Research article

Domestic wastewater treatment using Pt,Ni-RE (rare earth) electrodes

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Abstract: Electrochemical technologies can be used for the treatment of domestic wastewaters, by eliminating their organic pollutants. They have advantages over conventional methods, such as environmental compatibility, versatility, energy efficiency, safety and cost. The organic compounds degradation process is based on the production of OH radicals, formed during water electrolysis, which oxidize the organic molecules to CO_2. At the same time, hydrogen (H_2) is produced through reduction of the water in the effluent, which can be later used in a fuel cell. Present study seeks to find effective electrocatalysts to produce H_2 by electrolysis, using domestic wastewaters as the hydrogen source, with or without the addition of supporting electrolyte. Herein KOH is used as the supporting electrolyte, as the extra hydroxide can be used to degrade the organic matter. Nine different electrode materials are evaluated as cathodes for the hydrogen evolution reaction (HER) in a domestic wastewater. The tested materials include 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). Linear scan voltammetry measurements are conducted at temperatures ranging from 25 to 85 °C. Several kinetic parameters are calculated, such as the Tafel slopes, charge transfer coefficients and exchange current densities. The data obtained at the different electrode materials is compared and it is clear that Pt-RE alloys show superior activity for the HER. It is also noticeable that the wastewater effluent containing the supporting electrolyte leads to significantly better HER performances.

Keywords: domestic wastewater treatment; platinum; nickel; rare-earth alloys; hydrogen evolution reaction

1. Introduction

Rapid population growth has aggravated the water scarcity, turning this one of the main problems to be faced by world population in the XXIst 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, the 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 and creates multiple issues. In fact, poor water quality incurs into many economic costs related to 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. 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 [1,2].

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%) [1]. One of the most applied techniques in wastewater treatment is the use of activated carbon; it is a low-cost method but presenting efficiency only in hydrophobic compounds removal. 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 wastewater treatment, since domestic wastewaters normally have a conductivity around $120\,\text{mS}\,\text{m}^{-1}$, which is higher than fresh water $(50\,\text{mS}\,\text{m}^{-1})$ [1,3]. There are many reported studies on the degradation of organic compounds with electrolysis using anodes with high oxygen evolution reaction (OER) overpotential. Electrode materials such as SnO_2, PbO_2, RuO_2, IrO_2 and BDD (boron doped diamond) demonstrated to be efficient in the degradation of organic compounds, in combination with inert metals/metal oxides such as Ti, Pt, TiO_2 and Ta_2O_5, which add greater corrosion resistance and electrocatalytic activity [4,5]. Typical electrochemical methods use the OH^- present in the effluent to oxidize the organic compounds originating CO_2 [6-9]. Despite being a process with good environmental compatibility and versatility, it has high energy costs and uses expensive electrode materials, which compromises its viability.

Water electrolysis for hydrogen (H_2) production is one of the oldest and well-known electrochemical processes [10]. Therefore, to increase the economic viability of the wastewater treatment process, it is crucial to develop an efficient way to produce H_2 from wastewater electrolysis. The generated H_2 can be fed to a fuel cell that can partially power the wastewater treatment plant (WWTP), thereby reducing the energy costs of the process.

For the purpose of producing H_2 in an efficient and cost-effective way the most suitable electrodes for the process must be selected. Considering the high price of platinum (Pt), intensive research has been devoted to the development of the lower-cost nickel (Ni)-based electrodes as cathodes for hydrogen evolution reaction (HER), both in acid and in alkaline water electrolysis [11,12]. Recently,

Pt-rare earth (RE) and Ni-RE alloys have been reported to have good electrocatalytic activity as electrodes of direct borohydride fuel cells and for hydrogen evolution reaction (HER) in alkaline media [13-22]. For these reasons, herein Pt-RE and Ni-RE alloys are tested for the first time as electrodes for HER in a domestic wastewater effluent, with and without KOH addition. Specifically, the tested electrodes were Pt, Ni, and their alloys with RE elements, with the REs being cerium (Ce), samarium (Sm), dysprosium (Dy), and holmium (Ho). The four prepared Pt-RE alloys (Pt-Ce, Pt-Dy, Pt-Sm and Pt-Ho) were synthesized with equiatomic composition (50 at. % Pt) and the three Ni-RE alloys (Ni-Ce, Ni-Dy and Ni-Sm) were prepared with 10 at. % RE composition.

Voltammetric measurements are used to compare the performance of the tested materials and to calculate several kinetic parameters that characterize the HER on these electrodes.

