



Selective recovery of copper, nickel and zinc from ashes produced from *Saccharomyces cerevisiae* contaminated biomass used in the treatment of real electroplating effluents

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ABSTRACT

The aim of this work was to seek an environmentally friendly process for recycling metals from biomass-sludges generated in the treatment of industrial wastewaters. This work proposes a hybrid process for selective recovery of copper, nickel and zinc from contaminated biomass of *Saccharomyces cerevisiae*, used in the bioremediation of electroplating effluents. The developed separation scheme comprised five consecutive steps: (1) incineration of the contaminated biomass; (2) microwave acid (HCl) digestion of the ashes; (3) recovery of copper from the acid solution by electrolysis at controlled potential; (4) recycle of nickel, as nickel hydroxide, by alcalinization of the previous solution at pH 14; (5) recovery of zinc, as zinc hydroxide, by adjusting the pH of the previous solution at 10. This integrated approach allowed recovering each metal with high yield (>99% for all metals) and purity (99.9%, 92% and 99.4% for copper, nickel and zinc, respectively). The purity of the metals recovered allows selling them in the market or being recycled in the electroplating process without waste generation.

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1. Introduction

Electroplating industries constitute a fast growing sector. These industries generate effluents containing significant concentrations of various heavy metals, which do not meet the wastewater limit discharge criteria. These metal plating effluent streams cannot be released in the environment or sent directly to the municipal sanitary sewers. Although these effluents contain heavy metals concentrations higher enough to pose a serious environmental hazard, the concentrations of metals present in these waste solutions are too low for being directly recovered. Therefore, these toxic metals should be removed and, ideally (due to the increase of metal prices and reserves exhaustion) recovered in order to be recycled. Due to all these reasons, the treatment of wastewaters, produced in the electroplating industries, has become important not only to meet increasing environmental stringent regulations but also as a factor of competitiveness improvement. The goal of achieving zero discharge, as well as the need to reduce industrial costs, induced the development of methodologies for recovering selectively heavy metals.

Several methods, namely chemical precipitation, ion-exchange, solvent extraction, reverse osmosis and the application of biological materials has been proposed to treat effluents from electroplating industries [1]. Among the different types of biomass, flocculent cells of *S. cerevisiae* seem to be particularly suitable for the treatment of metal-bearing effluents. Heat-inactivated flocculent brewing yeast cells combine an efficient removal of heavy metals [2,3] with a fast, eco-friendly and inexpensive method of cell separation from the treated effluents; the use of flocculent cells saves energy as it overcomes the need of using a solid–liquid separation technique (centrifugation or filtration) or cell immobilization (gel entrapment), which in large scale can be excessively expensive [4,5].

Even though a big research effort has been promoted in the development of biological-based alternatives for the purification of metal-bearing effluents, a limited attention has been dedicated to metals recovery for subsequent re-use or sale. Basically, two approaches can be pursued: (i) metals desorption from the biomass; (ii) biomass dissolution (with strong acids) or incineration. Metals desorption from the biomass allows achieving the regeneration of biomass and simultaneous metals recovery from the liquid phase. Theoretically, this process is desirable in order to keep the process costs down. In this sense, different desorption agents have been used, namely: diluted (0.1 mol l^{-1}) mineral (HCl, HNO_3 and H_2SO_4) [6–8] and organic acids (CH_3COOH) [9],

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ethylenediaminetetraacetic acid (EDTA) [6,9] and carbonates [6,8]. However, some practical difficulties (such as: damage of yeast cells as a result of the eluant treatment, successive reduction of yeast metal uptake during biosorption/desorption cycles and in some cases, like chromium(III), lower capacity to concentrate the metals in a small volume of solution [6,9] have been found, which compromises the feasibility of the desorption process. On the other hand, when biomass is inexpensive, like the use of brewer's yeast cells (a by-product from a fermentative industry), its dissolution or incineration is advantageous because it generates a concentrated solution of heavy metals; this aspect is particularly important as it can determine the feasibility of metals recovery.

The combustion of microorganisms and subsequent recovery of metals from ashes, by acid leaching, seems to be a promissory approach. This process reduces the amount of residues and concentrates metals. Later on, metals can be recovered from acid solutions by separation processes such as electrolysis or chemical precipitation.

Few studies have been performed for recovering selectively more than two different metal ions [10,11]. Selective recovery of copper, nickel and zinc with sodium sulphides was investigated by Fukuta et al. [12] (quoted by Tokuda et al. [11]); in this work, copper, nickel and zinc were recovered with a selectivity of 94.5%, 65.9% and 75.9%, respectively. Further studies on the selective precipitation of copper, nickel and zinc, using sulphides, enhanced the selectivity of metal precipitation for values higher than 95% [11]. However, the use of sulphides implies the application of adequate safety procedures since it is toxic and corrosive. In addition, the transport, storage and production of sulphides are expensive [13].

