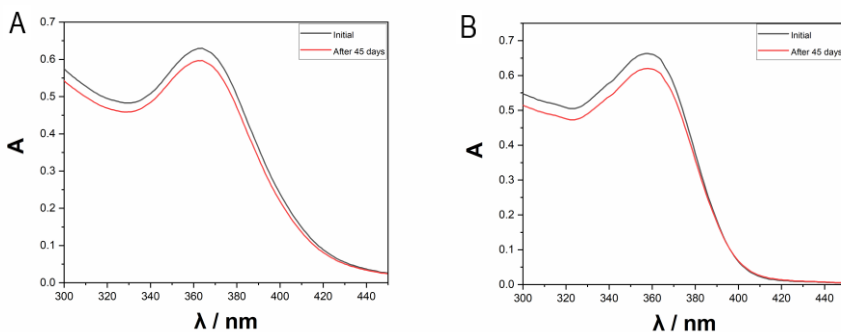


Fig. 9. UV-Vis spectrum of TC solution. Experimental conditions: A) pH=6, B) pH=8, [TC]=20 ppm, T=20°C.

The wavelength of maximum absorption in the acidified solution, as can be seen in Figure 9 A, was $\lambda=364$ nm and for the basified one, as can be seen in Figure 9 B, was $\lambda=358$ nm.

After 45 days of the preparation of both solutions and saved under dark, a new UV-Vis spectrum has been recorded and TOC measurements have been made, observing that the absorbance values remain almost constant and the mineralization percentage was negligible, which affirms its lengthy half-life in aqueous medium and consequently, its potential danger versus the generation of new microorganisms resistant to current antibiotics.

6.3.2. Catalytic performance

The kinetic degradation of TC through the PMS activation on the synthesized deposits of CoNi has been studied by varying a series of parameters to optimize the conditions for removing this type of pollutant from water.

As it is a heterogeneous catalyst and therefore, the catalytic process takes place on the surface of the catalyst, in this case, on the CoNi alloy, the adsorption-desorption equilibrium must occur to achieve a faster degradation process. For this purpose, the substrate was left in the cuvette with the 2.5 mL of TC. It has been determined that this is achieved within 10 minutes of contact with the TC solution, when the absorbance measurements remain constant, as can be seen in Figure 10 and 11. It is due to this fact that for each measurement of all these experiments, an interval of 30 minutes have been left at the beginning to achieve this equilibrium.

The relationship between the surface charge and pH is an important factor. As discussed in Figure 8, TC at pH 6 is neutrally charged and at pH 8 is negatively charged, so depending on the surface charge, the molecule will be more or less attracted to the alloy.

At time 0, when 0.1 mL PMS is added into the cuvette, it is fully demonstrated how the TC degradation process is initiated, as can be observed an abrupt drop in the pollutant concentration for all the type of catalysts and conditions studied.

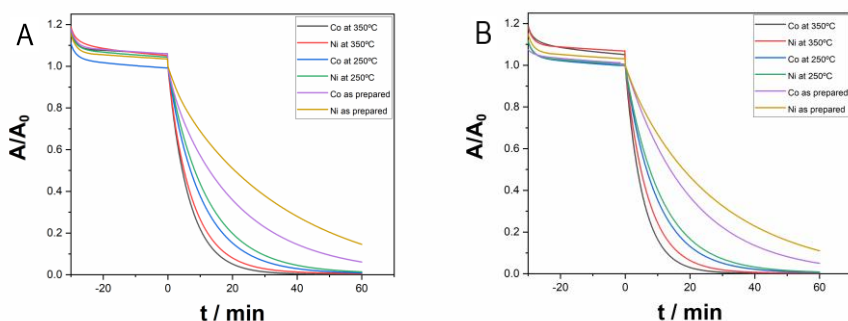


Fig. 10. Catalytic degradation of TC in different catalysts. Experimental conditions: A) pH=6, B) pH=8, $[TC]_0=20$ ppm, $[PMS]_0=0.3$ mM, $T=20^\circ\text{C}$.