With this work, it is intended to propose a new alternative for wastewater treatment based on electrochemical technologies, which results in water recovery with minimization of the total amount of non-treated discharged water and reduced treatment costs caused by a process simplification (Figure 1).
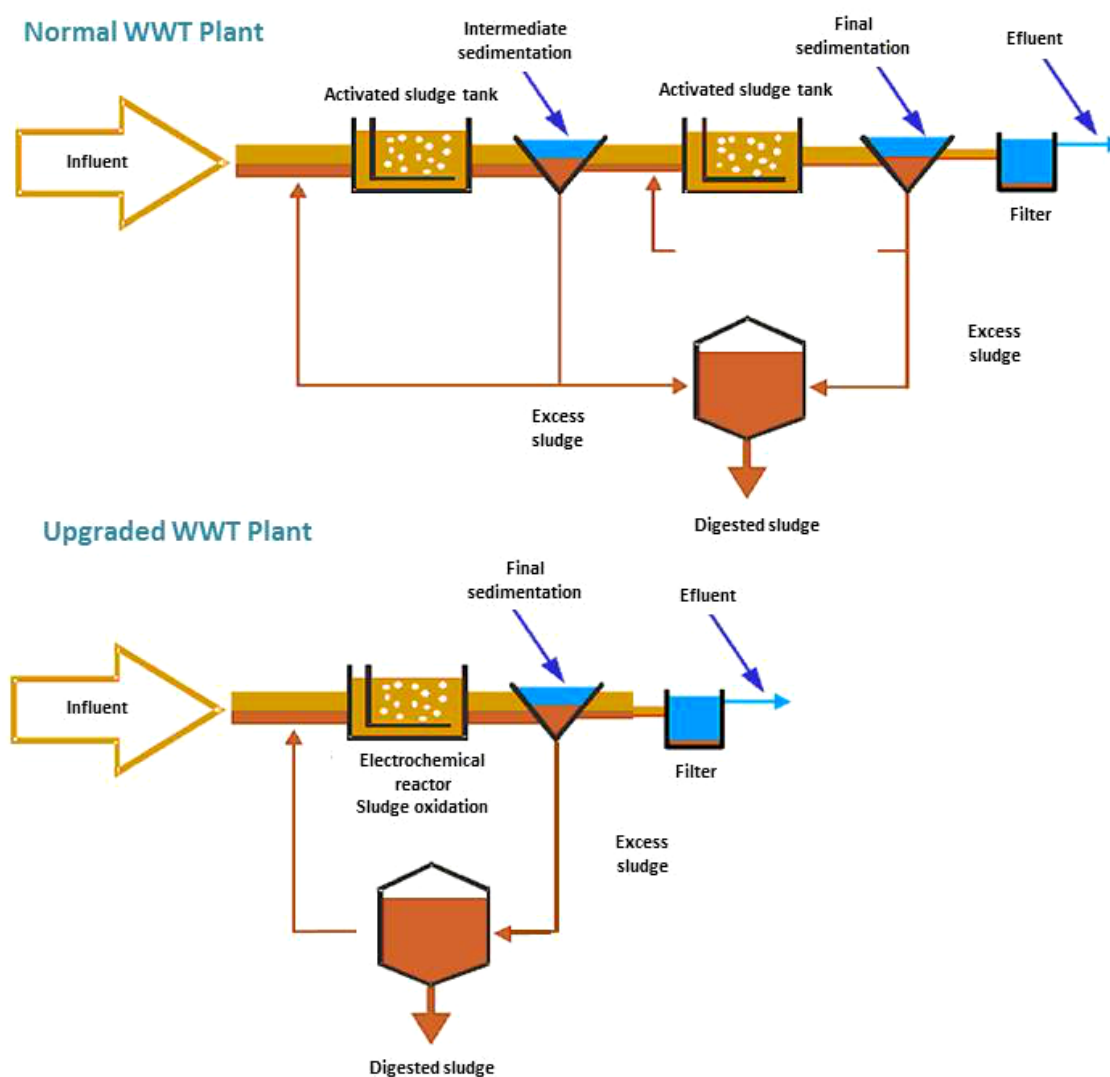

Figure 1. Normal wastewater treatment plant (WWTP) flowchart (above) and upgraded WWTP flowchart (below).

