

## Waste-to-Energy - Energy recovery from domestic wastewater

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### ABSTRACT

This work focuses water electrolysis studies, with several different cathode materials, to find effective electrocatalysts to produce H<sub>2</sub> using an effluent from municipal wastewater treatment as a hydrogen source. Tests are done with or without the addition of electrolyte, being the electrolyte selected KOH. The study consists in applying cyclic voltammetry at different temperatures, ranging between 25 and 85 °C and using the Tafel and Butler-Volmer scientific models to obtain the kinetic parameters. The electrodes used were the stainless steel 304 (SS304), platinum (Pt) and platinum-rare earth (Pt-RE) binary alloys, and nickel (Ni) and Ni-RE alloys, with the REs being cerium (Ce), samarium (Sm), dysprosium (Dy), and holmium (Ho). It was possible to conclude that, the addition of KOH improves considerably the efficiency of the electrochemical process. The activation energy obtained with a Ni electrode with KOH addition was 228kJ mol<sup>-1</sup>. It was also made a study of the anodic reaction with Pt electrodes. It was also performed in a study involving electrolysis of synthetic urine, using Pt and Ni electrodes.

**Keywords:** Energy; Environment; Hydrogen; Wastewater.

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### INTRODUCTION

Rapid population growth has aggravated the water scarcity, turning this one of the main problems to be faced by world population in the XXI<sup>st</sup> century. Water sustains humans' health, food production, and economic development. In developing countries, approximately 3.5 million deaths related to inadequate water supply, sanitation and hygiene occur each year. It is estimated that over 80% of used water worldwide is not collected or treated. Unfortunately, population without access to sanitation services is still increasing. The rate at which sanitation programs are being introduced to communities is far lower than the rate of overall population growth, resulting in more underserved people,

despite the attempts to increase coverage. Furthermore, the population growth results in overcrowding, exacerbating sanitation issues. The discharge of untreated waste into water systems is one of the most common sanitation problems. This creates multiple issues, poor water quality incurs many economic costs: degradation of ecosystem services; health-related costs; impacts on economic activities such as agriculture, industrial production and tourism; increased water treatment costs; and reduced property values among others. Contaminating the water sources also has an indirect effect on health, by exposing foods, such as vegetables and fish, to the pathogens present in contaminated water. Not only does this

contaminate the food supply, but it also reduces the amount of available food.<sup>1,2</sup>

Wastewater treatment is essential to protect water resources, the environment, and human health. The main pollutant groups present in wastewaters are organic, such as proteins (40-60%) carbohydrates (25-50%) and fats (10%).<sup>1</sup> Many techniques are being used to treat wastewaters, with some advantages and disadvantages, such as the use of activated carbon, which has low cost but is mainly successful for the removal of hydrophobic compounds. In this frame, public, scientific and industrial communities search for innovative processes for wastewater treatment that improve the offer of conventional depuration processes, by increasing the efficiency and reducing the associated economic and environmental impacts.

Electrochemical processes are a good alternative for water treatment, since domestic wastewaters normally have a conductivity around  $120 \text{ mS m}^{-1}$ , which is higher than fresh water ( $50 \text{ mS m}^{-1}$ ).<sup>1,3</sup> There are many reported studies on the degradation of organic compounds with electrolysis using anodes with high oxygen evolution reaction (OER) overpotential, such as  $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{RuO}_2$ ,  $\text{IrO}_2$  and BDD (Boron Doped Diamond) that make organic degradation more efficient, combined with inert metals/metal oxides like Ti, Pt,  $\text{TiO}_2$  and  $\text{Ta}_2\text{O}_5$  that add a greater corrosion resistance and electrocatalytic activity.<sup>4,5</sup> This method consists in using the  $\text{OH}^-$  present in the effluent to oxidize the organic compounds

originating  $\text{CO}_2$ .<sup>6-9</sup> Despite being a process with a better environment compatibility and versatility, these kinds of electrode materials are very expensive and have energy costs that compromise its viability.

One of the things that electrochemistry is well known for, is for producing hydrogen ( $\text{H}_2$ ) from water electrolysis. So, to increase the economic viability of the process, it is needed an efficient way to produce  $\text{H}_2$  from wastewater electrolysis. The generated  $\text{H}_2$  can be fed to a fuel cell that can partially power the wastewater treatment plant, thereby reducing the energy costs of the process.

