Purification of nickel or cobalt ion containing effluents by electrolysis on reticulated vitreous carbon cathode

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ABSTRACT

The study is aimed at improving a methodology to purify nickel or cobalt ion containing effluents by an electrochemical filter. Consequently, a cell with reticulated vitreous carbon (RVC) cathode for Ni and Co depletion was designed to analyze, at room temperature and pH equal to 6, flowrates and cathodic potentials able to affect the electrochemical process. Starting with Ni and Co initial concentration of 150 ppm, it is possible to reach a concentration lower than 0.1 ppm for both metals in less than 1 h, with a flowrate of about 1300 ml/min and for a catholyte volume of 1000 ml, under mass transport control conditions (for Ni − 1.1 V and for Co − 1.2 V cathodic potential versus Standard Calomel Electrode (SCE)). Moreover, the proposed work studied the process kinetics and fluid dynamics through the use of dimensionless relations such as Reynolds and Sherwood numbers. In addition considerations on current efficiency for reduction of both metal ions were done.

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1. Introduction

Material recovery and the need not to compromise the environment are two factors that today are no longer negligible. This becomes of more relevance if resources are strategic materials and wastes, containing pollutants to the environment, are harmful to humans.

The many sectors using batteries (with Ni and Co content) tend to constantly increase their demand, and strong increase in the production goes along with large amounts of exhausted batteries, which enhances the disposal problems. Indeed, being "hazardous waste", they must be collected separately and treated appropriately before their final discharge in controlled landfills. In this field, technologies for exhausted battery recycling (Lupi et al., 2006; Pasquali and Lupi, 2003; Pistoia et al., 2001; Wang et al., 2005) assume fundamental importance, in order to both recover and reuse metals, as in producing electrochemically alloys for hydrogen evolution reaction in electrolysis processes (Lupi et al., 2009, 2011, 2013), as well as to make inert such wastes, so they can be disposed of in accordance with local regulations. The selective recovery of metals is extremely advantageous not only from the economic aspect, closely linked to the purity degree of recovered metals, but also from the environmental aspect as saving natural resources and impact on the environment and human health. Despite those treatments, the Ni and Co are not completely recovered and the process solid or liquid effluents contain metal concentration that exceeds limits allowed by environmental legislation.

Electrochemical technologies have recently attracted attention, for they allow metal recovery in their most valuable form (zero-oxidation state), without requiring addition of chemicals, and thereby not generating byproducts which would later require treatment or confinement. Moreover, electro-recovered metals and waters treated using these electrochemical methods can be reused in the same process. That avoids
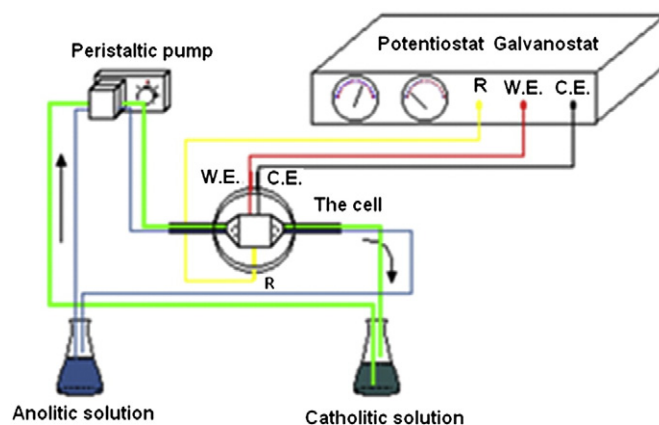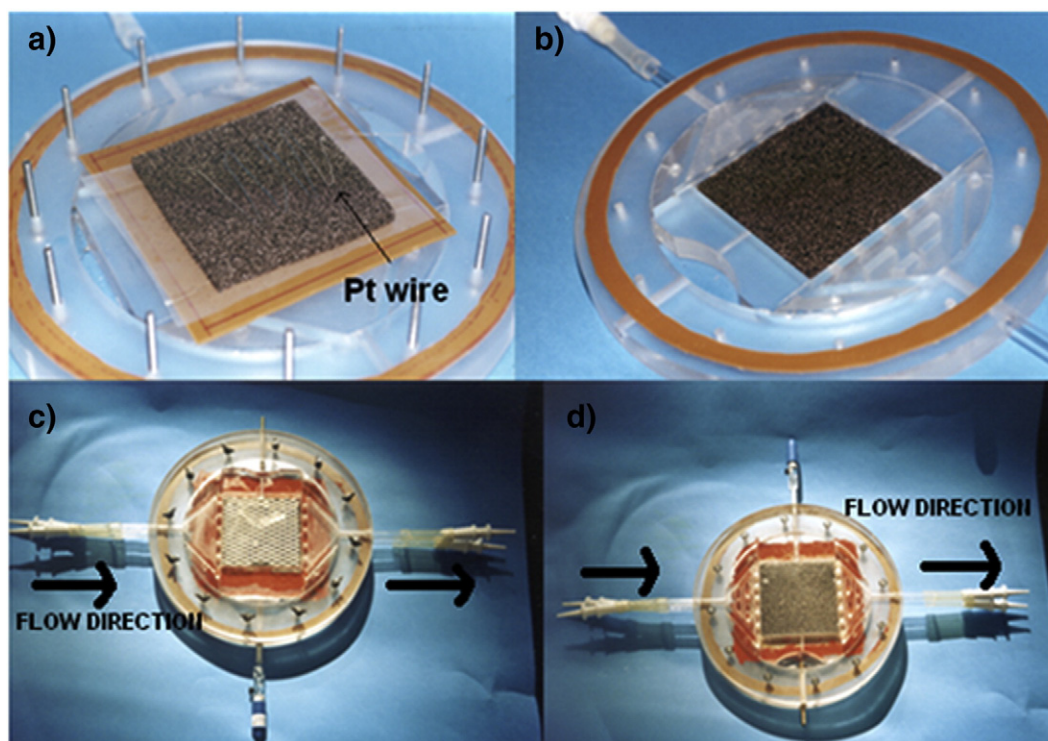