The main aim of this work was to develop a nearly closed cycle for recycling selectively, with high yield and purity, heavy metals from yeast cells contaminated with copper, nickel and zinc, coming from the treatment of real electroplating effluents. For this purpose, contaminated biomass was, firstly, incinerated. Then, ashes were totally acid digested under microwave conditions. From this solution, copper, nickel and zinc were selective and efficiently recovered with high purity by implementing a hybrid separation process; this separation procedure combines electrodeposition followed by a sequential alkaline precipitation. Finally, the possibility of re-using the metals, with lower purity, in the electroplating process or selling them is discussed.

2. Materials and methods

2.1. Incineration of contaminated biomass

An effluent from an electroplating industry containing copper, nickel and zinc was treated with heat-inactivated brewing cells of *Saccharomyces cerevisiae*. After effluent treatment, contaminated biomass was collected and dried at 45 °C.

Kinetic incineration studies were performed at 550 °C in a muffle furnace (Nabertherm, L5/C6), using incineration trays containing 15 g of dried contaminated biomass. At defined intervals of time, incineration trays were taken, cooled down in a dessicator and weighed. This procedure was repeated until constant weight. These experiments were done in duplicate.

2.2. Microwave acid digestion of ashes

About 200 mg of ashes obtained as described above and 4.5 ml of HCl 1 mol l⁻¹ were placed in a polytetrafluoroethylene vessel. Digestion of ashes was performed in a microwave digester (Anton Paar, Multiwave 3000), using one cycle of 20 min and another one of 45 min, both with continuous radiation of 800 W. Then, 4.5 ml of

HCl 1 mol l⁻¹ was added and another cycle of digestion (45 min with a continuous radiation of 800 W) was applied. A new batch containing 200 mg of ashes was added to the previous acid solution and a new cycle of digestion was applied (45 min with a continuous radiation of 800 W). In all cases, the cycles were preceded by a heating ramp of 15 min (heating rate: 53 W/min). After the heating ramp, the final temperature ranged between 200 and 220 °C.

To control the efficiency of the microwave acid digestion, copper, nickel and zinc concentrations were determined in the acid solution, after the digestion of the first and second batches of ashes, by atomic absorption spectroscopy with flame atomization (AAS-FA) in a PerkinElmer AAnalyst 400 spectrometer (Norwalk, CT, USA). The concentrations of copper, nickel and zinc obtained in the acid digested solution were 3.5, 2.8 and 4.3 g l⁻¹, respectively.

2.3. Copper recovery by electrolysis at controlled potential

Before copper electrolysis, the pH of the acid digested solution was raised up to pH 2. Copper electrolysis was conducted using a batch reactor containing three electrodes. The cathode was a platinum net; a platinum wire and an electrode of Ag/AgCl (KCl 3 mol l⁻¹) were used as anode and reference electrodes, respectively.

Deposition of copper was attained by applying a constant cathodic potential of -0.6 V [Ag/AgCl (KCl 3 mol l⁻¹)] with a potentiostat (Autolab, PGSTAT 302). A volume of 40 ml of acid solution was used, under constant agitation (500 rpm), at 35 °C or 40 °C. Current intensity was monitored along the deposition time; it was assumed that electrodeposition was finished when current stabilized. At the end of copper electrolysis, copper concentration was quantified in the remained acid solution by AAS-FA for determining the efficiency of metal recovery. For controlling the selective recovery of copper, nickel and zinc were quantified, by AAS-FA, after redissolving the deposited metal in nitric acid.

These experiments were done in duplicate.

2.4. Computer chemical simulations

Chemical speciation calculations were carried out using the MINEQL+ software (version 4.5) [14]. Metal speciation analysis with MINEQL+ generates chemical equilibrium concentrations of all species being considered in the model by the program reactions, based on component stability constants and molar concentrations. Computational simulations were performed considering the total concentrations of nickel and zinc, which remained in the acid solution after copper deposition, and the solubility product constants [15].

2.5. Selective recovery of nickel and zinc by alcalinization

After copper deposition, the mass of sodium hydroxide (NaOH) necessary to adjust the pH of the remaining solution up to 14 was theoretically calculated taken into account the amount of hydroxide necessary to raise the pH from 2 to 14 plus the amount of hydroxide necessary to convert nickel and zinc to nickel hydroxide [Ni(OH)₂ (s)] and tetrahydrozincate(II) [Zn(OH)₄²⁻ (aq.)]; due to the high ionic strength of the solution, calculation of pH was performed considering the OH⁻ activity instead of OH⁻ concentration. The pH of the solution was adjusted by addition of small pellets of solid NaOH in order to minimize volume variation. Then, the suspension was centrifuged (2800 × g, 10 min) and nickel recovered as a precipitate of Ni(OH)₂. Nickel precipitate was washed two times with 10 ml of NaOH, at pH 14 and different times (one to four) with 10 ml of NaOH at pH 10; after each washing step, the solid was recovered by centrifugation (2800 × g, 10 min). Subsequently, the pH of the supernatant solution was adjusted to 10, by addition of

HCl 37%, in order to precipitate zinc, as zinc hydroxide, $\text{Zn}(\text{OH})_2(\text{s})$. After that, the suspension was centrifuged ($2800 \times g$, 10 min) to recover the precipitate of zinc hydroxide. This precipitate was further washed different times (one to three) with NaOH, at pH 10, and recovered by centrifugation ($2800 \times g$, 10 min).