In order to find a way to produce  $\text{H}_2$  in an efficient and cost-effective way, adequate electrodes must be selected. In this work, the tested electrodes were platinum (Pt), nickel (Ni), and their alloys with some rare earth (RE) elements, with the RE being cerium (Ce), samarium (Sm), dysprosium (Dy), and holmium (Ho). Pt-RE and Ni-RE alloys have been recently reported to have good activity as anodes of direct borohydride fuel cells and as cathodes for hydrogen evolution reaction (HER) in alkaline water electrolysis.<sup>10-15</sup> For these reasons, herein Pt-RE and Ni-RE alloys are tested as electrodes for HER in domestic wastewaters, with and without KOH addition. Cyclic voltammetry measurements are used to compare the performance of the tested materials and to calculate several kinetic parameters that characterize the HER on these electrodes.

## EXPERIMENTAL

### Preparation of the electrodes

Pt-Ce, Pt-Dy, Pt-Sm and Pt-Ho binary alloys were prepared with equiatomic composition (50 at. % Pt). Ni-Ce, Ni-Dy and Ni-Sm binary alloys were prepared with 10 at. % RE composition. Alloys buttons were prepared according to the standard procedures,<sup>16,17</sup> with each of the elements being weighed according to their stoichiometric amounts, sealed in tantalum

crucibles under inert gas (argon) and induction heated under argon flux, continuously shaking the crucibles to ensure homogenization. Ni buttons were obtained from a high purity Ni rod by melting it in an arc furnace.

The electrodes were prepared by gluing these buttons to a copper wire with silver paint (SPI, high purity), using a thin

glass tube to protect the wire, and then mounted in an epoxy resin (resin to hardener ratio=5:1, Buehler EpoxiCure Epoxy Resin 20-8130-032 and Hardener 20-8132-008). After drying the Epoxy resin, the electrodes surfaces were polished using SiC paper (Struers) of decreasing grit sizes (1200,

2400, 4000). A commercial Pt electrode (Metrohm 6.0305.100) was also used for comparison purposes. Table 1 shows the geometric areas of the tested electrodes.

The SS304 electrode was prepared by cutting a stainless steel slab, making a square piece with 2x2 cm.

Table 1 - Geometric areas of the nine tested electrodes.

Electrode	Pt	Pt-Ce (50%)	Pt-Sm (50%)	Pt-Dy (50%)	Pt-Ho (50%)	Ni	Ni-Ce (10%)	Ni-Sm (10%)	Ni-Dy (10%)	SS 304
Area / cm <sup>2</sup>	1.00	0.14	0.09	0.23	0.23	0.79	0.40	0.53	0.39	8

### Electrochemical measurements

The electrochemical tests were carried out on a cylindrical glass cell with a capacity of 125 mL using a potentiostat/galvanostat from Princeton Applied Research/EG&G Model 273A. The cell temperature was ranged from 25 to 85 °C using a thermostatic bath (P-Selecta Ultraterm 6000383). A platinum (Pt) mesh was used as auxiliary electrode and a saturated calomel electrode (SCE, HANNA HI5412) was used as reference. Pt, Ni, and binary alloys of these elements with rare earths (RE = Ce, Sm, Dy, Ho) and SS304, were used as working electrodes.

It was prepared a solution of synthetic urine with composition according to Laube et al<sup>18</sup>, and the quantity is measured as shown in Table 4.1 for a volume of 250 ml with a pH of 6.0 ± 0.1 at 25°C (the solution initial pH was 5.0, and NaOH (≥99%) was used to reach that value) with a conductivity of 1594 ± 10 mS/m.

Table 0.1 - Overview of synthetic urine composition

Compound and purity	Supplier	Added mass (g)
NaCl (100%)	V.Reis	0.7418
KCl (100%)	Panreac	0.3965
CaCl <sub>2</sub>	V.P.	0.2765

Na <sub>2</sub> SO <sub>4</sub>	-	0.5516
KH <sub>2</sub> PO <sub>4</sub> (≥97%)	May & Baker Ltd	0.3551
NH <sub>4</sub> Cl (≥99.5%)	Sigma- Aldrich	0.2808
Urea (≥99.5%)	Merck	6.2305

The wastewater used throughout this study was an effluent provided from SIMTEJO (Portugal), an industry that provides a domestic wastewater treatment. The effluents were sampled at the outlet of the primary decantation process. The samples were collected and stored in polyethylene terephthalate bottles and kept in the fridge at the temperature of 4 °C until use. The wastewater has a pH of 7.0 ± 0.1 and a conductivity of 131 ± 10 mS m<sup>-1</sup> (25 °C, HANNA HI8733). For the experiments with addition of electrolyte, potassium hydroxide (KOH, 87%, Analar NORMAPUR) was added to the effluent sample to have a 5 M KOH concentration.

