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Electrolytic recovery of nickel and copper from acid pickling solutions used to treat metal surfaces

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the process have been identified (temperature, contact time and current density). In total about 60 tests were carried out on AW containing nickel and copper. The results of the tests carried out with copper-containing AW shows that removal yields are often higher than 50%; while the energy consumption is less than 15 kWh kg^{-1} of metal deposited. The best removal efficiency (100%) was achieved by applying a current density of 6 A dm^{-2} and the energy consumption was 2 kWh kg^{-1}. The tests carried out with AW containing nickel point out very low removal yields (< 20%) and very high energy consumption (even exceeding 300 kWh kg^{-1}). The best removal yield obtained, applying a current density of 3 A dm^{-2}, is 6.7% with an energy consumption of 40 kWh kg^{-1} of metal removed. A costs analysis based on Metal Exchange value was carried out. The cost analysis suggests that the results, in terms of removal and recovery, obtained for these metals, in particular for copper, are very promising for an industrial application.

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Pavia, December 11th, 2018

Dear Editor-in-Chief,
we would like to submit the manuscript titled "ELECTROLYTIC RECOVERY OF NICKEL AND COPPER FROM ACID PICKLING SOLUTIONS USED TO TREAT METAL SURFACES" for possible publication in *Water, Air, & Soil Pollution.*

This research focuses on the electrochemical recovery of copper and nickel from acid pickling solutions used to treat metal surfaces. This with a vision, increasingly stimulated internationally, of circular economy for waste. Using Hull cells, Beaker plating and electrolytic cells in pilote scale (capacity 30L), the most important parameters influencing the process have been identified (temperature, contact time and current density). In total about 60 tests were carried out on aqueous waste containing nickel and copper.

A costs analysis based on Metal Exchange value was conducted. The cost analysis suggests that the results, in terms of removal and recovery, obtained for these metals, in particular for copper, are very promising for an industrial application.

This paper is original and unpublished; it is not being considered for publication by any other journal.

Yours Sincerely,

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Electrolytic recovery of nickel and copper from acid pickling solutions used to treat metal surfaces

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ABSTRACT

The increased use of heavy metals in process industries often results in the generation of large quantities of wastewater (WW) and aqueous waste (AW) containing mixtures of heavy metals such as copper and nickel. This research focuses on the electrochemical recovery of copper and nickel from acid pickling solutions used to treat metal surfaces. Using Hull cells, Beaker plating and electrolytic cells in pilot scale (capacity 30L), the most important parameters influencing the process have been identified (temperature, contact time and current density). In total about 60 tests were carried out on AW containing nickel and copper. The results of the tests carried out with copper-containing AW shows that removal yields are often higher than 50%; while the energy consumption is less than 15 kWh kg^{-1} of metal deposited. The best removal efficiency (100%) was achieved by applying a current density of 6 A dm^{-2} and the energy consumption was 2 kWh kg^{-1}. The tests carried out with AW containing nickel point out very low removal yields (< 20%) and very high energy consumption (even exceeding 300 kWh kg^{-1}). The best removal yield obtained, applying a current density of 3 A dm^{-2}, is 6.7% with an energy consumption of 40 kWh kg^{-1} of metal removed. A costs analysis based on Metal Exchange value was carried out. The cost analysis suggests that the results, in terms of removal and recovery, obtained for these metals, in particular for copper, are very promising for an industrial application.

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1. INTRODUCTION

Pickling involves treating metal surfaces by removing the oxide layer, rust, encrustations, inorganic contaminants or other impurities from ferrous metals, copper or precious metals (Karakaya et al. 2018; Malamis et al. 2011).

A strong inorganic acid, such as HCl, is therefore used for pickling metal surfaces (Karakaya et al. 2018). These acid solutions are therefore rich in heavy metals such as copper and nickel. Two aspects must be taken into consideration: (i) these metals are in fact considered strategic metals and are widely used in various industrial processes, such as electrolytic plating, paint production, mineral processing, forging and the production of batteries (Coman et al. 2013; Karakaya et al. 2018; Peng et al. 2014); (ii) high concentrations of heavy metals are a problem when industrial wastewater (WW) or aqueous waste (AW) must be treated.

To treat AW, there are different types of processes commonly applied as: (i) coagulation-flocculation (Bourechech et al. 2018; Malamis et al. 2011), (ii) membrane processes (Renou et al. 2008), (iii) adsorption (de Freitas et al. 2018; Malamis et al. 2011; Renou et al. 2008), (iv) H_2O_2 based processes (Collivignarelli, Pedrazzani, et al. 2017) (v) Fenton process (Bourechech et al. 2018; Ishak et al. 2018) and (vi) biological degradation (Collivignarelli et al. 2018; Collivignarelli, Abbà, et al. 2017; Collivignarelli, Bertanza, et al. 2015; Renou et al. 2008). In any case, a high concentration of heavy metals in the AW to be treated means that the same metals are then present in high concentrations in the sludge. The latter may therefore not comply with regional and national regulations regarding the recovery of sludge in agriculture (Collivignarelli, Abbà, et al. 2015; EC 2010; Gunatilake 2015; Sharma et al. 2017).

It should be remembered that sludge can in fact be spread on agricultural land only if it meets the quality requirements (in particular concerning heavy metals and pathogens) established by European and national

legislation (EC 2010). The high concentration of metals in the sludge makes it impossible to recover it in agriculture (Sharma et al. 2017).

This implies the impossibility of recovering also the heavy metals contained in them, thus counteracting an essential point of the circular waste economy concept proposed by the European Commission (EC 2018).

The increased use of heavy metals in process industries often results in the generation of large quantities of dilute effluents containing mixtures of heavy metals such as copper and nickel (Fu and Wang 2011; Su and Ye 2017; Wang and Ren 2014). For this reason, in the last decades the search for the recovery of metal removal from WW and AW has advanced considerably. The main chemical-physical methods for removal and recovery of metals from industrial AW are (Awual 2015; Brooks 2018; Dermentzis et al. 2016; Fu and Wang 2011; Gunatilake 2015; Wang and Ren 2014): (i) chemical precipitation in the form of hydroxides or sulphides, (ii) nanofiltration or reverse osmosis membrane processes, (iii) ion exchange on resins, (iv) evaporation, (v) separation in the form of complexes, (vi) galvanocoagulation, (vii) bioadsorption and (viii) electrolysis.

Recently, with the aim of recovering heavy metals from WW, the combination of electrochemical and biological processes such as the Microbial Fuel Cell (MFC) and the Microbial Electrolysis Cell (MEC) has aroused considerable interest (Luo et al. 2015; Rodenas Motos et al. 2015, 2017). However, considerable amounts of electricity are still needed in the electrolysis cells for their operation. In comparison, bio-electrochemical systems can provide energy from bio-electrochemical degradation of organic compounds present in WW (Rodenas Motos et al. 2015, 2017).