2. Materials and Methods

2.1. 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 [14,16,19,21,22], with each of the elements being weighed according to their stoichiometric amounts. Specifically, the Pt-RE alloys were prepared by sealing the elements in tantalum crucibles under inert gas (argon, Ar) and induction heated under Ar flux, continuously shaking the crucibles to ensure homogenization. Ni-Ce and Ni-Dy alloys were synthesized by arc melting from starting metals in pieces in Ar atmosphere, and repeatedly melted to ensure homogeneity of the buttons. Ni-Sm alloy was prepared by melting stoichiometric amounts of the two elements placed in alumina crucibles in an induction furnace. A slight overpressure of Ar was maintained during the melting to reduce the Sm evaporation. Finally, the Ni button was obtained from a high purity Ni rod by melting it in an arc furnace.

The electrodes were prepared by gluing the alloy 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). The electrodes surfaces were polished using SiC paper (Struers) of decreasing grit sizes (1200, 2400, 4000) until reaching shiny smooth flat surfaces with nearly disk-like shape. SEM micrographs of the Pt-RE and Ni-RE alloy electrodes can be found in the authors' previous works [13-15,20]. A commercial Pt electrode (Metrohm 6.0305.100) was also used for comparison purposes. Table 1 shows the geometric areas of the tested electrodes. These areas were used for calculation of the current densities shown throughout the paper.

Table 1. Geometric areas of the nine tested electrodes.

Electrode (at. % RE)	Pt	Pt-Ce (50%)	Pt-Sm (50%)	Pt-Dy (50%)	Pt-Ho (50%)	Ni	Ni-Ce (10%)	Ni-Sm (10%)	Ni-Dy (10%)
Area (cm^2)	1.00	0.14	0.09	0.23	0.23	0.79	0.40	0.53	0.39

2.2. 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 ºC using a thermostatic bath (P-Selecta Ultraterm 6000383). A platinum (Pt) mesh was used as auxiliary electrode and a saturated calomel electrode (SCE, Hanna Instruments HI5412) was used as reference. Pt, Ni, and binary alloys of these elements with rare earths (RE = Ce, Sm, Dy, Ho) were used as the working electrodes. Specifically, nine different electrode materials were evaluated, namely four Pt-RE alloys (Pt-Ce, Pt-Dy, Pt-Sm, Pt-Ho) with 50 at. % RE, three Ni-RE alloys (Ni-Ce, Ni-Dy, Ni-Sm) with 10 at. % RE, and pure Pt and Ni electrodes.

The domestic wastewater used throughout this study was an effluent provided from Alcântara wastewater treatment plant (WWTP, Lisbon, Portugal). The Alcântara WWTP treats 42% of the catchment area around the counties of Lisbon, Oeiras and Amadora and it is the largest WWTP in Portugal. The tested effluents were sampled at the outlet of the primary decantation process. The

composition of municipal wastewaters varies significantly with the water consumption in households and infiltration and exfiltration during transport in the sewage system. The typical composition of domestic/municipal wastewater in a developed city is given in Table 2. The fractionation of nitrogen and phosphorus in the wastewater has influence on its treatment options [1]. Since most of the nutrients are normally soluble, they cannot be removed by conventional methods, namely settling, filtration, flotation or other means of solid-liquid separation, which increases the expectations on electrochemical processes to have a crucial role in the future wastewater treatment.

Table 2. Typical composition (mg L^{-1}) of raw municipal wastewater with minor contributions of industrial wastewater.

Parameter	Organic matter total			Volatile fatty acids	Nitrogen		Phosphorous	Volatile component
	Total	Soluble	Suspended		Total	Ammonia		
Concentration (mg L^{-1})	500	200	300	10	30	20	6	200

The collected samples were 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^{-1} (25 °C, Hanna Instruments HI8733). For the experiments with addition of supporting electrolyte, potassium hydroxide (KOH, 87%, Analar NORMAPUR) was added to have a 5 M KOH concentration in the effluent sample.

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, with and without the addition of KOH supporting electrolyte.

3.   Results and Discussion

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^{-1}, at 25 °C, inside the solution of the domestic wastewater effluent. The obtained polarization curves are shown in Figures 2A and 2B and the corresponding Tafel plots are shown in Figures 2C and 2D. The Pt-RE alloys clearly outperform the Pt electrode, with the higher currents being recorded with the Pt-Sm electrode. On the other hand, Ni-RE alloys show a performance similar to that of Ni.