Linear scan voltammetry was used to scan each of the nine electrodes' potential from the open circuit potential (OCP) up to a potential of -1.5 V vs. SCE, without the support of additional electrolytes and with the support of KOH.

## RESULTS AND DISCUSSION

The synthetic urine was used to study the influence of the conductivity, to compare to another solution with organics like the wastewater. Having a conductivity 10 times more than the effluent, it resulted on having 10 times more current density at a given voltage.

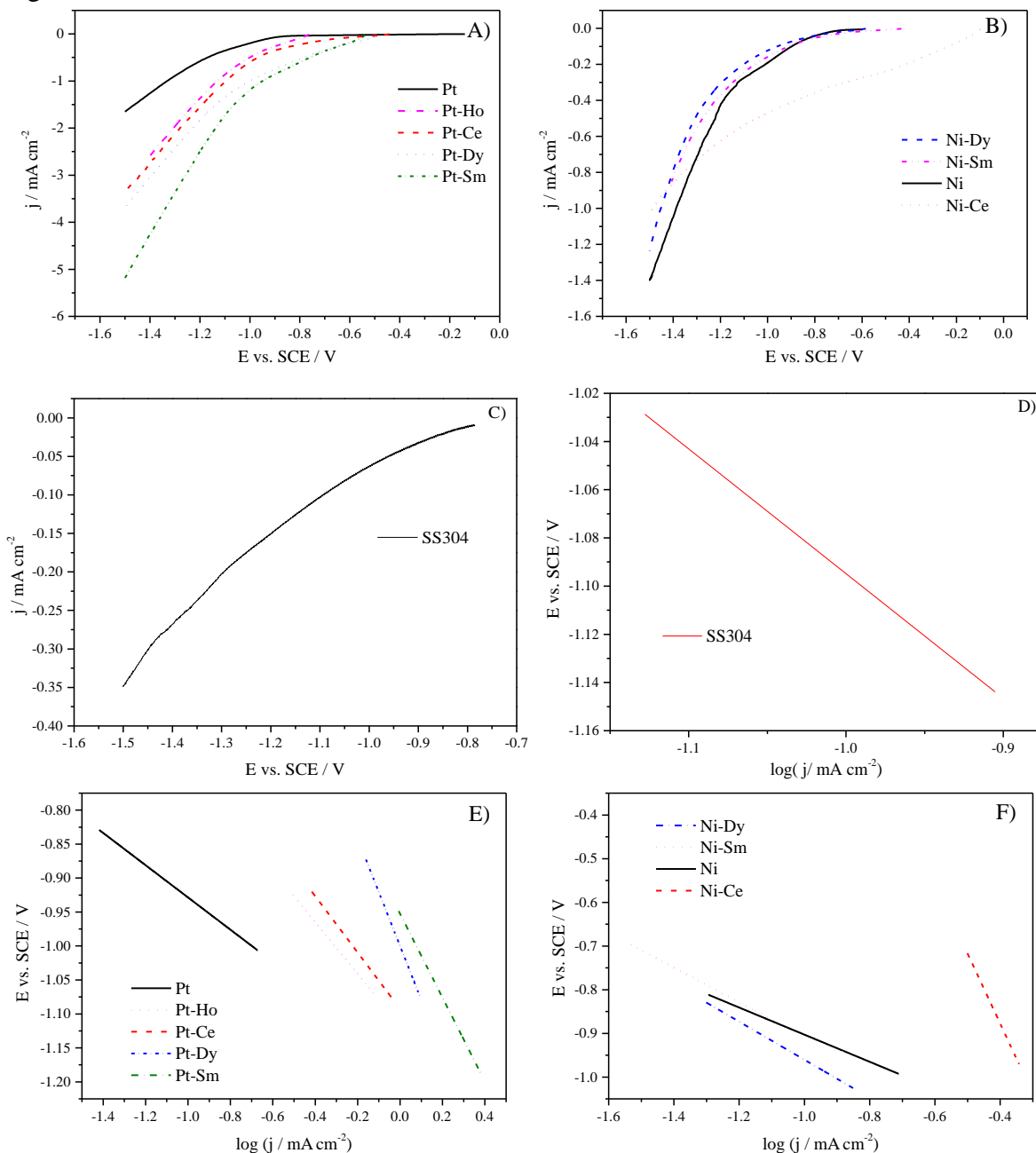


Figure 2. Polarization curves at 25 °C of Pt and Pt alloys (A), Ni and Ni alloys (B) and SS304 (C), and corresponding Tafel plots (E, F and D) in the domestic wastewater effluent.