However, one of the most promising technologies today is represented by electrodeposition (Dermentzis et al. 2016; Gunatilake 2015; Maarof et al. 2017). It demonstrates a feasible, low-cost and efficient approach for removing/recovering heavy metal ions (Lou et al. 2018). The electrodeposition process can

be carried out in order to remove heavy metals, such as copper and nickel, with high selectivity (Dermentzis et al. 2016; Liu et al. 2013; Lou et al. 2018). Regarding the electrolytic recovery of these two heavy metals, many studies have already been carried out (Dermentzis et al. 2016; Gunatilake 2015; Liu et al. 2013; Lou et al. 2018; Maarof et al. 2017).

It should be recalled that the recovery of heavy metals presents various advantages from an environmental point of view, including: (i) minimizing the impact of AW on biological treatments present in the treatment plants, allowing greater efficiency in those areas,(ii) the dispersion of the aforementioned metals into the environment (e.g. in sewage sludge) is reduced (Collivignarelli, Abba, et al. 2015) and (iii) the extraction and use of new virgin material is avoided with a view, increasingly stimulated at an international level, of circular economy for waste (EC 2018).

This research focuses on the electrochemical recovery of copper and nickel from acid pickling solutions used to treat metal surfaces. A significant aspect of this research are the three-step experiments that have been conducted. Firstly, the hull cells were used to identify the optical current density (I_x). Secondly, Beaker tests were conducted to identify the optimal operating parameters such as temperature and contact time. Finally, pilot-scale electrolytic cells were used to apply the optimal parameters on a larger scale. Based on optimal performance, an analysis of recovery costs was conducted. A comparison with the costs related to the purchase of "virgin" material was then presented.

2. MATERIALS AND METHODS

2.1 Aqueous waste characteristics

The experiments have been carried out using five AWs with high concentrations of metals: in two there is nickel and in the other three copper. The characteristics are shown in **Table 1**. As can be seen they are also characterized by a high concentration of COD and H_2O_2. These aspects must be taken into account in

the subsequent analysis of the results as high COD values favor the development of H^+ ions whose reduction, in competition with that of the metal ions of interest, slows down the deposition of the latter. Even high concentrations of H_2O_2 can hinder the deposition of the metal on the cathode (Balaji 2006).

Parameters	AW with nickel		AW with copper		
	A	B	C	D	E
Nickel [mg L^{-1}]	6000	19000	n.a.	n.a.	n.a.
Copper [mg L^{-1}]	n.a.	n.a.	22000	46000	74100
COD [mg L^{-1}]	14000	14000	40000	1250	3300
H_2O_2 [mg L^{-1}]	0-0.5	1	1	1	5
pH	5.5	6	1	1	1
Density [g mL^{-1}]	1.3	1.3	1.064	1.06	1.06
Electrical conductivity [µS cm^{-1}]	78100	89200	232000	20300	n.a.
Ammonia [mg kg^{-1}]	52203	38125	<50	<100	38125
Phosphates [mg kg^{-1}]	190000	107694	n.a.	n.a.	n.a.
Fluorides [mg kg^{-1}]	16572	4461	n.a.	n.a.	n.a.

n.a.: not available; AW: aqueous waste

Table 1 Characteristic of industrial AWs containing nickel (A, B) and copper (C, D, E)

COD, NH_4^+, H_2O_2, density, phosphates, fluorides, nickel, copper and electrical conductivity were measured according to the standard methods for water and wastewater (APHA 2012). pH and temperature (both with the use of a WTW Sentix 940-3 probe) were also measured.

2.2 Hull cell tests

The Hull cell allows to carry out preliminary laboratory tests to identify the main operative parameters. In these tests AWs containing copper (C, D and E) are used.

The main characteristic of the Hull cell (**Fig. 1 a**) is to have a cathode positioned with standard angle (0.22 π = 39.6 °) compared to the anode: in this way the cathode surface creates a continuous and determinable gradient of current density.

The technical characteristics of the laboratory Hull cell are:

- Cell volume: 267 mL;
- Anode material: Titanium activated with titanium oxides and iridium (DSA);
- Cathode material: stainless steel AISI 316;
- Treatment duration: 15 minutes.

The current distribution on the cathode is well represented by a logarithmic curve that can be expressed by the empirical formula (**Eq. 1**) (Pletcher and Walsh 1993):

$$I_x = 10i \cdot (C_1 - C_2 \cdot logx) \quad (1)$$

Where $\mathbf{I_x}$ is the current density [mA cm^{-2}]; **x** is the length of the deposit [cm], **i** is the current intensity [A] and $\mathbf{C_1}$ and $\mathbf{C_2}$ are two constants dependent on the cell used. (C_1 = 5.1 and C_2 = 5.24).

2.3 Beaker tests

According to the results obtained with Hull cell, other tests are carried out in a cell with flat and parallel electrodes on both copper and nickel AW in order to establish the optimal parameters for the pilot scale plant.

In these tests a glass beaker of 500 mL is used (**Fig. 1 b**). Several tests are carried out with varying temperature (from 25 to 50 °C), current density (from 3 to 30 A dm^{-2}) and deposition time (from 1.5 to 7 h). The current intensity is estimated by multiplying the optimal current density value, obtained from Hull cell tests, and the cathode area available for the electroplating.

The materials of anode and cathode are respectively: activated titanium or graphite for the anode and steel or brass for the cathode depending on the chemical compatibility with the solution to be treated.

2.4 Pilot scale tests

The pilot scale plant, as can be shown in **Figure 1 (c and d)**, consists of: a chamber in Moplen where the electrolytic cell (30 L) is located, a tank placed under the cell of 120 L and another compartment containing the pump and the flowmeter that allow the recirculation at a fixed range of solution. Inside the electrolytic cell and the reservoir are placed two Pt100 thermal resistances to monitor the temperature; a heating element is placed in the tank to heat the solution. In a compartment located above the pump is placed the current rectifier and the electrical panel through which it's possible to set the current intensity and the duration of the test. The anode and cathode materials are respectively lead (5 mm thick) and stainless steel AISI 316 (5 mm thick). The tested AW consists of a mixture of C, D and E containing copper.

FIGURE 1 HERE

2.5 Costs analysis

To assess whether the aforementioned process may or may not be used for the recovery of copper or nickel as a valid alternative to the use of new raw material, the economic aspect must be taken into consideration. The analysis was carried out on the combination of treatment conditions which, for each of the two heavy metals, gave the best results in terms of removal efficiency.