To determine the efficiency of nickel and zinc recovery, as well as to characterize the purity of the precipitates, concentrations of copper, nickel and zinc were determined by AAS-FA, after appropriate dissolution of the precipitates in HNO_3 20% (v/v). Sodium and chlorides can also be present as impurities in the precipitates. Sodium concentration was determined by Emission Atomic Spectroscopy (EAS) in a PerkinElmer AAnalyst 400 spectrometer (Norwalk, CT, USA). Concentration of chlorides was determined as the difference between the total amount of the dried precipitate weighted gravimetrically and the sum of copper, nickel, zinc (all in the form of metal hydroxide) and sodium quantified in the precipitate. All determinations were done at least in duplicate.

3. Results and discussion

A real electroplating effluent containing 20, 22 and 25 mg l^{-1} of copper, nickel and zinc, respectively, was collected from a Portuguese electroplating industry. This effluent was efficiently treated by using a hybrid technology, which combines chemical precipitation with heat-inactivated cells of *S. cerevisiae* [16]. This process allowed reducing metal concentrations, in the treated effluent, to values below the Portuguese and US-EPA legal limits of discharge [16]. However, these heavy metals were only transferred from a liquid (effluent) to a solid phase (yeast cells) generating toxic sludges with high metal concentrations. Thus, a process to recover efficient and selectively copper, nickel and zinc from the contaminated biomass was required to be developed.

For heavy metals recovery, the first step should be the extraction of metals from biomass. As it was reported above, desorption of metals from biomass presents some difficulties. Alternatively, biomass can be dissolved using concentrated mineral acids or incinerated. In the present work, biomass incineration and subsequent digestion of ashes was chosen due to the following reasons: (i) the incineration originates a drastic reduction of the mass of the residues generated as a consequence of the bioremediation process used on the treatment of the effluent; (ii) the subsequent acid digestion of the ashes leads to the achievement of a concentrated solution of heavy metals, which is a key factor on the feasibility of metals recovery process.

3.1. Incineration of contaminated biomass

Contaminated yeast cells were incinerated and converted into ashes at 550°C to assure that organic matter was eliminated without formation of extremely recalcitrant compounds [17]. Preliminary incineration studies with different amounts of contaminated biomass (2, 10 and 15 g) have shown similar periods of time to complete incineration of biomass (data not shown). Thus, further incineration studies were performed using 15 g of contaminated biomass.

Kinetics studies of mass thermal decreasing were performed at 550°C . As it can be seen in Fig. 1, after 15 min and 4 h of incineration, a mass reduction of 83.1% and 97.6% was achieved, respectively. Total mineralization of the organic matter (incineration until a constant weight was attained) present in the sludges was obtained after 12.5 days (300 h) of incineration, which corresponded to a final mass decrease of 98.7%. The increasing of the incineration time up 300 h did not reveal a great decrease of the biomass ($\Delta\text{weight} = 1.1\%$) when compared with the decrease observed after 4 h. From these results, we concluded that an incineration time of

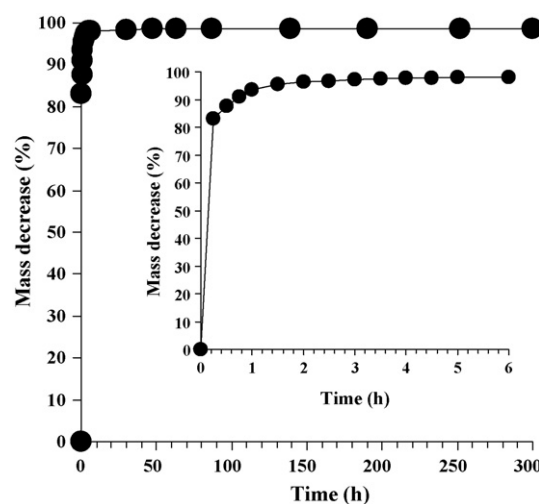


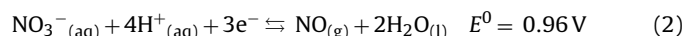
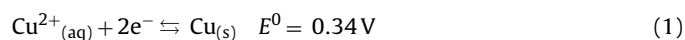
Fig. 1. Evolution of yeast cells mass loss. 15 g of *S. cerevisiae* brewer's yeast cells, used in the bioremediation of an electroplating effluent and loaded with heavy metals, was incinerated at 550°C until constant weight. Each point represents the mean of two replicates.