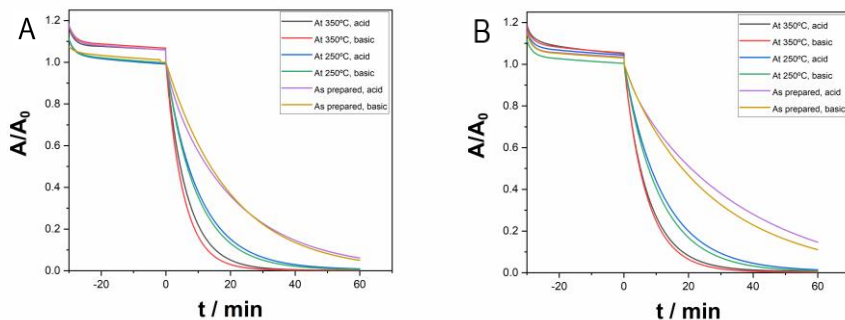


Fig 11. Catalytic degradation of TC in different pH conditions A) Co sample B) Ni sample.

Experimental conditions: $[TC]_0=20$ ppm, $[PMS]_0=0.3$ mM, $T=20^\circ\text{C}$.

The first parameters to be analyzed were the effect of the heat treatment applied to the sample, the alloy composition and under which acid-base conditions the most rapid degradation occurs.

As can be seen in Figures 10 and 11, in all samples and indifferently of pH, the pollutant can be removed with very high efficiency from water. However, it is evident that the catalytic process depends on some variables.

The most obvious one is the heat treatment applied. It can be observed that those samples which have been subjected to a treatment at 350°C are those which present a faster degradation, where passed 30 minutes, the degradation process is almost absolute, followed by samples with a treatment at 225°C and finally the as prepared. Therefore, the treatment at high temperature, confers a better PMS activation and consequently, higher is the TC removal performance.

The application of the heat treatment on the samples stimulates the oxidation of cobalt and nickel in the substrate and the formation of oxides on the surface, in which the reversible redox cycles Co(II)/Co(III) and Ni(II)/Ni(III) contributes to reactive oxygen radicals, which improve the catalytic efficiency for PMS activation as described in Figure 1 [9, 14].

At the same time, for the same heat treatment, it is possible to differentiate which alloy is more efficient. It can be observed that Co samples show a higher degradation efficiency than Ni samples with independence of the pH conditions.

As can be seen in Figure 11, pH is another determining factor for the kinetics of the degradation reaction. In basic conditions, the process is faster than not in acidic, maintaining the order already established above, where samples treated at 350°C are the ones with the fastest

reaction rate, followed by the ones treated at 225°C and finally the samples without any treatment, and those Co samples.

It is known that the reactivity of pollutants increases with the increasing deprotonation degree. As it is explained in Figure 8, at pH 8 TC presents as an anion, so it has higher reactivity than TC as neutral at pH 6 [9]. Also, the adsorption degree of TC on the catalyst plays a fundamental role, since at more adsorbed molecules, greater is the degradation, that is why at basic pH, where there is a higher and faster adsorption, the kinetics is faster.

The kinetics rate constants and their reaction order have been determined by the integral method and it has been concluded that TC degradation follows a pseudo-first order kinetics. Reactions rate constants are shown in Table 2:

Thermic treatment	$k_{Ni\ samples} / \text{min}^{-1}$		$k_{Co\ samples} / \text{min}^{-1}$	
	pH 6	pH 8	pH 6	pH 8
As prepared	0.0308	0.0454	0.0361	0.0499
At 225°C	0.0772	0.0882	0.0860	0.0962
At 350°C	0.1046	0.1469	0.1323	0.1733

Table 2. Rate constants for the different pH, heat treatments and samples.

Results show what has already been observed with the absorbance measurements. It can be seen that the treatment at higher temperature, confers a highest kinetic constant, and therefore, a better TC removal performance. The value of the rate constants with the 350°C treatment multiplies its value by more than 3 with respect to the as prepared ones. It can also be seen that Co samples have a greater degradation performance by its higher rate constants. Experiments carried out at pH 8 are also the most effective.

Moreover, the efficiency of the catalyst has been assessed by TOC measurements. In this way, the amount of TC that has been mineralized can be known. TOC and mineralization data are shown in Table 3.

Sample	Thermic treatment	pH	TOC / ppm	Mineralization / at %
Cobalt-rich	As prepared	6	4.30 (0.06)	78.4
		8	3.76 (0.15)	81.0
	225°C	6	1.96 (0.06)	90.1
		8	1.10 (0.05)	94.4
	350°C	6	0.12 (0.01)	99.4
		8	0.02 (0.05)	99.9
Nickel-rich	As prepared	6	6.79 (0.02)	65.9
		8	5.86 (0.10)	70.4
	225°C	6	2.80 (0.15)	85.9
		8	2.01 (0.07)	89.8
	350°C	6	0.79 (0.06)	96.0
		8	0.43 (0.05)	97.8

Table 3. TOC and mineralization results for each sample respect the initial solutions. pH=6: $[TC]_0=19.9$ ppm, pH=8: $[TC]_0=19.8$ ppm.