The cost related to the recovery of copper and nickel ($Cr_{heavy\ metal}$) was calculated (**Eq. 2**) considering the consumption of energy per kg of recovered metal calculated as a product between the energy consumed

per unit of mass (E) and the cost of electricity ($C_{c.energy}$). For the latter, the gross European average cost for 2018 was assumed (ARERA 2018).

$$Cr_{heavy\ metal}\left[€\ kg^{-1}_{heavy\ metal}\right] = E\left[kWh\ kg^{-1}_{heavy\ metal}\right] * C_{e.energy}[€\ kWh^{-1}] \quad (2)$$

The cost related to the possible purchase of new raw material (copper or nickel) ($Cb_{heavy\ metal}$) was assessed (**Eq. 3**) by taking into consideration the cost of the metal ($V_{heavy\ metal}$) (LME 2018) and the average Euro/US$ exchange rate (change) for the last year calculated from October 2017 until October 2018 (ECB 2018).

$$Cb_{heavy\ metal}\left[€\ kg^{-1}_{heavy\ metal}\right] = \frac{V_{heavy\ metal}\left[US\$\ t^{-1}_{heavy\ metal}\right]}{change\ [US\$\ €^{-1}]*1000} \quad (3)$$

In order to still have convenience in recovery, the value of maximum energy consumption (E_{max}) was calculated by setting the cost related to the recovery of copper and nickel ($Cr_{heavy\ metal}$) equal to the cost related to the possible purchase of new raw material ($Cb_{heavy\ metal}$) through the following formula (**Eq. 4**):

$$E_{max}\left[kWh\ kg^{-1}_{heavy\ metal}\right] = \frac{Cb_{heavy\ metal}\left[€\ kg^{-1}_{heavy\ metal}\right]}{C_{e.energy}[€\ kWh^{-1}]} \quad (4)$$

3. RESULTS AND DISCUSSION

3.1 Hull cell

The tests carried out using the Hull cell with AW containing copper have been used to determine the most important parameters that affect the process. As shown in **figure 2a**, the length of metal deposition (i.e., the cathode region that is covered by the plated metal) depends on the applied current intensity and the initial Cu^{2+} concentration. The results suggest that as the current intensity (i) increases and, under equal conditions, the metal deposit increases.

Furthermore, it is shown as the initial concentration of Cu^{2+} increases, the length of the deposit (x) and the current density (I_x) decrease significantly to almost nullify (x= 1cm; I_x< 0.5 A dm^{-2}) in the case of AW E. Thus, the amount of metal deposition obtained, increases with the increase of optimum current density, calculated with the previous empirical formula (**Eq. 1**); this is in fact related to the applied current intensity and the initial concentration of metals in the AW.

The experiments always show a decrease in the cell voltage during the tests (between 0.1 and 0.89 V). The appearance of metal deposition is coppery, thin with good quality (**figure 2b**); it has been observed that, with the passage of time and the increase in thickness, the deposition of copper becomes discontinuous and contains more impurities.

FIGURE 2 HERE

3.2 Beaker tests

The results obtained with the beaker tests suggest that the removal yields of nickel, from the AW A and B, are between 1 and 10% (**Figure 3a**) according to the study of (Borges Porto et al. 2017) on a real case that showed also a rather low removal yield (around 36%). However, this result contrasts with other recent studies that have obtained higher removal rates from 90 to 100% (Coman et al. 2013; Liu et al. 2013; Peng et al. 2014). The energy consumption of the tests, carried out using nickel-containing AW, is between 40 and 350 kWh kg^{-1} of Ni^{2+} deposited (**Figure 4**). The lower value obtained is in total agreement with that reported by the study of (Peng et al. 2014) (25 ÷ 30 kWh kg^{-1} of Nickel deposited) although in our study we are operating with an initial concentration of two orders of magnitude higher. As suggested in (**Figure 3b**), the removal yields of copper from the AW C and D are higher than nickel removal yields and they vary between 20% and 100%. The test results, with the exception of only one,

suggest an energy consumption between 2 and 17 kWh kg^{-1} of Cu^{2+} deposited. It is a significantly lower value compared to nickel tests.

These results are in agreement with the scientific literature: for example, (Britto-Costa and Ruotolo 2015) have obtained the removal of Cu^{2+} with an energy consumption of 1.7 kWh kg^{-1} of Cu^{2+} deposited. Moreover, (Britto-Costa et al. 2014) found values from 2.5 and 9.6 kWh kg^{-1} as energy consumption during their tests.

During the experiments it was observed that the presence of oxygen contrasts and makes the metal deposition more difficult. Another important aspect suggested by test is that low metal concentrations involve very low removal yields with consequently higher specific energy consumption. This result is in agreement with (Britto-Costa and Ruotolo 2015) study about copper removal. They explained that electrowinning can be successfully obtained with high removal yields particularly when the copper ion concentration is high.

Moreover, as (Coman et al. 2013) explains, electrolytic process and particularly electrodeposition can be successfully applied for Ni^{2+} removal/recovery from WWs and AW when the concentration of the metal in solution is high because otherwise the control of the process is very difficult and the yields are very low.

As regards I_x analysis, the results show that the optimal current density value for an effective removal of Cu^{2+} is equal to 3 A dm^{-2} while for the removal of the Ni^{2+} it is necessary to operate with higher values (6 or 10 A dm^{-2}). The result of copper is in agreement with the bibliography. For example, (Ahmed Basha et al. 2008) have tested the electrolytic removal of copper by detecting optimal current density values of about 2 A dm^{-2}, other conditions being equal. They also tested a higher current density (4 A dm^{-2}). In the second case, lower removal results were obtained (30% against 80%). The influence of current density on nickel removal is confirmed, for example, by studies of (Orhan et al. 2002) that have found a greater removal of nickel by operating with higher current densities.

The tests show that the optimal temperature for the deposition and removal of Cu^{2+} is equal to 25 °C, (this value of T is obtained thanks to the Joule effect and presence of electric current) while for the removal of Ni^{2+} ions it is necessary to increase the temperature up to 50 °C providing additional thermal energy. Regarding the optimal temperature for copper removal, the literature is rather discordant. The results obtained are in agreement with those obtained from (Britto-Costa and Ruotolo 2015) which verified that an increase in the temperature of the electrolyte causes a decrease in the electrodeposition rate. Also (Orhan et al. 2004) have found an optimal temperature for the removal of Cu2 + equal to 20 °C. As regards the temperature as a process parameter for the removal of nickel, what the results suggest is in complete agreement with what, for example, stated by (Orhan et al. 2002). They varied the temperature of the electrolyte between 20 and 65 °C and found that the recovery of nickel is in fact only possible at temperatures above 50 °C.

During the tests, the COD was also monitored. The results show that there was a removal rate between 10 and 56% for all types of AW (A, B, C and D). The variability seems to depend on the initial composition of the AW.

FIGURE 3 HERE

FIGURE 4 HERE

3.3 Pilot scale test

According to beaker tests results, a pilot scale tests are carried out only on copper-containing AW. The main result, achieved with pilot scale plant (shown in **figure 5**), is that the contact time doesn't seem to have a significant influence on the removal yields.

The influence of temperature has also been investigated. An increase (from 25 to 40 °C), with equal other conditions, produces a slight increase in the rate of removal of Cu^{2+}, but lower than that shown in the study of (Britto-Costa et al. 2014).