4 h should be used because it allows a significant mass decrease and saving of energy consumption.

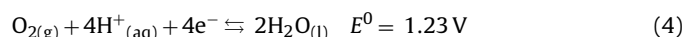
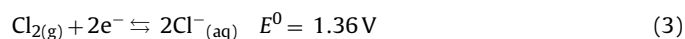
3.2. Ashes digestion

A microwave acid digestion with closed vessels was used to maximize the leaching of copper, nickel and zinc from the ashes. Closed vessels allow high pressures, which results in temperatures higher than the acid boiling point; as a consequence, the digestion process is accelerated [18]. This method also consumes a small volume of acid, which assures a relatively low sample dilution. Consequently, high metals concentrated solutions are obtained.

Because sulphuric, nitric and hydrochloric acids are economic and widely used in the electroplating industries, we started by evaluating the feasibility of using each one of these acids in the ashes digestion. Copper, nickel and zinc react with diluted sulphuric acid to form metal sulphates, which crystallise at room temperature [19]. So, sulphuric acid could not be used in the acid digestion of the ashes because it would not allow a subsequent selective recovery of each metal. Additionally, nitric acid did not meet the requirements for being used in the subsequent selective recovery of metals by electrolysis; in the presence of nitrates, besides copper, nitrates reduction also occurs in the cathode according to reactions (1) and (2), respectively [20]:



Nitric oxide, $\text{NO}_{(\text{g})}$, rapidly reacts with atmospheric oxygen and is converted to brown nitrogen dioxide, $\text{NO}_{2(\text{g})}$, a toxic gas by inhalation. Moreover, gas evolution at the cathode decreases the electroplating rate and can create porous metal deposits [21]. Hydrochloric acid can be used to digest the ashes without formation of crystals. Additionally, subsequent recovery of copper can be obtained by electrolysis without chlorides gas evolution at the anode because chlorides only evolves at a more anodic potential than water oxidation:



Previous calculations have shown that HCl 1 mol l^{-1} should be enough to dissolve totally the heavy metals present in the ashes.

Previous studies allowed optimizing other experimental conditions (volume of acid, time of digestion and power conditions) (data not shown). The digestion of 400 mg (200 plus 200 mg) of ashes, with HCl 1 mol l⁻¹ under the experimental conditions described in Section 2.2, allowed the total dissolution of copper, nickel and zinc. The acid digestion of the ashes resulted in a solution containing 3.5, 2.8 and 4.3 g l⁻¹ of copper, nickel and zinc, respectively.

In the next steps, selective recovery of copper, nickel and zinc from the acid digestion solution, followed by the evaluation of possible metals reinsertion in the electroplating production process, was studied.

3.3. Selective recovery of copper, nickel and zinc

3.3.1. Copper recovery by electrolysis at a controlled potential

Electrolysis can be applied as a metal recovery process when sufficiently large differences in the metals reduction potentials of the metals to be removed occurs [22]. Preliminary studies have shown that copper deposition already occurs at a cathodic potential of -0.4 V/[Ag/AgCl (KCl 3 mol l⁻¹)] at room temperature. However, an increase of the cathodic deposition potential improves copper deposition rate [23] but can eventually co-deposit nickel and zinc. It was verified that no co-deposition of nickel and zinc occurs at a cathodic potential of -0.6 V/[Ag/AgCl (KCl 3 mol l⁻¹)] ; thus, this potential was selected for recovering copper from the acid digested solution. For this purpose, firstly, the pH of the acid digested solution was raised up to pH 2. Subsequently, copper was electrodeposited at 35 °C or 40 °C and constant agitation (500 rpm). Fig. 2 shows the variation of the current intensity with time. In the first 60 min of deposition, no appreciable decrease of the current intensity was observed for both temperatures assayed. This fact can be explained by the high concentration of Cu²⁺ in solution that must undergo previous reduction to Cu⁺ before being reduced to Cu⁰ and deposited in the platinum electrode [23]. Then, a rapid decrease of the current intensity was observed for both temperatures tested. The kinetics of copper deposition at 40 °C was faster than at 35 °C (Fig. 2). When the current intensity stabilized, it was assumed that copper electrodeposition was finished. In fact, after 90 min of electrolysis, at 40 °C, a residual copper concentration of 30 mg l⁻¹ was present in solution, which corresponded to a recovery of 99.1%. At 35 °C, the kinetic of copper deposition was slower and after 130 min of electrolysis, a copper residual concentration of 7 mg l⁻¹ was achieved, corresponding to 99.8% of metal removal. These data demonstrate that the rise of cell temperature from 35 to 40 °C, reduced considerably the time of electrolysis (about half-hour) without a significant decrease of the yield of copper recovery.