TOC measurements allow us to confirm even more strongly what was previously concluded, as those samples that were heat-treated, cobalt-rich and in a basic medium, are the ones that present a better PMS activation, as can be seen in the table, where the mineralization percentage for these conditions is almost 100%. Even so, it is important to highlight the high performance of all the samples, where after 1 hour, the mineralization for untreated samples ranges between 60-80%, for samples treated at 225°C between 85-95% and for samples treated at 350°C always exceeding 95%.

6.3.3. PMS concentration effect

As observed in the previous experiments, with a 0.3 mM PMS concentration, TC degradation using a heat-treated sample at 350°C is almost complete. Therefore, experiments with 0.2 mM and 0.1 mM PMS solutions have been carried out to observe their efficiency too.

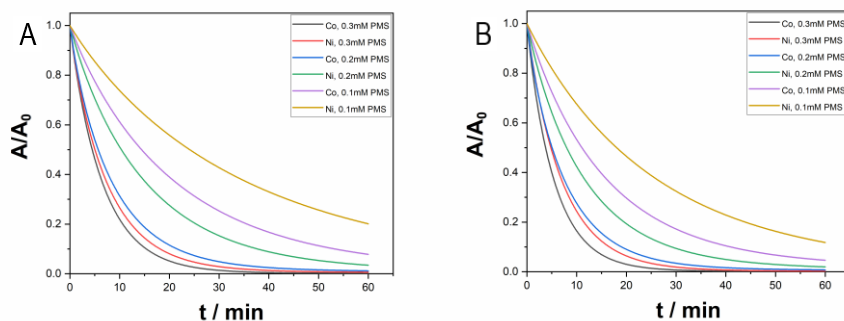


Fig 12. Catalytic degradation of TC in different pH conditions and different PMS concentrations. Experimental conditions: A) pH=6 B) pH=8, $[TC]_0=20$ ppm, samples treated at 350°C , $T=20^\circ\text{C}$.

It can be seen at Figure 12 that the PMS concentration is a determining factor in the degradation of TC. It is observed that as PMS concentration decreases, the rate at which it degrades decreases, being the least effective solution the 0.1 mM one and the most effective solution the 0.3 mM. The hierarchy followed is in line with the concluded above, where substrates with a higher cobalt composition have a higher efficacy.

The kinetics rate constants and their order have been determined again by the integral method and it has been concluded that for all the systems under study TC degradation follows a pseudo-first order kinetics. Reactions rate constants are shown in Table 4:

[PMS] / mM	k Ni samples / min ⁻¹		k Co samples / min ⁻¹	
	pH 6	pH 8	pH 6	pH 8
0.3	0.1046	0.1469	0.1323	0.1733
0.2	0.0603	0.1032	0.0751	0.1150
0.1	0.0265	0.0437	0.0356	0.0550

Table 4. Rate constants for the different pH, PMS concentration and samples.

By means of the information provided by Table 4, as higher the PMS concentration is, higher is the kinetic constant and therefore faster is the degradation process. The increased PMS concentration would produce more reactive species to degrade TC [7], it is why at 0.3 mM PMS the degradation rate is higher.

6.3.4. Light effect

The efficiency of the catalytic process in contact with visible light is another parameter that has been studied, where at the same time as the PMS was added, the solution was irradiated with light. It can be observed that the degradation process is much faster than those previously studied, as after 5 minutes a strong decrease of TC can already be seen, as observed in Figure 13, while in dark conditions it was observed around the minute 15, as observed in Figure 10 and 11. This is also confirmed by the kinetics constants values, Table 5, which are much higher with light contact than those calculated previously (Table 2), where the degradation took place in dark conditions. As in previous sections, it is observed that the most efficient system is with Co sample and at basic pH, in fact, at these conditions, rate constants double its values with respect to the measurements made in dark.