Then, the polarization curves were repeated with same nine electrode materials, but after the addition of 5 M KOH to the domestic wastewater effluent (Figs. 3A, 3B

Using the domestic wastewater effluent, the potential of each of the nine electrode materials was scanned from the OCP up to a potential of -1.5 V vs. SCE, using a scan rate of 0.5 mV s<sup>-1</sup>, at 25 °C (Figs. 2A, 2B and 2C). The corresponding Tafel plots are shown in Figs. 2E, 2F and 2D.

and 3C), as it has been reported by Boggs et al.<sup>7</sup> that the alkaline electrolyte addition facilitates the electrolysis processes, enhancing both the organics oxidation

reactions as well as the hydrogen evolution reaction (HER). The corresponding Tafel

plots are also shown in Figs. 3D, 3E and 3F.

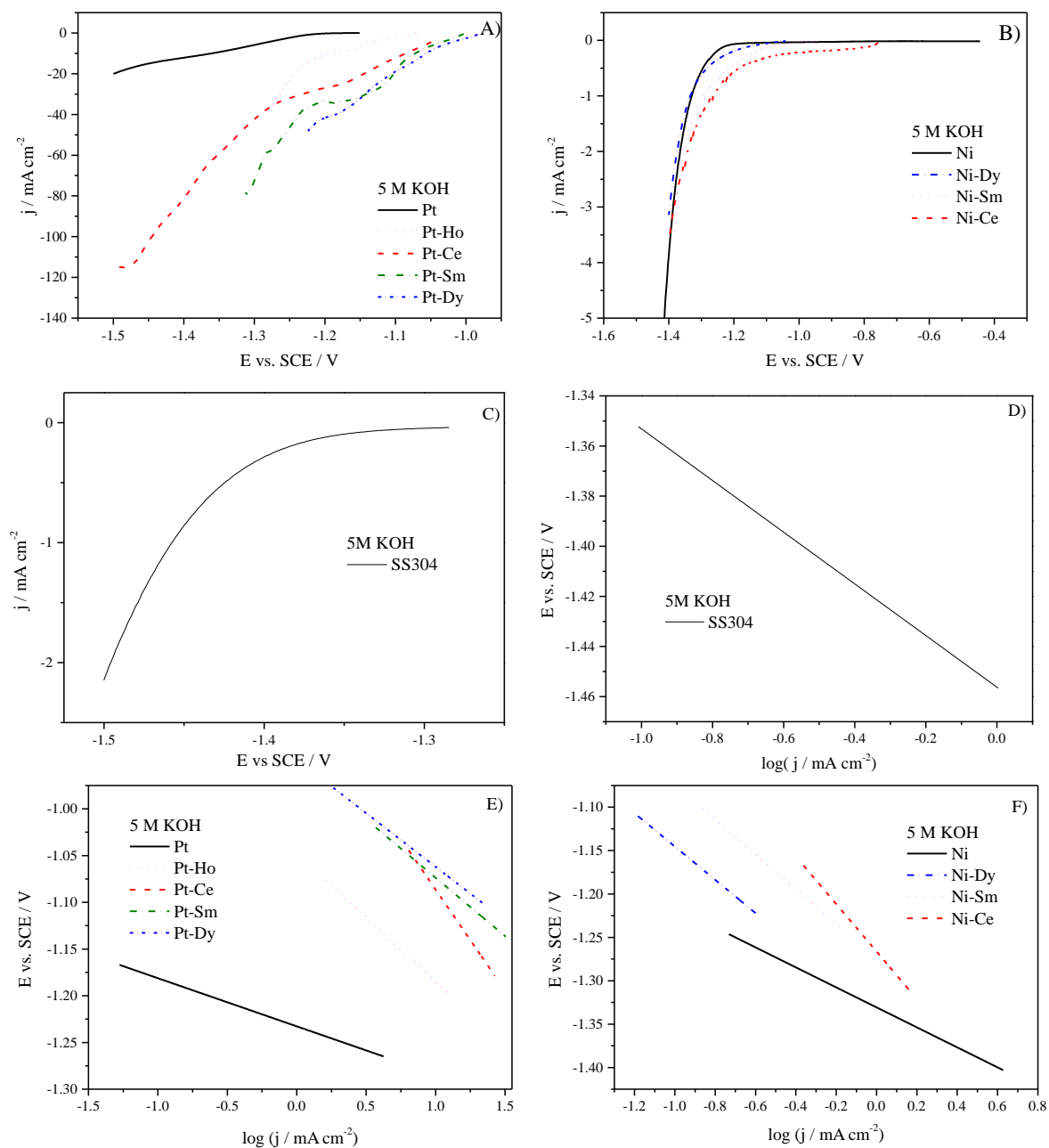


Figure 3. Polarization curves at 25 °C of Pt and Pt alloys (A), Ni and Ni alloys (B) SS304 (C), and corresponding Tafel plots (E, F and D) in the domestic wastewater effluent after 5 M KOH addition.