Finally, contrary to other recent studies (Min et al. 2018), a current density increasing, at least in the tested values (from 3 to 10 to A dm^{-2}), doesn't seem to have a positive influence in the copper removal yields. The results, on the other hand, seem to suggest a slight decrease in the rate of removal of Cu^{2+} with the increase in current density in accordance with what was already reported by (Ahmed Basha et al. 2008).

FIGURE 5 HERE

3.4 Costs analysis

	Copper	**Nickel**
Best removal efficiency	Current density= 6 A dm^{-2}; T= 40 °C; deposition time= 4 h; pH= 1	Current density= 3 A dm^{-2}; T= 50 °C; deposition time= 4 h; pH= 6
E [kWh $kg^{-1}_{heavy\ metal}$]	2	40
C_{energy} [€ kWh^{-1}]	0.2207	0.2207
$V_{heavy\ metal}$ [US$ $kg^{-1}_{heavy\ metal}$]	6.28	12.45
change [$ $€^{-1}$]	1.1882	1.1882
$Cr_{heavy\ metal}$ [€ $kg^{-1}_{heavy\ metals}$]	0.44	8.83
$Cb_{heavy\ metal}$ [€ $kg^{-1}_{heavy\ metals}$]	5.29	10.48
E_{max} [kWh $kg^{-1}_{heavy\ metals}$]	24	47

Table 2 Analysis and comparison of metal recovery costs and costs for the purchase of new metals taking into consideration the treatments that showed the best removal efficiencies

Taking into consideration the treatments that showed the best removal efficiency and considering, for the recovery of metals, only the energy costs, the main result obtained with the analysis of recovery costs and the costs for the purchase of new metals (reported in **Table 2**) is that in both cases the costs for the recovery of metals are lower than the costs for the purchase of new metals, in particular in the case of copper. This is in agreement, for example, with the results of (Min et al. 2018) which have applied an electrolytic process for economically recovery of highly-purified copper.

The results obtained from the economic analysis suggest that the convenience in recovering nickel is lower than copper due mainly to two factors: (i) poor efficiency of nickel removal by electrolytic process (ii) high energy consumption linked to metal recovery. However, it should be recalled that, on the one hand, the costs for recovery in this analysis have been simplified by not taking into account, for example, the costs of depreciation of the plant or the costs of the reagents, on the other hand if the metals are not removed from the AW and recovered there would be additional disposal costs not considered here. Indeed, AW containing high concentrations of heavy metals generally generates high management and disposal costs (Barakat 2011).

This analysis also suggests that in order to have convenience in recovery, the maximum value of energy consumption (E_{max}) is higher for nickel (47 kWh kg^{-1}) than copper (24 kWh kg^{-1}). This is because the Ni^{2+} has a higher sales price (LME 2018) thus making the recovery process convenient even with the use of more energy.

4. CONCLUSIONS

The results of the tests carried out with copper-containing AW are very positive considering high removal yields obtained and low energy consumption required; in particular, removal yields are often higher than 50%; while the energy consumption is less than 15 kWh kg^{-1} of metal deposited.

The best removal efficiency (100%) was achieved by applying a current density of 6 A dm^{-2}, a temperature of 40 °C, pH around 1 and a deposition time of 4 h, the energy consumption was 2 kWh kg^{-1}. Based on the price of copper on Metal Exchange, this electrochemical treatment is considered reliable if energy consumption is less than 24 kWh kg^{-1} of copper removed. So, we can say that the results obtained for this metal are very promising.

Regarding the results obtained from the tests carried out with AW containing nickel, very low removal yields (< 20%) are achieved with high energy consumption (even exceeding 300 kWh kg^{-1}) for an industrial scale application.

The best removal yield obtained, applying a current density of 3 A dm^{-2}, a temperature of 50 °C with a deposition time of 4 h and pH around 6, is 6.7% with an energy consumption of 40 kWh kg^{-1} of metal removed. In this case, electrochemical treatment is considered to be reliable, since energy consumption has been found to be less than 47 kWh kg^{-1} of deposited nickel (calculated according to the price of nickel on Metal exchange). The cost analysis suggests that the results, in terms of removal and recovery, obtained for these heavy metals, in particular for copper, are very promising for an industrial application.

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References:

Ahmed Basha, C., Bhadrinarayana, N. S., Anantharaman, N., & Meera Sheriffa Begum, K. M. (2008). Heavy metal removal from copper smelting effluent using electrochemical cylindrical flow reactor. *Journal of Hazardous Materials*, *152*(1), 71–78. doi:10.1016/j.jhazmat.2007.06.069

APHA. (2012). *Standard Methods for the Examination of Water and Wastewater*. *American Public Health Association, American Water Works Association, Water Environment Federation* (22nd Editi.). https://www.mwa.co.th/download/file_upload/SMWW_1000-3000.pdf. Accessed 30 October 2018

ARERA. (2018). *Relazione Annuale sullo stato dei servizi e sull'attività svolta - Volume I| Stato dei Servizi*. Milano. https://www.arera.it/allegati/relaz_ann/18/RAvolumeI_2018.pdf

Awual, M. R. (2015). A novel facial composite adsorbent for enhanced copper(II) detection and removal from wastewater. *Chemical Engineering Journal*, *266*, 368–375. doi:10.1016/j.cej.2014.12.094

Balaji, R. (2006). *Preparation and characterization of electrodeposits form methane sulphonic acid bath | PhD Thesis*.

Barakat, M. A. (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, *4*(4), 361–377. doi:10.1016/j.arabjc.2010.07.019

Borges Porto, M., Barbosa Alvim, L., & de Almeida Neto, A. F. (2017). Nickel removal from wastewater by induced co-deposition using tungsten to formation of metallic alloys. *Journal of Cleaner Production*, *142*(4), 3293–3299. https://www.sciencedirect.com/science/article/pii/S0959652616317711

Bourechech, Z., Abdelmalek, F., Ghezzar, M., & Addou, A. (2018). Treatment of leachate from municipal solid waste of Mostaganem district in Algeria: Decision support for advising a process treatment. *Waste Management & Research*, *36*(1), 68–78. doi:10.1177/0734242X17739970

Britto-Costa, P. H., Pereira-Filho, E. R., & Ruotolo, L. A. M. (2014). Copper electrowinning using a pulsed bed three-dimensional electrode. *Hydrometallurgy*, *144–145*, 15–22. doi:10.1016/j.hydromet.2014.01.014

Britto-Costa, P. H., & Ruotolo, L. A. M. (2015). Copper Electrowinning using a Spouted-Bed Electrochemical Reactor. *Química Nova*, *38*(5), 657–662. doi:10.5935/0100-4042.20150068

Brooks, C. S. (2018). *Metal Recovery from Industrial Waste*. Taylor and Francis Ltd.