The polarization curves presented in Figures 3A and 3B reproduce the behavior of the same nine electrode materials after addition of 5 M KOH to the domestic wastewater effluent. The addition of this strongly alkaline supporting electrolyte facilitates the electrolysis processes, enhancing both the organics oxidation reactions and the hydrogen evolution reaction (HER), as it has been reported by Boggs et al. [7]. The corresponding Tafel plots are also shown in Figures 3C and 3D.
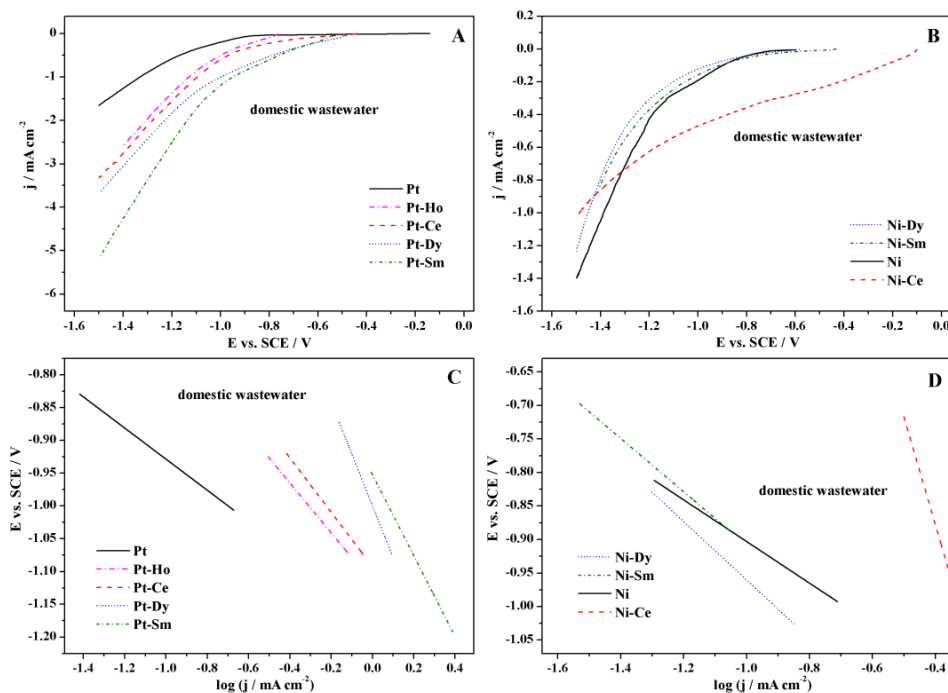
Figure 2. Polarization curves at 25 ºC of Pt and Pt-RE alloys (A) and of Ni and Ni-RE alloys (B), and corresponding Tafel plots (C and D) in the domestic wastewater effluent.
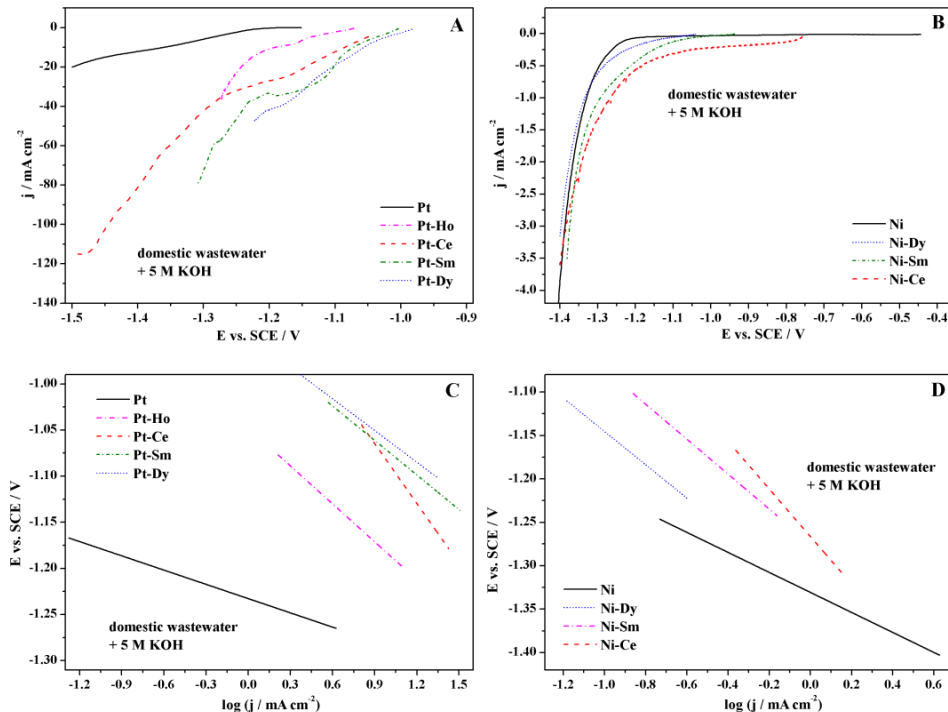