The cathodic polarization curves for Pt and Pt-RE alloys, represented in Figs. 2 and 3, show that for a given electrode potential the Pt-RE alloys lead to higher currents than Pt electrodes on both situations with and without addition of KOH. For the Ni and Ni-RE alloys in the absence of KOH, the polarization curves show much lower currents than those obtained for Pt and Pt-RE electrodes (Fig. 2). Furthermore, no obvious differences were

observed between the curves of Ni and of the Ni-RE alloys, for the wastewater solution with no added KOH (Fig. 2). After KOH addition, the Ni-RE alloys outperform the Ni electrode, especially for lower overpotentials. In fact, in the effluent with KOH, the Ni-RE alloys present an activity similar to that of Pt but inferior to that of the Pt-RE alloys (Fig. 3). As for the SS304 electrode, its polarization curve has the lowest current density on both

with no added KOH (Fig. 2) and after KOH (Fig. 3).

So, from the cathodic polarization curves shown in A, B and C of Figs. 2 and 3, it is possible to apply the Tafel method to get the Tafel plots shown in D, E and F of Figs. 2 and 3, which allow us to obtain specific parameters that characterize the HER in these electrode materials, namely the Tafel slopes,  $b$ , the charge transfer coefficients,  $\alpha$ , and the exchange current densities,  $j_0$ . Basically, the Tafel analysis consists on using Eq. 1 to adjust straight lines to a selected overpotential,  $\eta$ , zone of the polarization curves,

$$\eta = a + b \log j \quad (1)$$

where  $a$  represents  $(2.3RT \log j_0)/\alpha nF$  and  $b$ , the Tafel slope, corresponds to  $2.3RT/\alpha nF$ , with  $R$  being the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  the temperature in Kelvin,  $\alpha$  the charge transfer coefficient,  $n$  the number of exchanged electrons in the rate determining step (which is 1), and  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ).

By application of Eq. 1 to the graphic representation of the Tafel plots, in the form of  $E$  vs.  $\log j$ , as shown in Figs. 2 and 3 (D, E and F), without and with addition of KOH electrolyte, respectively it is possible to obtain the HER kinetic parameters. Table 2 shows a comparison, at  $25 \text{ }^\circ\text{C}$ , of the kinetic parameters obtained for the nine electrode materials in the domestic wastewater effluent, with and without KOH.

Table 2. Comparison of the calculated parameters for the hydrogen evolution reaction at  $25 \text{ }^\circ\text{C}$  without and with 5 M KOH addition to the domestic wastewater, in the nine tested electrodes.

		Pt	Pt-Ce	Pt-Sm	Pt-Dy	Pt-Ho	Ni	Ni-Ce	Ni-Sm	Ni-Dy	SS304
Without 5M KOH	$\alpha$	0.25	0.14	0.10	0.07	0.11	0.19	0.04	0.15	0.13	0.11
	$b / \text{mV dec}^{-1}$	237	417	617	791	380	311	1616	398	458	518
	$j_0 / \text{mA cm}^{-2}$	$4.66 \times 10^{-5}$	$2.73 \times 10^{-2}$	$2.14 \times 10^{-1}$	$2.15 \times 10^{-1}$	$1.17 \times 10^{-1}$	$1.04 \times 10^{-2}$	$1.14 \times 10^{-1}$	$6.33 \times 10^{-3}$	$1.48 \times 10^{-2}$	$2.51 \times 10^{-2}$
With 5M KOH	$\alpha$	0.64	0.32	0.51	0.59	0.55	0.51	0.22	0.31	0.31	0.57
	$b / \text{mV dec}^{-1}$	46	182	115	100	108	115	274	188	192	103
	$j_0 / \text{mA cm}^{-2}$	$1.86 \times 10^{-2}$	6.15	2.47	1.81	1.20	$1.90 \times 10^{-8}$	$1.38 \times 10^{-2}$	$4.20 \times 10^{-2}$	$5.26 \times 10^{-2}$	$2.14 \times 10^{-2}$