The purity of the metallic copper, recovered at 40 °C, was very high, 99.9%, containing minor amounts [0.05% and 0.07% (w/w)] of nickel and zinc, respectively. Similar copper purity (higher than 99.5 mol%) had been reported by Doulakis *et al.* [23] when copper was recovered, under potentiostatic conditions, from a synthetic chloride solution containing a mixture of cadmium, copper, lead and zinc ions.

The results obtained in the present work show that copper can be efficient and rapidly recovered, as metallic copper with high purity, from the acid digestion solution containing multiple metal ions (copper, nickel and zinc) using a cathodic potential of -0.6 V [Ag/AgCl (KCl 3 mol l⁻¹)] under mild temperature (40 °C) and agitation (500 rpm) conditions.

The obtained metallic copper can be sold in the market or reintroduced in the copper plating baths (sulphate copper acid baths, fluoroborate acid baths, copper pyrophosphate-plating baths and brass plating solutions) at the production process [24].

If electroplating industries use baths of nickel-zinc alloys, the acid digested solution remained after the electrodeposition of copper, which contains nickel and zinc, can be directly reintroduced in

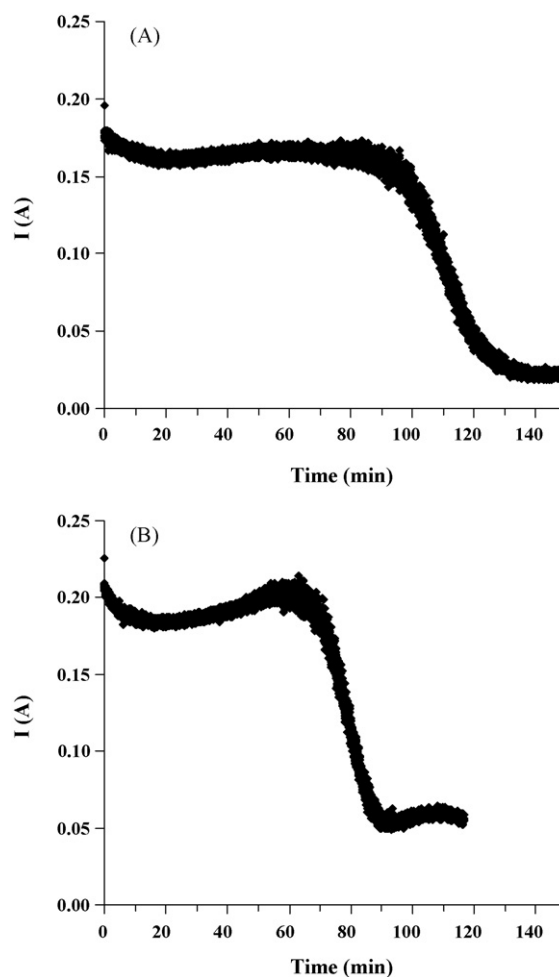
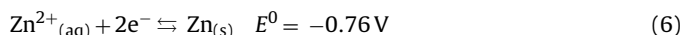
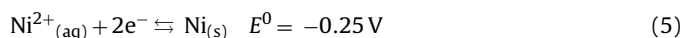


Fig. 2. Evolution of intensity current profile of copper electrodeposition. The pH of the acid digestion solution was adjusted at pH 2 and copper was electrodeposited at -0.6 V/[Ag/AgCl (KCl 3 mol l⁻¹)], at 35 °C (A) or 40 °C (B).

the production process to prepare those plating baths. If this application is not practicable, selective recovery of nickel and zinc is required.

3.3.2. Selective recovery of nickel and zinc

Firstly, the selective recovery of nickel from the remaining acid digested solution by electrolysis, at a controlled potential, was evaluated. The feasibility of the process would allow recovering nickel, in the metallic form, while zinc would remain in solution. The gap of potential between the standard reduction potentials of nickel and zinc (reactions (5) and (6), respectively, presented below) is 0.50 V:



This means that, from a theoretical point of view, deposition of nickel without simultaneous co-deposition of zinc should be possible. In order to determine the cathodic deposition potential where nickel and zinc are reduced, polarization studies were carried out applying a linear potential sweep from 0 to -2 V versus Ag/AgCl (KCl 3 mol l⁻¹) using single metal ion component solutions at pH 2. Nickel started to deposit at a cathodic potential of -0.95 V/[Ag/AgCl (KCl 3 mol l⁻¹)] and zinc at a cathodic potential of -1.2 V/[Ag/AgCl (KCl 3 mol l⁻¹)] (data not shown). These experimental results evidenced that the gap of potential between the beginning of nickel and zinc deposition is very tight (0.25 V) and does not allow a complete separation of these two metals by electrolysis.