Collivignarelli, M. C., Abbà, A., Bertanza, G., & Barbieri, G. (2017). Treatment of high strength aqueous wastes in a thermophilic aerobic membrane reactor (TAMR): performance and resilience. *Water Science and Technology*, *76*(12), 3236–3245. doi:10.2166/wst.2017.492

Collivignarelli, M. C., Abbà, A., Bertanza, G., Setti, M., Barbieri, G., & Frattarola, A. (2018). Integrating novel (thermophilic aerobic membrane reactor-TAMR) and conventional (conventional activated sludge-CAS) biological processes for the treatment of high strength aqueous wastes. *Bioresource Technology*, *255*, 213–219. doi:10.1016/j.biortech.2018.01.112

Collivignarelli, M. C., Abba, A., Padovani, S., Frascarolo, M., Sciunnach, D., Turconi, M., & Orlando, M. (2015). Recovery of Sewage Sludge on agricultural land in Lombardy: current issues and regulatory scenarios. *Environmental Engineering and Management Journal*, *14*(7), 1477–1486. doi:10.30638/eemj.2015.159

Collivignarelli, M. C., Abbà, A., Padovani, S., Frascarolo, M., Sciunnach, D., Turconi, M., & Orlando, M. (2015). Recovery of sewage sludge on agricultural land in Lombardy: current issues and regulatory scenarios. *Environmental Engineering and Management Journal*, *14*(7), 1477–1486. doi:10.30638/eemj.2015.159

Collivignarelli, M. C., Bertanza, G., Sordi, M., & Pedrazzani, R. (2015). High-strength wastewater treatment in a pure oxygen thermophilic process: 11-year operation and monitoring of different plant configurations. *Water Science and Technology*, *71*(4), 588–596. doi:10.2166/wst.2015.008

Collivignarelli, M. C., Pedrazzani, R., Sorlini, S., Abbà, A., & Bertanza, G. (2017). H2O2 Based Oxidation Processes for the Treatment of Real High Strength Aqueous Wastes. *Sustainability*, *9*(2), 244. doi:10.3390/su9020244

Coman, V., Robotin, B., & Ilea, P. (2013). Nickel recovery/removal from industrial wastes: A review. *Resources, Conservation and Recycling*, *73*, 229–238. doi:10.1016/j.resconrec.2013.01.019

de Freitas, F., Battirola, L. D., & de Andrade, R. L. T. (2018). Adsorption of Cu2+ and Pb2+ Ions by Pontederia rotundifolia (L.f.) (Pontederiaceae) and Salvinia biloba Raddi (Salviniaceae) Biomass. *Water, Air, & Soil Pollution*, *229*(11), 349. doi:10.1007/s11270-018-4005-9

Dermentzis, K., Marmanis, D., Christoforidis, A., Kokkinos, N., & Stergiopoulos, D. K. (2016). Recovery of metallic nickel from waste sludge produced by electrocoagulation of nickel bearing electroplating effluents. In *4th International Conference on Sustainable Solid waste Management* (pp. 23–25).

EC. (2010). *Environmental, economic and social impacts of the use of sewage sludge on land | Part II: Report on Options and Impacts*. http://ec.europa.eu/environment/archives/waste/sludge/pdf/part_ii_report.pdf

EC. (2018). Circular Economy: Implementation of the Circular Economy Action Plan. *European Commission*. http://ec.europa.eu/environment/circular-economy/index_en.htm. Accessed 31 October 2018

ECB. (2018). Euro reference exchange rate: US dollar (USD). *European Central Bank*. https://www.ecb.europa.eu/stats/policy_and_exchange_rates/euro_reference_exchange_rates/html/eurofxref-graph-usd.en.html. Accessed 23 October 2018

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*, *92*(3), 407–418. doi:10.1016/j.jenvman.2010.11.011

Gunatilake, S. K. (2015). Methods of Removing Heavy Metals from Industrial Wastewater. *Journal of Multidisciplinary Engineering Science Studies*, *1*(1), 12–18. http://www.jmess.org/wp-content/uploads/2015/11/JMESSP13420004.pdf

Ishak, A. R., Hamid, F. S., Mohamad, S., & Tay, K. S. (2018). Stabilized landfill leachate treatment by coagulation-flocculation coupled with UV-based sulfate radical oxidation process. *Waste Management*, *76*, 575–581. doi:10.1016/j.wasman.2018.02.047

Karakaya, E., Aras, M. S., Erdoğan, M., Karagül, S. Ç., Ersoy, M. K., & Karakaya, İ. (2018). An Electrochemical Procedure for Copper Removal from Regenerated Pickling Solutions of Steel Plants (pp. 275–281). doi:10.1007/978-3-319-72362-4_24

Liu, Y., Wu, X., Yuan, D., & Yan, J. (2013). Removal of nickel from aqueous solution using cathodic deposition of nickel hydroxide at a modified electrode. *Journal of Chemical Technology & Biotechnology*, *88*(12), 2193–2200. doi:10.1002/jctb.4085

LME. (2018). Copper and Nickel prices. *London Metal Exchange*. https://www.lme.com/. Accessed 23 October 2018

Lou, W., Cai, W., Li, P., Su, J., Zheng, S., Zhang, Y., & Jin, W. (2018). Additives-assisted electrodeposition of fine spherical copper powder from sulfuric acid solution. *Powder Technology*, *326*, 84–88. doi:10.1016/j.powtec.2017.12.060

Luo, H., Qin, B., Liu, G., Zhang, R., Tang, Y., & Hou, Y. (2015). Selective recovery of Cu2+ and Ni2+ from wastewater using bioelectrochemical system. *Frontiers of Environmental Science & Engineering*, *9*(3), 522–527. doi:10.1007/s11783-014-0633-5

Maarof, H. I., Daud, W. M. A. W., & Aroua, M. K. (2017). Recent trends in removal and recovery of heavy metals from wastewater by electrochemical technologies. *Reviews in Chemical Engineering*, *33*(4). doi:10.1515/revce-2016-0021

Malamis, S., Katsou, E., & Haralambous, K. J. (2011). Study of Ni(II), Cu(II), Pb(II), and Zn(II) Removal Using Sludge and Minerals Followed by MF/UF. *Water, Air, & Soil Pollution*, *218*(1–4), 81–92. doi:10.1007/s11270-010-0625-4

Min, X., Luo, X., Deng, F., Shao, P., Wu, X., & Dionysiou, D. D. (2018). Combination of multi-oxidation process and electrolysis for pretreatment of PCB industry wastewater and recovery of highly-purified copper. *Chemical Engineering Journal*, *354*, 228–236. doi:10.1016/j.cej.2018.07.212

Orhan, G., Arslan, C., Bombach, H., & Stelter, M. (2002). Nickel recovery from the rinse waters of

plating baths. *Hydrometallurgy*, *65*(1), 1–8. doi:10.1016/S0304-386X(02)00038-5