$k_{\text{Ni samples}} / \text{min}^{-1}$		$k_{\text{Co samples}} / \text{min}^{-1}$	
pH 6	pH 8	pH 6	pH 8
0.199	0.292	0.288	0.388

Table 5. Rate constants for the different pH and samples with light contact. Experimental conditions:

$[\text{TC}]_0=20$ ppm, $[\text{PMS}]_0=0.3$ mM, $T=20^\circ\text{C}$, $P= 5\text{mW}$

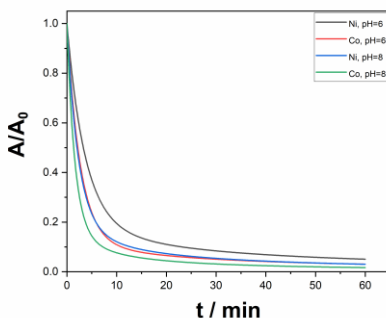


Fig 13. Catalytic degradation of TC in different catalysts. Experimental conditions: $[\text{TC}]_0=20$ ppm,

$[\text{PMS}]_0=0.3$ mM, $T=20^\circ\text{C}$, $P= 5\text{mW}$.

TOC measurements confirm that the light irradiation of the catalytic system is a determining factor for the activation of PMS and the rapid degradation of TC, as the percentage of mineralization is almost 100% for both catalysts and both pH conditions, as can be observed

in Table 6. This is likely because of the combination of the radicals formed by Co-mediated PMS activation as was observed in Figure 1 and photolytic activation of PMS, where two mechanisms might be involved [9]. The first consists of breaking the O-O bond following Eq. 1.



The second consists of the activation of PMS by the products generated by the radiation of water, as presented in Eq. 2 and 3.



It has been determined that if the TC solution, without the action of PMS, is only treated with light irradiation, the photolysis process does not occur.

Sample	pH	TOC / ppm	Mineralization / at %
Cobalt-rich	6	0.01 (0.03)	99.9
	8	0.02 (0.02)	99.9
Nickel-rich	6	0.05 (0.03)	99.8
	8	0.03 (0.01)	99.8

Table 6. TOC and mineralization results for Co and Ni sample respect the initial solutions. Acid solution: $[\text{TC}]_0=19.9$ ppm, basic solution $[\text{TC}]_0=19.8$ ppm.

6.3.5. Contact time

The contact time of the sample with the TC and PMS solution has been studied to know its influence on the PMS activation by the catalyst. It has been studied for a time of 3.8, 7.5, 15, 30 and 60 minutes, where after this time, the alloy was removed, and the degradation reaction was allowed to continue until 60 minutes.

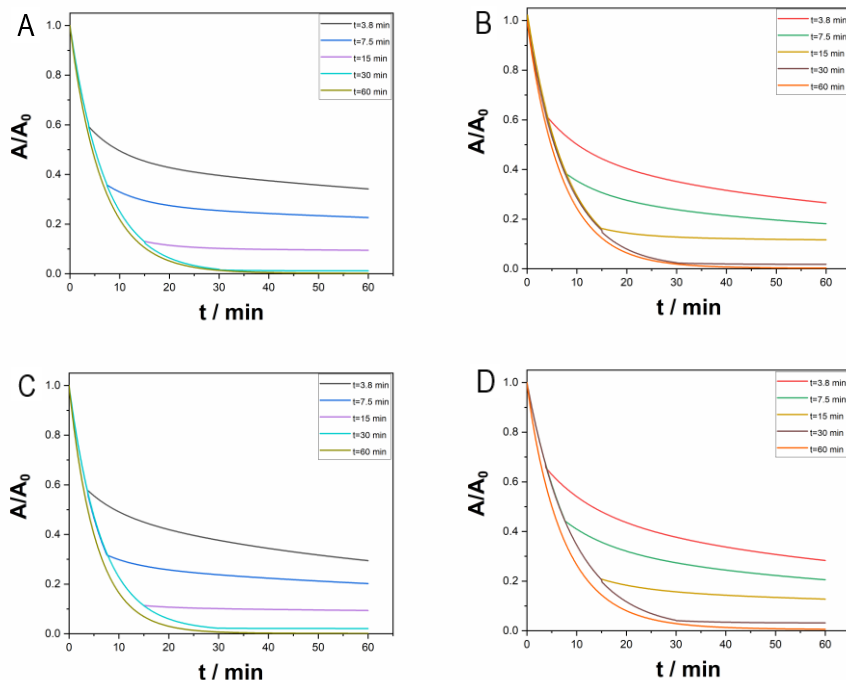


Fig 14. Catalytic degradation of TC in different catalysts removing it after different times. Experimental conditions: A) Co sample, pH=6, B) Ni sample, pH=6, C) Co sample, pH=8, D) Ni sample, pH=8, $[TC]_0=20$ ppm, $[PMS]_0=0.3\text{mM}$, $T=20^\circ\text{C}$.

Figure 14 shows that the removal of the sample plays a very important role, having in consideration factors such as pH and the type of catalyst, as the degradation rate decreases drastically when the alloy is removed, but it can be seen how the reaction goes on even if the catalyst is not present.