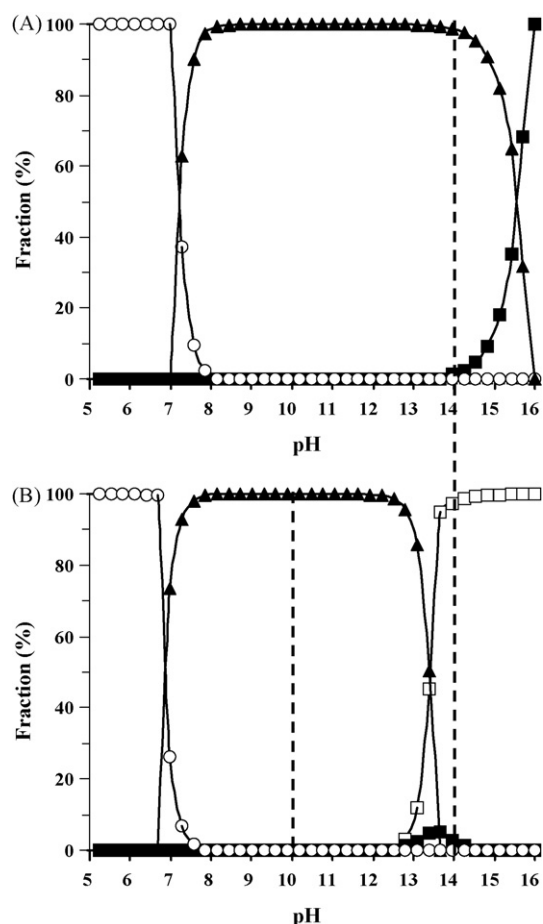


Fig. 3. Species distribution diagrams of nickel and zinc at different pH values. 2.8 g l⁻¹ of nickel (A) and 4.3 g l⁻¹ of zinc (B) were considered. The different species of metals in solution were calculated with a chemical equilibrium computer program (MINEQL+) and assuming the total concentrations of metals present in the acid digested solution: free metal ion, M²⁺(aq) (○), M(OH)_{2(s)} (▲) M(OH)_{3⁻(aq)} (■) and M(OH)_{4²⁻(aq)} (□).

As it was already mentioned above, selective sequential recovery of nickel and zinc processes were recently developed and described in the literature to separate these metal ions, as metal sulphides precipitates from multi-metal systems [11]. However, the handling of sulphides poses severe adequate safety procedures and its transport, storage and production are expensive [13].

Taking into account the impossibility of nickel and zinc recovery by electrolysis, with high purity, it was decided to develop a separation process based on an alkaline precipitation scheme. For this purpose, theoretical chemical distributions diagrams were done, using the MINEQL+ program, assuming the concentrations of nickel and zinc present in the remaining acid digested solution, 2.8 and 4.3 g l⁻¹, respectively, in the pH range between 5 and 16 (Fig. 3). Chemical distributions diagrams predict that both metal ions start to precipitate at about pH 7. For pH value higher than 13, zinc hydroxide starts to redissolve, as complexes of Zn(OH)_{4²⁻(aq)}, being totally soluble at about pH 14 (Fig. 3B). At this pH, nickel should still be found precipitated as Ni(OH)_{2(s)} (Fig. 3A). The analysis of these chemical distribution diagrams pointed out that a new strategy for selective recovery of nickel and zinc could be drawn based on the different solubility behaviour of nickel and zinc under alkaline conditions.

According to the information obtained from the chemical distributions diagrams of nickel and zinc (Fig. 3), the pH of the remaining acid digested solution was raised up to pH 14. Since the final pH

Table 1
Recovery and purity of the precipitate of nickel hydroxide.

	Without wash	Washing steps at pH 10 ^a			
		1	2	3	4
Recovery (%)	97 ± 5	100 ± 1	96 ± 5	98 ± 6	100 ± 1
Purity (%)	8 ± 1	40 ± 1	63 ± 7	77 ± 2	92 ± 7

^a The precipitate was previously washed two times with NaOH at pH 14; subsequent washing steps were carried out at pH 10.

Table 2
Recovery and purity of the precipitate of zinc hydroxide.

	Washing steps at pH 10			
	0	1	2	3
Recovery (%)	100 ± 3	95 ± 6	88 ± 4	100 ± 6
Purity (%)	55.3 ± 0.1	97 ± 2	99 ± 1	99.4 ± 0.8

was very high and thus could not be measured accurately, the mass of sodium hydroxide necessary to adjust the pH was theoretically calculated (for further details see Section 2.5). Under these conditions, 97% of nickel was recovered (Table 1), as nickel hydroxide, and zinc remained totally soluble. Nickel hydroxide was recovered with a purity of 8% (Table 1); sodium and chlorides constituted the main impurities (about 90%) present in the precipitate (Fig. 4). Minor amounts (less than 2%) of copper and zinc were present in the precipitate (Fig. 4). At this stage, this precipitate can be reused for adjusting the nickel concentration in the Watts electroplating baths; these baths usually present a concentration of 30–60 g l⁻¹ of NiCl₂·6H₂O and sodium does not affect the electrodeposition performance [24]. Additional washing steps for recovering nickel hydroxide are necessary to be implemented if a more pure compound is desirable.