Orhan, G., Gurmen, S., & Timur, S. (2004). The behavior of organic components in copper recovery from electroless plating bath effluents using 3D electrode systems. *Journal of Hazardous Materials*, *112*(3), 261–267. doi:10.1016/j.jhazmat.2004.05.012

Peng, C., Jin, R., Li, G., Li, F., & Gu, Q. (2014). Recovery of nickel and water from wastewater with electrochemical combination process. *Separation and Purification Technology*, *136*, 42–49. doi:10.1016/j.seppur.2014.08.025

Pletcher, D., & Walsh, F. C. (1993). *Industrial Electrochemistry*. Dordrecht: Springer Netherlands. doi:10.1007/978-94-011-2154-5

Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., & Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials*, *150*(3), 468–493. doi:10.1016/j.jhazmat.2007.09.077

Rodenas Motos, P., Molina, G., ter Heijne, A., Sleutels, T., Saakes, M., & Buisman, C. (2017). Prototype of a scaled-up microbial fuel cell for copper recovery. *Journal of Chemical Technology & Biotechnology*, *92*(11), 2817–2824. doi:10.1002/jctb.5353

Rodenas Motos, P., ter Heijne, A., van der Weijden, R., Saakes, M., Buisman, C. J. N., & Sleutels, T. H. J. A. (2015). High rate copper and energy recovery in microbial fuel cells. *Frontiers in Microbiology*, *6*. doi:10.3389/fmicb.2015.00527

Sharma, B., Sarkar, A., Singh, P., & Singh, R. P. (2017). Agricultural utilization of biosolids: A review on potential effects on soil and plant grown. *Waste Management*, *64*, 117–132. doi:10.1016/j.wasman.2017.03.002

Su, F., & Ye, S. (2017). Zinc and Copper Recovery from Smelter Waste Stream Case Study. *Geo-Resources Environment and Engineering*. doi:10.15273/gree.2017.02.012

Wang, H., & Ren, Z. J. (2014). Bioelectrochemical metal recovery from wastewater: A review. *Water*

Research, *66*, 219–232. doi:10.1016/j.watres.2014.08.013

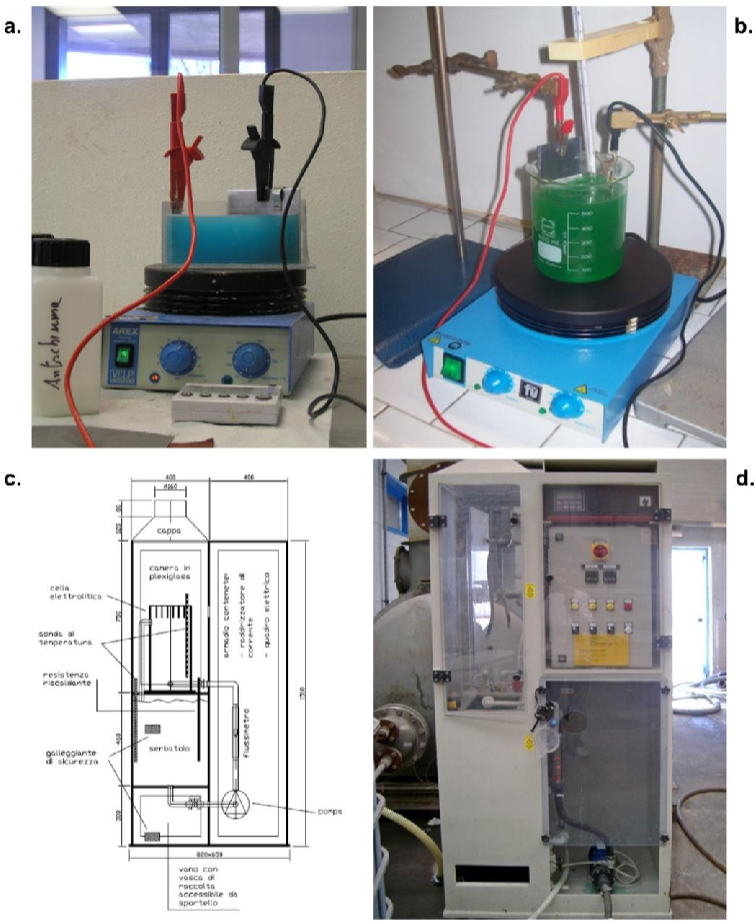

Fig. 1 (a) Hull cell, (b) Beaker test, (c) Pilot scale plant's scheme and (d) Pilot scale plant's figure *(graphics program: Microsoft Power Point)*

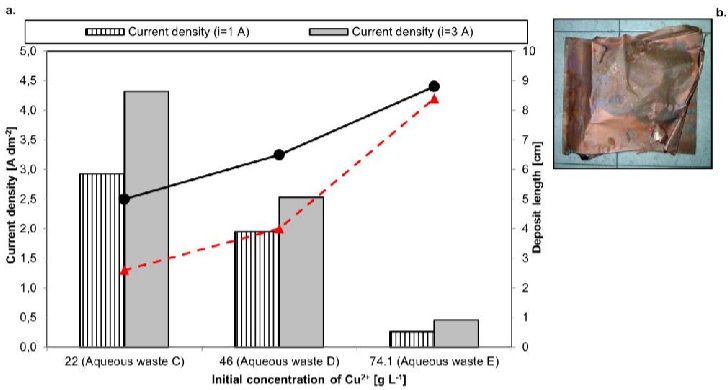

Fig. 2 (a) Results of Hull cell tests with contact time equal to 15 min and (b) Cu^{2+} deposition after 15 minutes *(graphics program: Microsoft Power Point)*

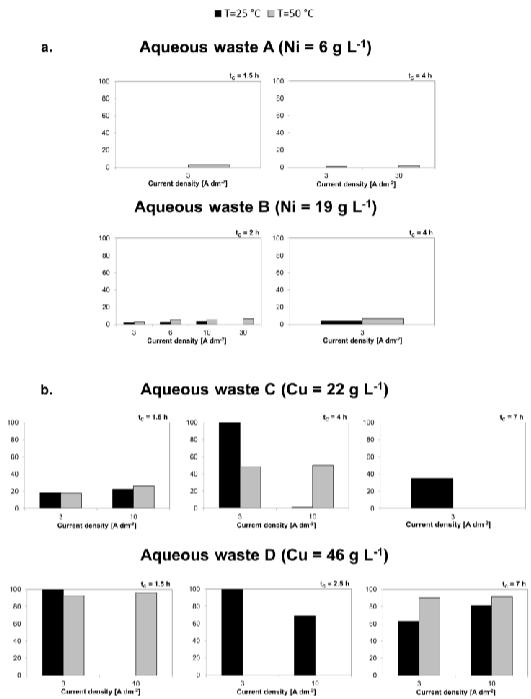

Fig. 3 (a) Results of beaker tests on AW A and B: nickel removal yield (% percentage); (b) results of beaker tests on AW C and D: copper removal yield (% percentage) *(graphics program: Microsoft Power Point)*