Fig. 1. Experimental apparatus schema.

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Fig. 2. Electrochemical cell: a) anodic plate with the silicon layer, the membrane, the first rectangular piece of RVC cathode and Pt wire, one above the other in sequence; b) cathodic plate with the second rectangular piece, before closing the cell; c) anodic side of the assembled cell; d) cathodic side of the assembled cell.

economic loss during treatment, and reduces both water consumption and environmental impact.

In particular, when the metal ion concentration of the solution is very low, or at the end of electrodeposition process, the mass transport may become the limiting step, and use of electrodes with high specific area may be required. This is one of the reasons for the very large success obtained by three-dimensional electrodes, RVC, in the electrochemical treatment of wastewater (Bertazzoli et al., 1998; Czerwinski et al., 2010; Dell'Era et al., 2008; Dutra et al., 2000; Friedrich et al., 2004; Lanza and Bertazzoli, 2000; Pletcher et al., 1991; Podlaha and Fenton, 1995; Polcaro et al., 1999; Ramalan et al., 2012; Tangirala et al., 2010; Tramontina et al., 2002; Widner et al., 1998).

Moreover, because of the low current of metal reduction, the reactions related to the solvent reduction, can become important and can affect the faradic yield of the process. If the main reactions are kinetically controlled, a higher current efficiency could be obtained by working at lower cathodic potential, but it must be controlled in the range at which metal reduction is under mass transport control for having the maximum value of deposition rate. In this context, the aim of this work is to emphasize how, by using electrochemical method, and in particular with the use of three-dimensional electrodes such as RVC ones, it is however possible, to obtain a satisfactory decrease of Ni and Co metal ions in solution. Specifically in this paper, starting from the results obtained in a previous work (Lupi et al., 2005), in particular by considering the after treated electrolyte, as Ni or Co containing effluents, a comparison between the electrochemical depletion of those divalent ions, by using RVC cathode has been done, highlighting the differences

and all the parameters that can affect the process such as, first and foremost, the working electrode potential and the flow rate. Furthermore a dimensionless analysis for each ionic species has been performed determining different results for the two ions.

2. Experimental

2.1. Apparatus

Flow cell, especially designed, with three electrodes in flow-by configuration was used to perform experimental tests. Peristaltic pumps are used to recirculate the solution between the reservoirs and the two compartment of electrolytic cell. The electrochemical cell, made in Plexiglas, is constituted by cathodic and anodic compartments. Within the cathodic compartment there are two rectangular pieces of RVC between which is inserted a platinum wire to bring out electrical contact from the cell. The two compartments are separated by an anionic membrane 125×125 mm (BDH Laboratory Supplies). A cell outline is shown in Fig. 1, while in Fig. 2 the cell configuration and the flow direction are illustrated. In particular in Fig. 2a) the anodic plate, the silicon layer, the membrane, the first rectangular piece of RVC cathode and Pt wire are shown, one above the other in sequence; in Fig. 2b) the cathodic plate with the second rectangular piece is shown before closing the cell. In Fig. 2c) it is shown the anodic side of the assembled cell, the flow

Table 1
Characteristics of reticulated vitreous carbon model LS190727 JV of Goodfellow.

Porosity	%	97
Density	g/cm^3	0.05
Specific surface	cm^2/cm^3	27
Dimensions	mm^3	$100 \times 100 \times 6.5$
3-d electrode volume	cm^3	127

Table 2
Electrolysis operative conditions for Ni.

Catholyte and anolyte volume [ml]	1000 ml
Catholyte solution	NiSO$_4$° 150 ppm in Na$_2$SO$_4$ 0.1 M
Anolyte solution	Na$_2$SO$_4$ 0.5 M
Working potential (SCE) [V]	$-1.0 - -1.3$ V
range	(mass transport control conditions)
Flowrate [ml/min]	500; 1300
pH	≈ 6