In order to eliminate possible vestigial amounts of zinc impurities, the precipitate of nickel hydroxide was firstly washed with a

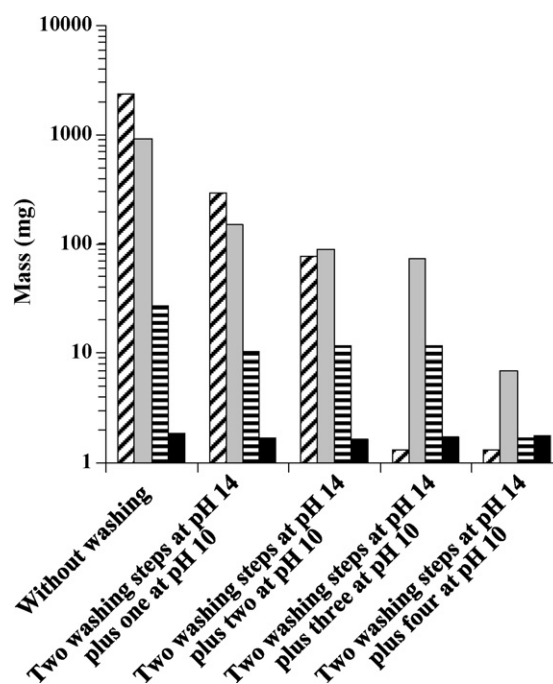


Fig. 4. Evolution of the decrease of contaminants present in the nickel hydroxide precipitate with the washing steps. Amounts of chlorides (bar with sloping lines), sodium (grey bar), zinc hydroxide (bar with horizontal lines) and copper hydroxide (black bar) present in the nickel hydroxide precipitate.

Table 3
Concentration of metals determined in the washing waters of nickel hydroxide.

Metal concentration (mg l ⁻¹)	Washing waters ^a					
	1st	2nd	3rd	4th	5th	6th
Cu	1.5	0.41	0.35	0.13	0.04	0.08
Ni	0.7	1.1	1.2	1.2	4.9	4.8
Zn	1.5 × 10 ³	5.9 × 10 ²	3.0 × 10 ²	15	1.4	0.4

^a The first two washing steps were performed with NaOH at pH 14; the other ones were done with NaOH at pH 10.

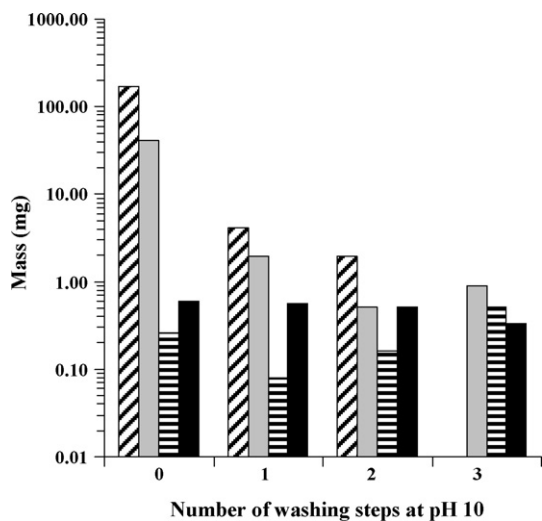


Fig. 5. Evolution of the decrease of contaminants present in the zinc hydroxide precipitate along the washing steps at pH 10. Amounts of chlorides (bar with sloping lines), sodium (grey bar), nickel hydroxide (bar with horizontal lines) and copper hydroxide (black bar), present in the zinc hydroxide precipitate.

sodium hydroxide solution at pH 14. Since at this pH, zinc is totally soluble (Fig. 3B), this washing approach allows eliminating any possible amount of zinc, which remained in the precipitate. Next, the precipitate was washed with a sodium hydroxide solution at pH 10 for eliminating sodium and chlorides from the precipitate. As it can be seen in Table 1, the purity of the precipitate increased significantly (from 8% to 92%) with no appreciable reduction of the recovery yield. In addition, Fig. 4 also evidences that the increase of purity was mainly due to the leaching of sodium and chlorides from the precipitate. The nickel hydroxide obtained in this work, with a purity of 92%, can be sold for industrial purposes (e.g. production of nickel–cadmium and nickel–manganese batteries) [25].

Chemical distribution diagram of zinc (Fig. 3B) evidences, that at pH 10, zinc should be completely precipitated as Zn(OH)₂(s). So, in the next step, the pH of the remained supernatant solution was adjusted at pH 10 and zinc was totally recovered as a precipitate of zinc hydroxide (Table 2). The precipitate was recovered with a purity of 55.3%, being sodium and chlorides the main impurities present in the precipitate (Fig. 5); only vestigial amounts of copper and nickel were present in the precipitate (Fig. 5). The recovered zinc hydroxide can be reintroduced in the chloride electroplating

Table 4
Concentration of metals determined in the washing waters of zinc hydroxide.