Figure 3. Polarization curves at 25 ºC of Pt and Pt-RE alloys (A) and of Ni and Ni-RE alloys (B), and corresponding Tafel plots (C and D) in the domestic wastewater effluent after 5 M KOH addition.

For a given electrode potential the Pt-RE alloys always lead to higher currents than Pt electrodes, on both situations with and without addition of KOH supporting electrolyte. The cathodic polarization curves represented in Figures 2 and 3 support these results for Pt and Pt-RE alloys. As for the polarization curves for the Ni and Ni-RE alloys in the absence of KOH, they show much lower currents than those obtained for Pt and Pt-RE electrodes (Figure 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 (Figure 2). However, after KOH addition, the Ni-RE alloys slightly outperform the Ni electrode, especially for lower overpotentials. In fact, in the effluent with KOH supporting electrolyte, the Ni-RE alloys present an activity in the same order of that of Pt but inferior to that of the Pt-RE alloys (Figure 3).

With the application of the Tafel method (Equation 1) to the cathodic polarization curves shown in Figures 2 and 3 (A and B) it was possible to get the Tafel plots represented in Figures 2 and 3 (C and D), which enable the calculation of specific parameters, such as Tafel slopes (*b*) the charge transfer coefficients (*α*) and the exchange current densities (*j₀*). These parameters allow characterizing the HER in these electrode materials. The Tafel analysis consists on using Equation 1 to adjust straight lines to a selected overpotential (*η*) zone of the polarization curves,

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

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 J mol^{-1} K^{-1}), *T* the temperature in Kelvin, *α* 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 C mol^{-1}).

By application of Equation 1 to the graphic representation of the Tafel plots, in the form of *E* vs log *j*, as shown in Figures 2 and 3 (C and D), without and with the addition of KOH supporting electrolyte, respectively, it is possible to obtain the HER kinetic parameters. Table 3 shows a comparison, at 25 °C, of the kinetic parameters obtained for the nine electrode materials in the domestic wastewater effluent, with and without 5 M KOH addition.

Table 3. Parameters calculated for the hydrogen evolution reaction at the nine tested electrodes at 25 ºC without and with supporting electrolyte addition to the domestic wastewater.

	Without 5 M KOH			With 5 M KOH		
	α	*b* (mV dec^{-1})	*j₀* (mA cm^{-2})	*α*	*b* (mV dec^{-1})	*j₀* (mA cm$^{-2)}$)
Pt	0.25	237	4.66×10^{-5}	0.64	46	1.86×10^{-2}
Pt-Ce	0.14	417	2.73×10^{-2}	0.32	182	6.15
Pt-Sm	0.1	617	2.14×10^{-1}	0.51	115	2.47
Pt-Dy	0.07	791	2.15×10^{-1}	0.59	100	1.81
Pt-Ho	0.11	380	1.17×10^{-1}	0.55	108	1.2
Ni	0.19	311	1.04×10^{-2}	0.51	115	1.90×10^{-8}
Ni-Ce	0.04	1616	1.14×10^{-1}	0.22	274	1.38×10^{-2}
Ni-Sm	0.15	398	6.33×10^{-3}	0.31	188	4.20×10^{-2}
Ni-Dy	0.13	458	1.48×10^{-2}	0.31	192	5.26×10^{-2}

As can be seen from Table 3, α and j_0 values increase with the 5 M KOH addition, whereas b values decrease, which indicates that the HER process is more favorable in the wastewater with added KOH. For Pt, the obtained b value of 46 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 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.

Additional cathodic polarization curves were obtained in the 25–85 ºC range to evaluate the effect of temperature on HER kinetics. Figure 4 shows the temperature effect on the Tafel plots obtained with Pt and Ni electrodes, in the wastewater solutions, with and without KOH addition.