6.3.6. Reusability and stability

The stability and reusability of the substrates were evaluated:

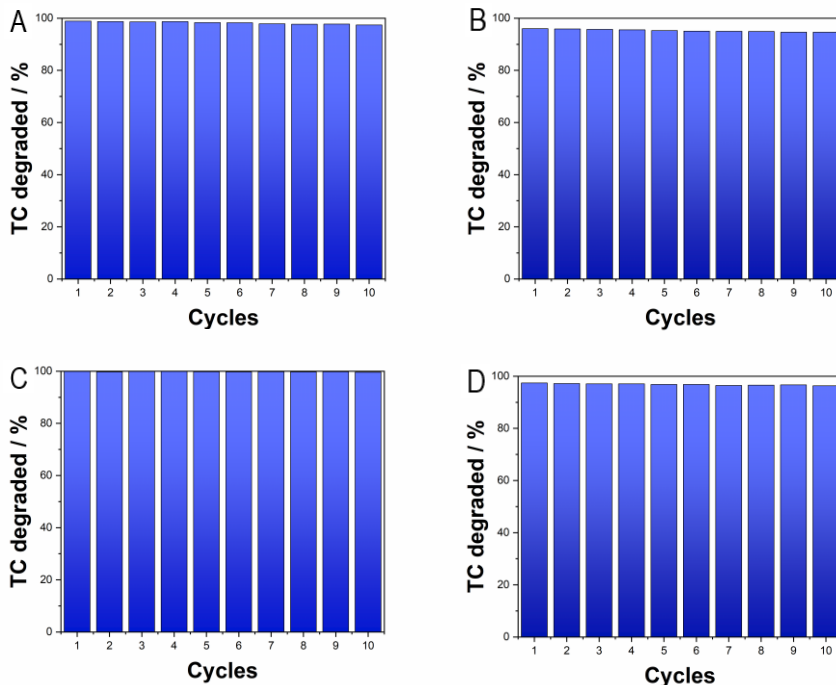


Fig 15. TC degradation after 60 minutes using the same catalyst for each measurement in ten consecutive cycles runs. A) Co, pH=6, B) Ni, pH=6, C) Co, pH=8, D) Ni, pH=8. Experimental conditions: $[TC]=20\text{ppm}$, $[PMS]=0.3\text{mM}$, $T=20^\circ\text{C}$.

It can be seen in Figure 15 how after 10 catalytic cycles of one hour each for the same substrate, the percentage of TC degradation is maintained: in the case of the Co samples with a degradation of almost 100% and for the Ni samples with a degradation grade of more than 95%, both in the basic and in the acidic solution. Thus, the catalysts are stable and can be reused.

7. CONCLUSIONS

It has been concluded that the PMS/CoNi catalytic system is very efficient in removing persistent organic pollutants (POPs) by advanced oxidation processes (AOPs), so it could be an interesting proposal to be applied in wastewater treatment plants in order to eliminate these pollutants from our waters, and consequently, from the environment. However, the catalytic effectivity is subjected to some of the parameters analyzed.

The most effective substrates are the cobalt-rich ones (Co samples), substrates that allow to be reused for several experiments without losing efficacy, and under basic pH.

Samples which have been heat treated are more effective than the as prepared ones, where Co samples treated at 350°C have a mineralization percentage of nearly 100%, and Ni samples treated at 350°C around 97% after 60 minutes.

Working with a higher PMS concentration (0.3 mM) and visible light irradiation, a greater TC degradation is observed, where the amount of organic compound removed is for both substrates and pH almost 100%.

The degradation process continues with no contact with the catalyst, but at a reduced rate. Therefore, it will be important to keep the solution in contact with the sample during the degradation.

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9. ACRONYMS

CoNi	Cobalt and Nickel alloy
DES	Deep Eutectic Solvent
POPs	Persistent Organic Pollutants
AOPs	Advanced Oxidation Processes
TC	Tetracycline
PMS	Peroxymonosulfate
PS	Persulfate
ChCl	Choline Chloride
FE-SEM	Field Emission Scanning Electron Microscopy
TOC	Total Organic Carbon
UV-Vis	UV-Visible
CV	Cyclic Voltammetry
Co solution	0.03 M NiCl ₂ and 0.14 M CoCl ₂
Ni solution	0.14 M NiCl ₂ and 0.03 M CoCl ₂
Co sample	Cobalt-rich sample
Ni sample	Nickel-rich sample
j-t	Current-time
A	Absorbance