As can be seen from Table 2,  $\alpha$  and  $j_0$  values increase with the KOH addition, whereas  $b$  values decrease, which indicates that the HER process is more favorable in the wastewater with KOH. For Pt, the obtained  $b$  value of  $46 \text{ mV dec}^{-1}$  is typical of a mechanism where the Heyrovsky reaction is the rate determining step (RDS), suggesting that on the Pt electrode the HER proceeds following the Volmer-Heyrovsky pathway, meaning that one electron is exchanged in each electrochemical step. For Ni, the  $b$  value of  $115 \text{ mV dec}^{-1}$  is typical of

a mechanism where the Volmer step is the RDS, which means that HER on Ni follows a Volmer-Tafel pathway. For the Pt-RE and Ni-RE alloys, the Volmer-Tafel mechanism also seems to be dominant.

To evaluate the effect of temperature on HER kinetics, the cathodic polarization curves were obtained in the  $25 - 85 \text{ }^\circ\text{C}$  range. Figure 4 shows the temperature effect on the Tafel plots obtained with Pt, Ni and SS304 electrodes, in the wastewater solutions, with and without KOH addition.

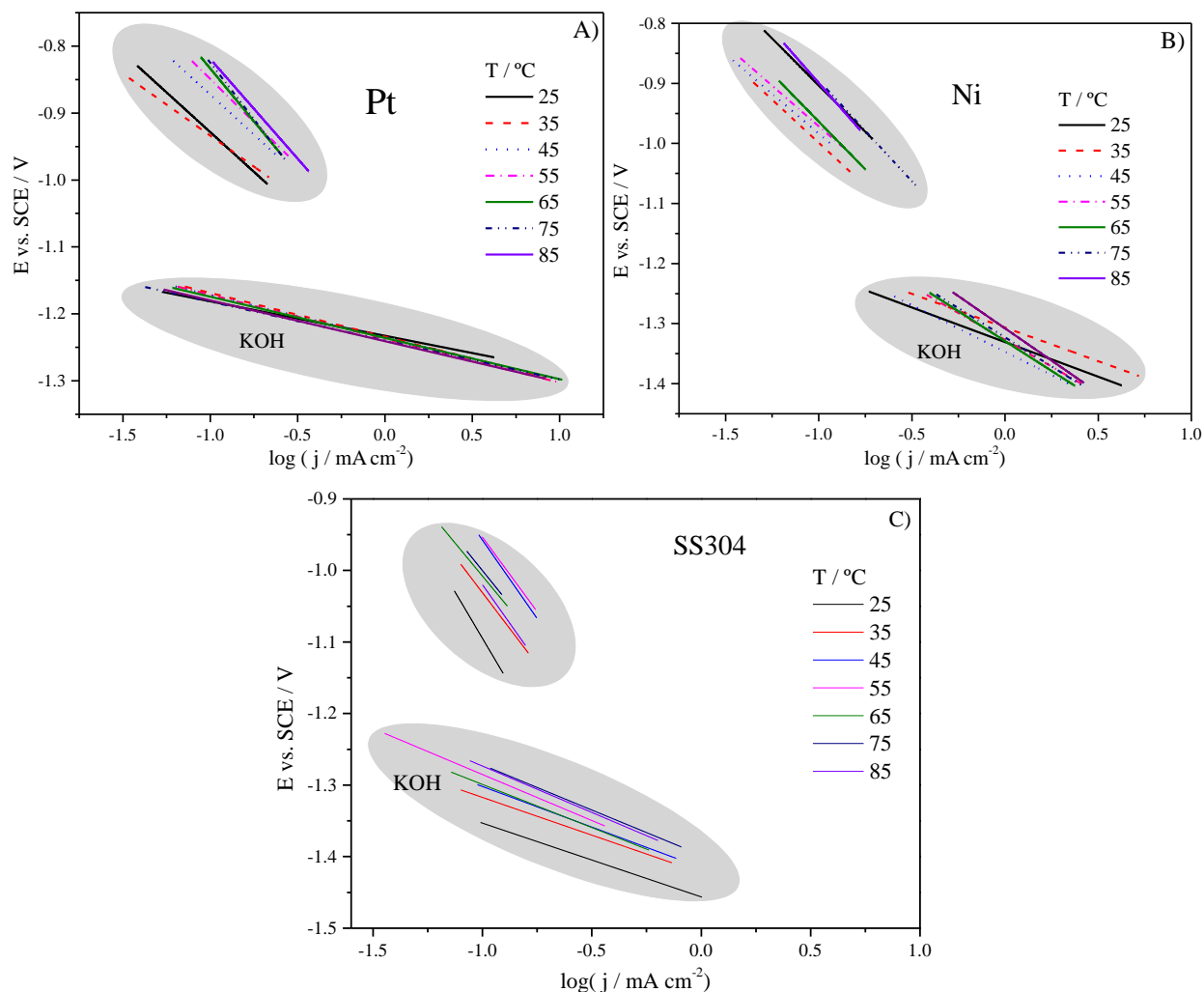


Figure 4. Effect of temperature, ranging from 25 to 85 °C, on the Tafel plots of Pt (A), Ni (B) and SS304 (C) electrodes, in the presence and in the absence of 5 M KOH.

As can be seen from the figure, an increase in the solution temperature leads to an improvement of the catalytic activity of the electrodes. Figure 4 also shows that the KOH addition completely changes the zone of the Tafel plots. The increase in the solution pH shifts the electrode potential to much more negative values and leads to much lower Tafel slopes, which is a sign of increased electrocatalytic activity for HER. In other words, Figure 4 shows that upon

KOH addition, a small increase in the overpotential leads to a large increase in the HER currents, which is what is expected for a practical electrolysis system.

Tafel analysis (Eq. 1) was also done for these materials in the temperature range between 25 and 85 °C. Table 3 summarizes the calculated parameters in the selected temperature range, for Pt, Ni and SS304 electrodes, in the domestic wastewater solutions, with and without KOH addition.