As can be seen from Figure 4, 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 substantial increase in the HER currents, which is what is expected for a practical electrolysis system.
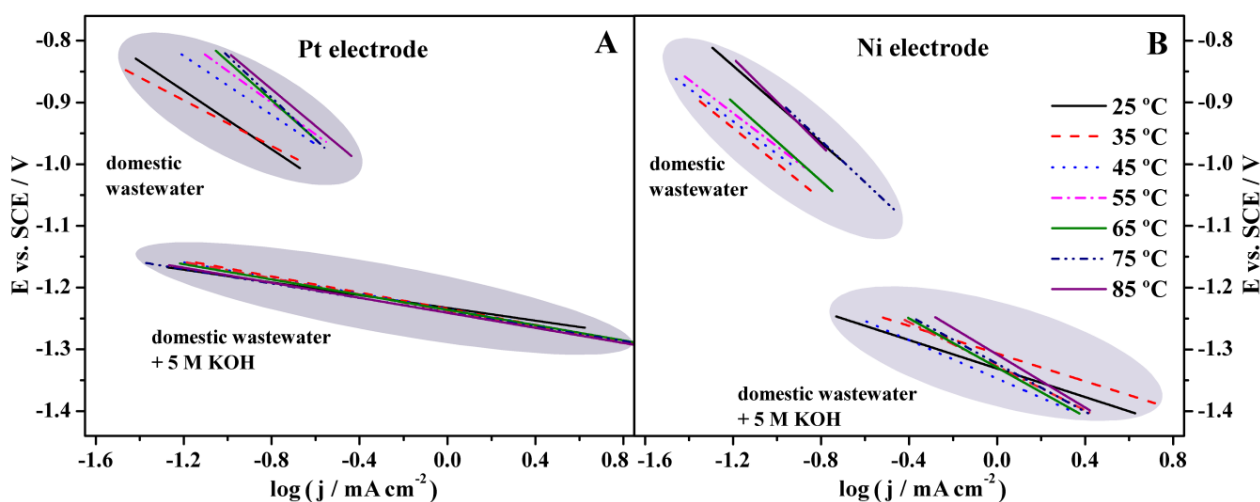

Figure 4. Effect of temperature, ranging from 25 to 85 ºC, on the Tafel plots of Pt (A) and Ni (B) electrodes, in the presence and in the absence of KOH supporting electrolyte.

Tafel analysis (Equation 1) was also done for these materials in the temperature range between 25 and 85 ºC. Table 4 summarizes the calculated parameters in the selected temperature range, for Pt and Ni electrodes, in the domestic wastewater solutions, with and without KOH addition.

The calculated parameters show that in the absence of KOH supporting electrolyte, the HER is hindered in both Pt and Ni, 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.

Table 4. 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	α	0.25	0.36	0.23	0.26	0.22	0.21	0.24
(without KOH)	b/mV dec^{-1}	237	171	278	253	309	326	292
	j_0/mA cm^{-2}	4.66×10^{-5}	5.94×10^{-3}	2.32×10^{-4}	2.55×10^{-4}	1.03×10^{-3}	1.38×10^{-3}	1.01×10^{-3}
Ni	α	0.19	0.22	0.24	0.24	0.22	0.20	0.19
(without KOH)	b/mV dec^{-1}	311	283	259	271	311	337	376
	j_0/mA cm^{-2}	1.04×10^{-2}	6.89×10^{-3}	6.64×10^{-3}	4.43×10^{-3}	3.21×10^{-3}	3.52×10^{-2}	7.59×10^{-3}
Pt	α	0.64	0.58	0.69	0.71	0.75	0.77	0.77
(with 5 M KOH)	b/mV dec^{-1}	46	53	46	46	44	45	46
	j_0/mA cm^{-2}	1.86×10^{-2}	2.37×10^{-2}	1.69×10^{-2}	1.86×10^{-2}	1.86×10^{-2}	1.85×10^{-2}	8.26×10^{-3}
Ni	α	0.51	0.56	0.39	0.36	0.33	0.35	0.33
(with 5 M KOH)	b/mV dec^{-1}	115	109	160	171	204	198	215
	j_0/mA cm^{-2}	1.90×10^{-8}	1.84×10^{-6}	7.95×10^{-4}	3.86×10^{-3}	3.47×10^{-2}	4.02×10^{-2}	1.21×10^{-1}

In fact, with the Pt electrode, the process does not seem to improve with the temperature increase—as it typically 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 mV dec^{-1}, reveal that the Heyrovsky step is the RDS with the Pt electrode (after KOH addition), independently of the solution temperature. These results reinforce that the HER mechanism proceeds on the Pt electrode via the Volmer-Heyrovsky pathway. As previously reported, αn values ranging from 1.3 to 1.5 have been interpreted by setting $n = 2$ to get α values of ca. 0.65–0.75, as it is the case of present 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 the corresponding decrease in α, 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 supporting 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.