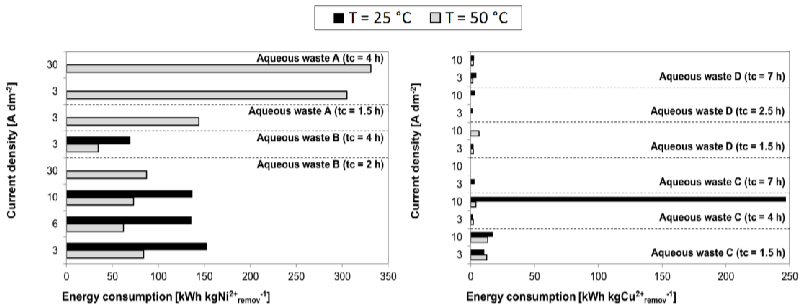

Fig. 4 Results of beaker tests: energy consumption *(graphics program: Microsoft Power Point)*

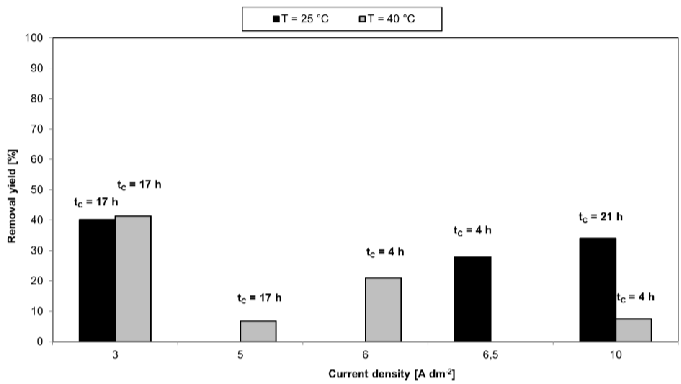

Fig. 5 Results of Pilot scale tests: performance of copper removal *(graphics program: Microsoft Power Point)*

Fig1

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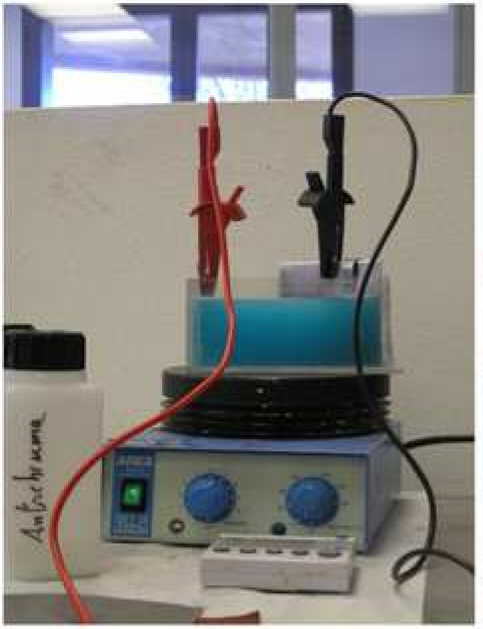
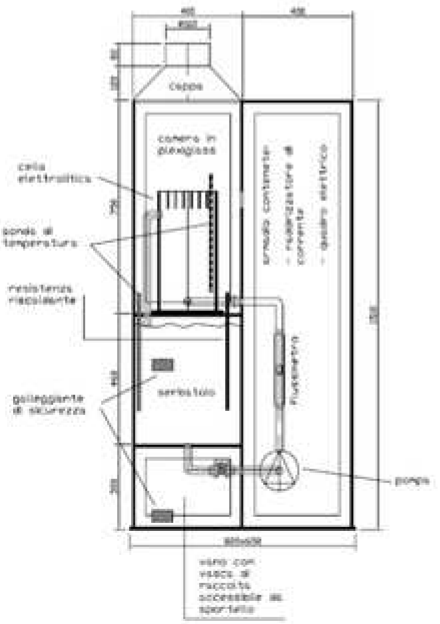
a.



b.

c.



d.

Fig2

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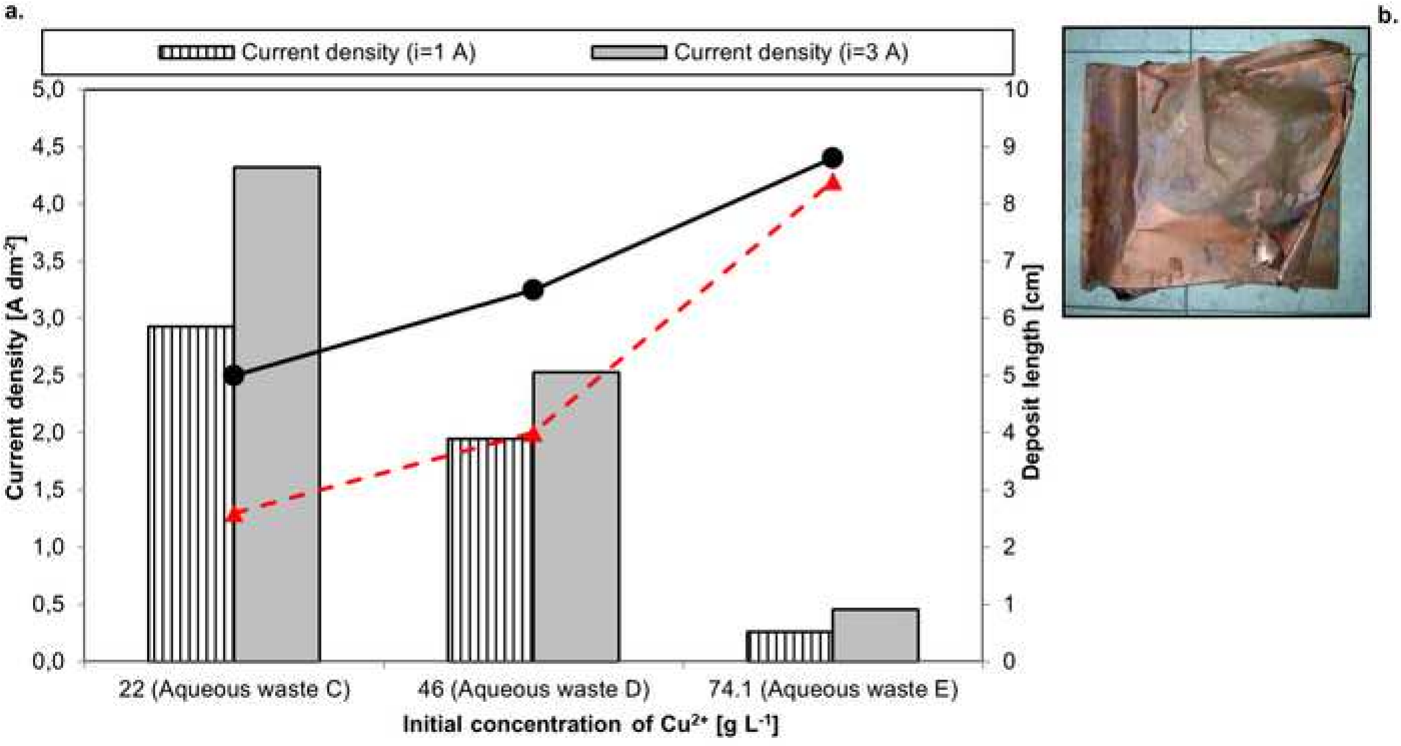