Table 3. Effect of temperature on the HER parameters obtained from Tafel equation (with and without KOH) for Pt and Ni electrodes.

	T / °C	25	35	45	55	65	75	85
Pt (wastewater without KOH)	$\alpha$	0.25	0.36	0.23	0.26	0.22	0.21	0.24
	$b / \text{mV dec}^{-1}$	237	171	278	253	309	326	292
	$j_0 / \text{mA cm}^{-2}$	4.66	5.94	2.32	2.55	1.03	1.38	1.01
		$\times 10^{-5}$	$\times 10^{-3}$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$
Ni	$\alpha$	0.19	0.22	0.24	0.24	0.22	0.20	0.19

(wastewater without KOH)	$b / \text{mV dec}^{-1}$	311	283	259	271	311	337	376
	$j_0 / \text{mA cm}^{-2}$	1.04 $\times 10^{-2}$	6.89 $\times 10^{-3}$	6.64 $\times 10^{-3}$	4.43 $\times 10^{-3}$	3.21 $\times 10^{-3}$	3.52 $\times 10^{-2}$	7.59 $\times 10^{-3}$
SS304 (wastewater without KOH)	$\alpha$	0.11	0.15	0.14	0.16	0.18	0.18	0.16
	$b / \text{mV dec}^{-1}$	518	401	439	416	369	379	432
	$j_0 / \text{mA cm}^{-2}$	2.51 $\times 10^{-2}$	2.37 $\times 10^{-2}$	3.01 $\times 10^{-2}$	3.13 $\times 10^{-2}$	1.65 $\times 10^{-2}$	2.21 $\times 10^{-2}$	3.47 $\times 10^{-2}$
	$\alpha$	0.64	0.58	0.69	0.71	0.75	0.77	0.77
Pt (wastewater with 5 M KOH addition)	$b / \text{mV dec}^{-1}$	46	53	46	46	44	45	46
	$j_0 / \text{mA cm}^{-2}$	1.86 $\times 10^{-2}$	2.37 $\times 10^{-2}$	1.69 $\times 10^{-2}$	1.86 $\times 10^{-2}$	1.86 $\times 10^{-2}$	1.85 $\times 10^{-2}$	8.26 $\times 10^{-3}$
Ni (wastewater with 5 M KOH addition)	$\alpha$	0.51	0.56	0.39	0.36	0.33	0.35	0.33
	$b / \text{mV dec}^{-1}$	115	109	160	171	204	198	215
	$j_0 / \text{mA cm}^{-2}$	1.90 $\times 10^{-8}$	1.84 $\times 10^{-6}$	7.95 $\times 10^{-4}$	3.86 $\times 10^{-3}$	3.47 $\times 10^{-2}$	4.02 $\times 10^{-2}$	1.21 $\times 10^{-1}$
	$\alpha$	0.57	0.58	0.56	0.51	0.56	0.55	0.55
SS304 (wastewater with KOH addition)	$b / \text{mV dec}^{-1}$	103	105	113	129	121	126	130
	$j_0 / \text{mA cm}^{-2}$	2.14 $\times 10^{-2}$	3.55 $\times 10^{-2}$	2.33 $\times 10^{-2}$	1.38 $\times 10^{-2}$	2.66 $\times 10^{-2}$	4.21 $\times 10^{-2}$	3.72 $\times 10^{-2}$

The calculated parameters show that in the absence of KOH electrolyte, the HER is hindered in Pt, Ni and SS304, with no improvement of the process efficiency even at high operation temperatures. However, after KOH addition, there is a large increase in the HER currents.