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 Equation 2, where A is the Arrhenius pre-exponential factor and E_a is the activation energy.

$$\log j_0 = \log A - E_a/(2.3RT) \tag{2}$$

Figure 5 shows a typical Arrhenius plot, i.e., $\log j_0$ vs T^{-1}, for the Ni electrode in the domestic wastewater solution after 5 M KOH addition.

From the slope of the Arrhenius plots and by application of Equation 4, an E_a value of 117 kJ mol^{-1} was obtained. This value is a somewhat high compared with those typically obtained for HER in 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.
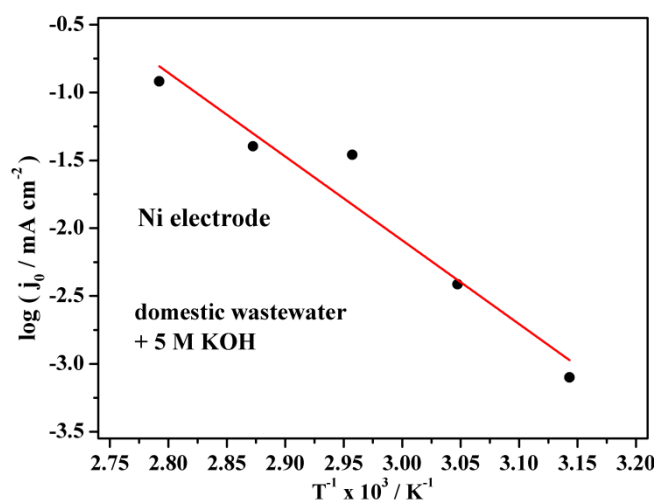
Figure 5. Arrhenius plot for Ni electrode in the wastewater solution containing 5 M KOH.

4. Conclusions

The present study intended to propose a new alternative for domestic wastewater treatment based on electrochemical technologies. The concept proposes to carry out a wastewater electrolysis process, with H_2 being produced at the cathode whereas the pollutants oxidation occurs at the anode.

Specifically, the HER in a domestic wastewater effluent was evaluated herein at Pt-RE and Ni-RE alloy electrodes and directly compared to the results obtained with single Pt and Ni metallic electrodes. The Pt-RE and Ni-RE alloy buttons were synthesized, embedded in an epoxy resin, and polished until reaching flat surfaces with disk-like shape, thus avoiding the contribution of support material and allowing the evaluation of their intrinsic HER activity.

The voltammetric measurements carried out with the nine tested electrode materials allowed calculating the most relevant kinetic parameters that characterize the HER on these materials. In the domestic wastewater without support electrolyte addition the Pt-RE electrodes always showed much better performance than the single Pt electrode, whereas there was no significant difference between the activity of Ni and Ni-RE electrodes. However, after adding the supporting electrolyte to the domestic wastewater sample, the Pt-RE and Ni-RE alloys showed a clear increase of their α and j_0 values, together with a Tafel slope decrease, which clearly indicate that the HER is more favorable in the wastewater with added KOH. Namely, the α values that initially ranged between 0.1 and 0.2 increase to ca. 0.3–0.6 after the supporting electrolyte addition.

The exceptionally high Tafel slopes in the domestic wastewater demonstrate that in the absence of KOH supporting electrolyte, the HER is strongly hindered in both Pt- and Ni-based electrodes, with no improvement of the process efficiency even at high operation temperatures. Notably, after KOH addition, there is a large increase in the HER currents, which is reflected in the much lower Tafel slopes. The low b value of 46 mV dec^{-1} obtained for Pt is typical of a mechanism where the Heyrovsky reaction is the rate determining step (RDS), suggesting that the HER proceeds on the Pt electrode following a Volmer-Heyrovsky pathway. As for Ni, the b value of 115 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.

In summary, the studied Pt-RE alloys lead to promising HER performances, especially in the 5 M KOH wastewater solution. Moreover, results show that the addition of KOH significantly enhances the HER in the domestic wastewater effluent, suggesting that a possible practical application of this electrochemical approach in a WWTP can only be run with good efficiency in the presence of a supporting electrolyte.

Conflict of Interest

The authors declare that they have no conflict of interest, financial or otherwise.