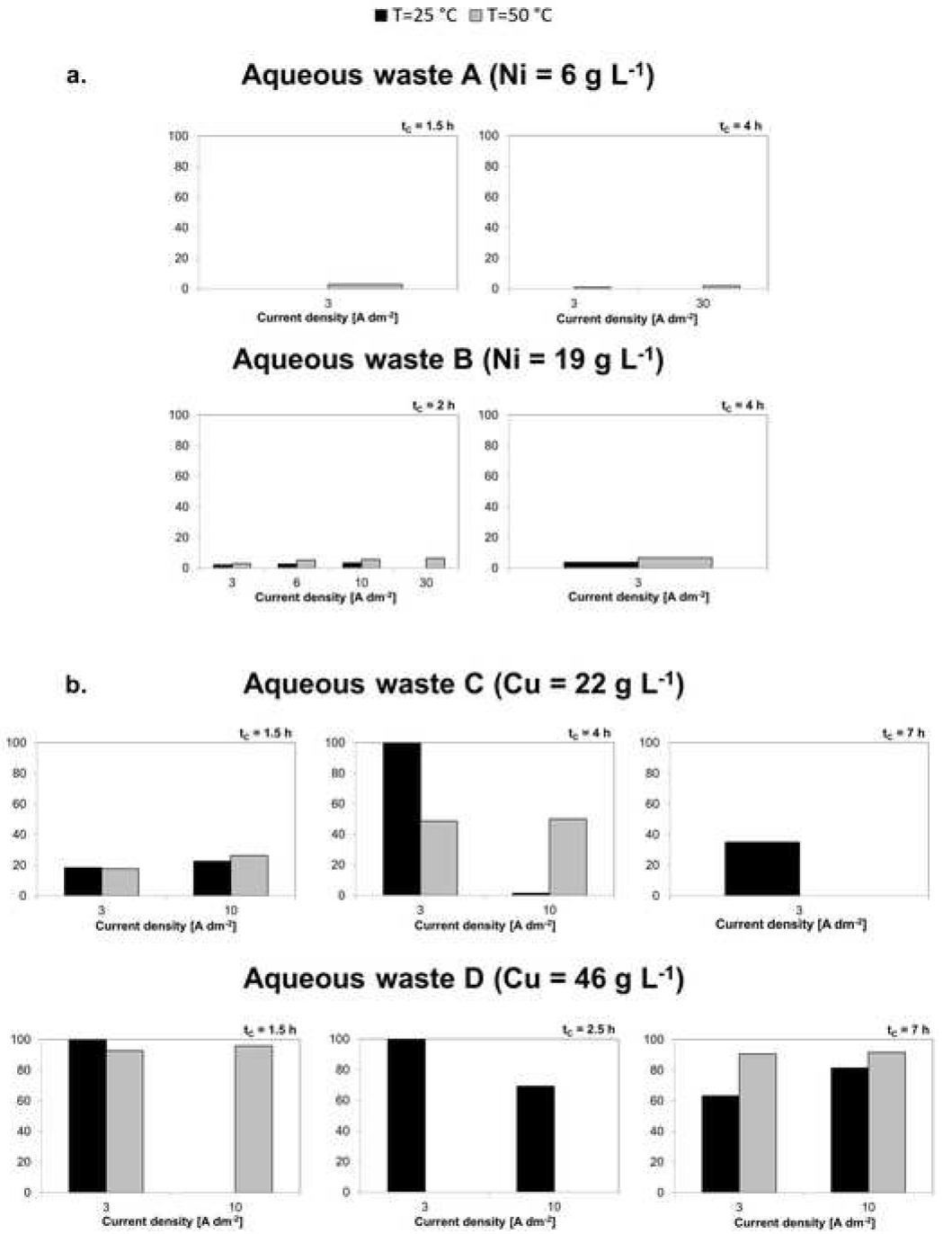

Fig4

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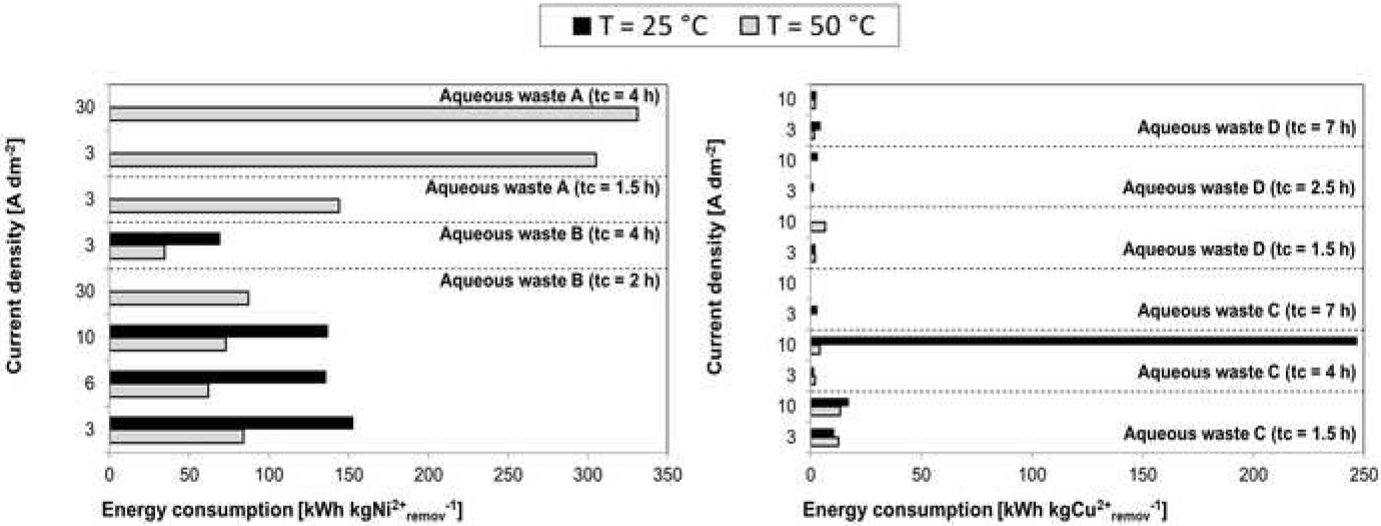

Fig5

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