Metal concentration (mg l ⁻¹)	Washing waters		
	1st	2nd	3rd
Cu	0.1	0.2	0.1
Ni	0.1	0.2	0.6
Zn	7.8	7.3	10

The washing steps were performed with NaOH at pH 10.

baths, since these baths present a concentration of 120 g l⁻¹ of NaCl [24].

If more pure zinc hydroxide is desirable, additional washing steps are needed. For this purpose, the precipitate was washed with a sodium hydroxide solution at pH 10 using one, two and three washing steps (Table 2 and Fig. 5). After one washing step, the purity of the precipitate increased to 97% (Table 2); this increase of purity was mainly due to the leaching of sodium and chlorides from the precipitate (Fig. 5). When two or three washing steps were implemented, almost all the remained sodium and chlorides present in the precipitate were leached and the purity of the precipitate increased to 99% and 99.4%, respectively, with no appreciable reduction of the recovery yield (Table 2). The introduction of washing steps for purifying nickel and zinc hydroxides generates small volumes of alkaline rinsing waters containing concentrations of

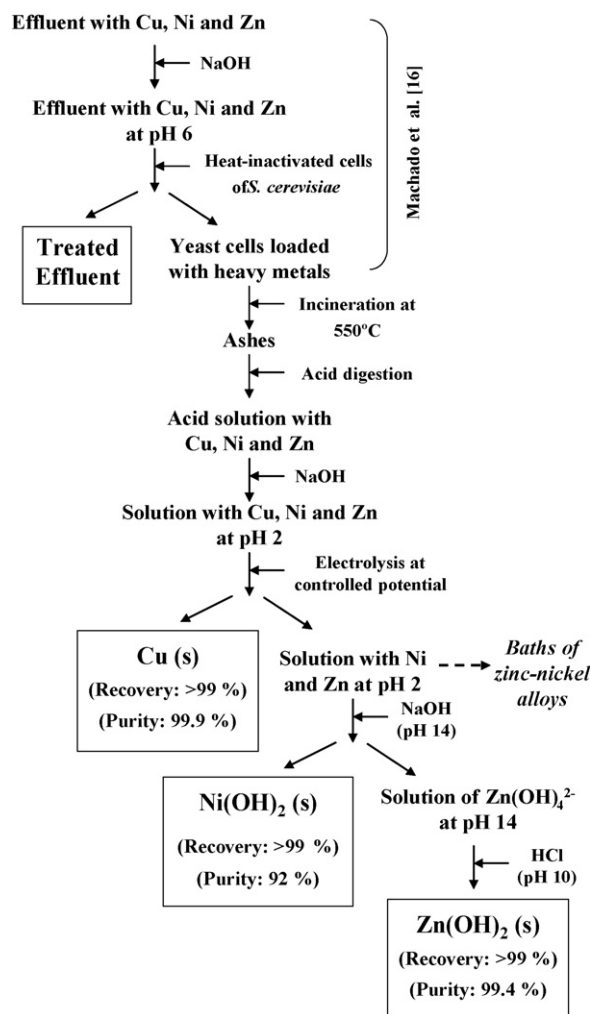


Fig. 6. Diagrammatic representation of the overall procedure proposed in the present work for removing and recovering selectively copper, nickel and zinc from contaminated yeast cells produced in the bioremediation of electroplating effluents.

nickel and zinc above the limits of discharge (Tables 3 and 4, respectively). In order that no residues are generated during the recycling process, we propose the incorporation of these rinsing waters plus the aqueous NaCl at pH 10, which remained after zinc hydroxide recovery, together with the effluents to be treated by biosorption.

4. Conclusions

In a previous work, a real electroplating effluent containing multi-elements was treated using an inter-technological process, which combines chemical precipitation with a biotechnological based process (heat-inactivated flocculent yeast cells of *S. cerevisiae*) [16]. In the present work, a nearly closed cycle for recovering selectively each metal was completed (Fig. 6). For this purpose, contaminated yeast cells, used in the bioremediation of electroplating effluents [16], were incinerated, the ashes were acid digested in a microwave assisted process and the metals present in the concentrated solution were sequential and selectively recovered by electrolysis (metallic copper) and alkaline precipitation (nickel and zinc as metal hydroxides).

The incineration step allowed, after 4 h, a reduction of 98% of the toxic mass. Additionally, metals (copper, nickel and zinc) present in the solution obtained after microwave acid digestion of the ashes were concentrated about 170 times.

This closed cycle constitutes an effluent-free process, which allows selective recovery of copper, nickel and zinc with high yield (>99% for all metals) and purity (99.9%, 92% and 99.4% for copper, nickel and zinc, respectively). The developed process can be easily implemented and constitutes a positive approach to the wastewater treatment since it combines the minimization of environmental liabilities with financial benefits (recovered metals can be re-sailed or re-used).

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