References

1. Henze M, Loosdrecht MCM, Ekama GA, et al. (2008) *Biological Wastewater Treatment: Principles, Modelling and Design*, London: IWA Publishing, chapter 3.
2. *That Bill Gates Shit-Water Machine Might Actually Change the World*, VICE Media LLC, 2015. Available from:
   http://www.vice.com/read/that-bill-gates-shit-water-machine-might-actually-change-the-world-185
3. Behar S (1996) *Testing the Waters: Chemical and Physical Vital Signs of a River*, Montpellier (VT): River Watch Network.
4. Daghrir R, Drogui P, Tshibagu J (2014) Efficient treatment of domestic wastewater by electrochemical oxidation process using bored doped diamond anode. *Sep Purif Technol* 131: 79-83.
5. Niu J, Maharana D, Xu J, et al. (2013) A high activity of Ti/SnO$_2$-Sb electrode in the electrochemical degradation of 2,4-dichlorophenol in aqueous solution. *J Environ Sci* 25: 1424-1430.
6. Ma W, Cheng Z, Gao Z, et al. (2014) Study of hydrogen gas production coupled with phenol electrochemical oxidation degradation at different stages. *Chem Eng J* 241: 167-174.
7. Boggs BK, King RL, Botte GG (2009) Urea electrolysis: direct hydrogen production from urine. *Chem Commun*: 4859-4861.
8. Cho K, Kwon D, Hoffman MR (2014) Electrochemical treatment of human waste coupled with molecular hydrogen production. *RSC Adv* 4: 4596-4608.
9. Ma H, Wang B, Luo X (2007) Studies on degradation of Methyl Orange wastewater by combined electrochemical process. *J Haz Mat* 149: 492-498.
10. Santos DMF, Sequeira CAC, Figueiredo JL (2013) Hydrogen production by alkaline water electrolysis. *Quim Nova* 36: 1176-1193.
11. Dalla Corte DA, Torres C, Correa PS, et al. (2012) The hydrogen evolution reaction on nickel-polyaniline composite electrodes. *Int J Hydrogen Energy* 37: 3025-3032.
12. McKone JR, Sadtler BF, Werlang CA, et al. (2013) Ni-Mo nanopowders for efficient electrochemical hydrogen evolution. *ACS Catal* 3: 166-169.
13. Santos DMF, Amaral L, Šljukić B, et al. (2014) Electrocatalytic activity of nickel-cerium alloys for hydrogen evolution in alkaline water electrolysis. *J Electrochem Soc* 161: F386-F390.

14. Cardoso DSP, Santos DMF, Amaral L, et al. (2015) Enhancement of hydrogen evolution in alkaline water electrolysis by using nickel-rare earth alloys. *Int J Hydrogen Energy* 40: 4295-4302.

15. Santos DMF, Figueiredo JL, Macciò D, et al. (2013) Platinum-rare earth electrodes for hydrogen evolution in alkaline water electrolysis. *Int J Hydrogen Energy* 38: 3137-3145.

16. Santos DMF, Šljukić B, Amaral L, et al. (2014) Nickel and nickel-cerium alloy anodes for direct borohydride fuel cells. *J Electrochem Soc* 161: F594-F599.

17. Santos DMF, Šljukić B, Sequeira CAC, et al. (2013) Electrocatalytic approach for the efficiency increase of electrolytic hydrogen production: proof-of-concept using Pt-Dy. *Energy* 50: 486-492.

18. Šljukić B, Milikić J, Santos DMF, et al. (2014) Electrocatalytic performance of Pt-Dy alloys for direct borohydride fuel cells. *J Power Sources* 272: 335-343.

19. Santos DMF, Šljukić B, Amaral L, et al. (2016) Nickel-rare earth electrodes for sodium borohydride electrooxidation. *Electrochim Acta* 190: 1050-1056.

20. Cardoso DSP, Santos DMF, Šljukić B, et al. (2016) Platinum-rare earth cathodes for direct borohydride-peroxide fuel cells. *J Power Sources* 307: 251-258.

21. Macciò D, Rosalbino F, Saccone A, et al. (2005) Partial phase diagrams of the Dy e Pt and Ho e Pt systems and electrocatalytic behaviour of the DyPt and HoPt phases. *J Alloys Compd* 391: 60-66.

22. Santos DMF, Saturnino PG, Macciò D, et al. (2011) Platinum-rare earth intermetallic alloys as anode electrocatalysts for borohydride oxidation. *Catal Today* 170: 134-140.