In fact, with the Pt electrode, the process does not seem to improve with the temperature increase – as it normally occurs in conventional alkaline water electrolysis –, with a fairly constant value for the Tafel slope and the exchange current density. Moreover, the  $b$  values ranging from 44 to 53  $\text{mV dec}^{-1}$ , reveal that the Heyrovsky step is the RDS with the Pt electrode (after KOH addition), independently of the solution temperature. This means that the HER mechanism proceeds on the Pt electrode via the Volmer-Heyrovsky pathway. As previously reported,  $\alpha$ n values ranging from 1.3 to 1.5 have been interpreted by setting alternatively  $n = 2$  to get  $\alpha$  values of ca. 0.65 - 0.75, as it is the case of our results. An acceptable kinetic interpretation might consist in postulating the reversible uptake of one electron, followed by the rate-determining uptake of a second electron.

As for the Ni electrode, although there is a slight increase in the  $b$  values, with corresponding decrease in  $\alpha$ , the clear increase of the  $j_0$  values show that the HER is enhanced with the temperature increase when using Ni electrodes in the domestic wastewater solution with KOH electrolyte. In this case, the  $b$  values suggest that the Volmer step is the RDS, being the HER at Ni electrodes controlled by the Volmer-Tafel mechanism.

The SS304 electrode can maintain the  $\alpha$  value with almost no variation and there's some increase of  $j_0$  by rising the temperature. The KOH addition enhance the HER, the  $b$  values are slightly increased with the temperature and its values suggest the Volmer step as RDS.

By plotting the obtained  $j_0$  values of as a function of temperature, it is possible to use the Arrhenius relation for calculation of the HER activation energies. The Arrhenius equation is given in Eq. 2, where  $A$  is the Arrhenius pre-exponential factor and  $E_a$  is the activation energy.

$$\log j_0 = \log A - E_a/(2.3RT) \quad (2)$$



Figure 4 shows a typical  $\log j_0$  vs.  $T^{-1}$  plot for the Ni electrode in wastewater

solution after KOH addition.

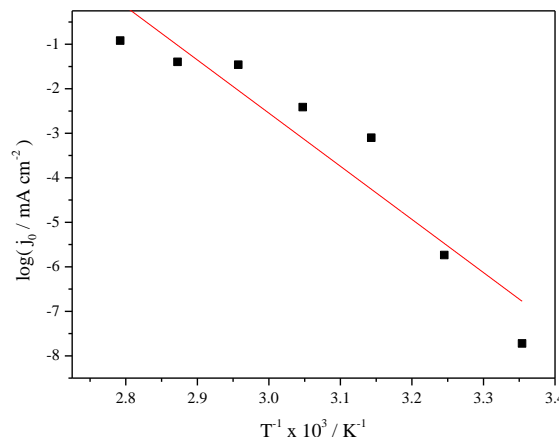


Figure 4. Arrhenius plot for Ni electrode in the wastewater solution containing 5 M KOH.

From the slope of the Arrhenius plots and by application of Eq. 4, an  $E_a$  value of  $228 \text{ kJ mol}^{-1}$  was obtained. This value is a bit too high compared with those obtained for conventional alkaline water electrolysis. However, it shows that the HER may be accomplished in a domestic wastewater, allowing  $H_2$  production with simultaneous anodic oxidation of the organic pollutants present in the effluent.

## CONCLUSIONS

This work intended to propose a new alternative for domestic wastewater treatment based on electrochemical technologies. The concept intends to carry out a wastewater electrolysis process, with  $H_2$  being produced at the cathode whereas the pollutants oxidation occurs at the anode. Herein the hydrogen evolution reaction (HER) in the wastewater was studied in ten different electrode materials, namely in Pt, Ni, and their alloys with rare earth elements (RE = Ce, Sm, Dy, Ho) and SS304. CV measurements allowed comparison of the performance of the tested materials and calculation of kinetic parameters that characterize the HER on these electrodes. Results show that the HER efficiency in the domestic wastewater effluent can be greatly improved by addition of KOH electrolyte.

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