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Research article

Purification of residual leach liquors from hydrometallurgical process of NiMH spent batteries through micellar enhanced ultra filtration

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ABSTRACT

Hydrometallurgical processes for the treatment and recovery of metals from waste electrical and electronic equipment produce wastewaters containing heavy metals. These residual solutions cannot be discharged into the sewer without an appropriate treatment. Specific wastewater treatments integrated with the hydrometallurgical processes ensure a sustainable recycling loops of the electrical wastes to maximize the metals recovery and minimize the amount of wastes and wastewaters produced. In this research activity the efficiency of ultrafiltration combined with surfactant micelles (micellar-enhanced ultrafiltration) was tested to remove metals form leach liquors obtained after leaching of NiMH spent batteries.

In the micellar-enhanced ultrafiltration, a surfactant is added into the aqueous stream containing contaminants or solute above its critical micelle concentration. When the surfactant concentration exceeding this critical value, the surfactant monomers will assemble and aggregate to form micelles having diameter larger than the pore diameter of ultrafiltration membrane. Micelles containing contaminants whose diameter is larger than membrane pore size will be rejected during ultrafiltration process, leaving only water, unsolubilized contaminants and surfactant monomers in permeate stream. The experiments are carried out in a lab-scale plant, where a tubular ceramic ultrafiltration membrane is used with adding a surfactant to concentrate heavy metals in the retentate stream, producing a permeate of purified water that can be reused inside the process, thus minimizing the fresh water consumption.

1. Introduction

The batteries are divided in two main categories: the primary and secondary cells. In the first ones, the internal chemical reactions are irreversible. In other words when all reagents are completely transformed in the final products, the cells are discharge and become unusable. Zinc-carbon, alkaline, silver, lithium are examples of primary cells. The second kinds of batteries are the rechargeable cells, whose charge can be completely reestablished by the application of an appropriate electrical energy. There are several types with different electrical properties, chemical compositions and dimensions. Acid-lead, lithium ions, nickel–cadmium (NiCd), zinc-nickel and nickel-metal-hydride batteries (NiMH) are examples of secondary cells. Every year around 800.000 tons of automotive batteries, 190.000 tons of industrial batteries and 160.000 tons of portable cells (30% of rechargeable) are placed on the European Union market in the European Union (European Commission, 2016a; b).

All batteries contain a series of dangerous metals, acid and basic solutions that cannot be released into the environment at the end of their useful life. For example, the lead batteries are considered highly toxic, for the presence of lead and sulfuric acid. According with EU directives (Directive, 2006/66/EC; Directive, 2008/103/EC) batteries are classified as hazardous waste. These directives encourage the European States to increase collection and recycling wastes. . Eurostat provides a series of data related to 2016 that show Belgium, Norway and Croatia are the most virtuous European countries with a ratio from collected spent batteries and those placed on the market exceeding 70%, followed by Czech Republic, Lithuania, Luxembourg, Hungary and Austria with a collection

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percentage equal or greater than 50%. Estonia and Latvia have a percentage close to 30%.

About Italy, 35.3% of batteries and accumulators has been properly collected in 2016. Eurostat also provides recycling data for spent batteries and accumulators. The data shall be updated to 2016. The percentages of recycling are higher than 90% for Hungary, Finland; followed by Austria, United Kingdom, Portugal, Croatia, Germany, Estonia and Belgium. For the other Countries of the European Union the recycling percentages are less than 70% (European Commission, 2016a; b; 2017).

In the production sector of hybrid cars, three types of batteries are used: lead-acid batteries, NiMH and Li-ion accumulators. The first type is doomed to disappear for the presence of dangerous materials and in part because it reduces the efficiency of the car. NiMH batteries contain (% wt/wt) 36–42% of Ni, 3–4% Co and 8–10% of rare earths (La, Ce, Pr and Nd) (Muller and Friedrich, 2006). The Li-ion batteries have a negative electrode in graphite while the positive one is metallic oxides ($LiCoO_2$, $LiFePO_4$ or $LiMn_2O_4$) and the electrolyte is a lithium salt in an organic solvent. The several materials of the batteries influence the performance, the cost and the environmental impact.

In Italy, more than 14.800 hybrid cars (1.43% respect to the total cars sold in Italy) and 751 electrical ones (0.07% respect to the total cars sold in Italy) were sold in 2014, more than 30% respect to 2013 (Moroni, 2014). The sale of this type of machines is still a market niche compared to the traditional machines, but in these years the scientific community is focusing on the recycling processes of the spent batteries to develop a suitable treatment to reduce their environmental impact and at the same time to recover metals such as nickel, manganese and critical materials such as graphite and rare earths (lanthanum, cerium, praseodymium). The recycling treatments can be classified as hydrometallurgical and pyrometallurgical processes. The first one consists of material dissolution using reagents (acids or base) and recovery of dissolved metals by selective precipitation, solvent extraction, crystallization and others chemical operations. These treatments are more or less complex and it is dependent on the initial material and on the elements to recover. In ppyrometallurgical processes furnaces, that work at high temperatures, are used to recover materials. Several companies treat spent batteries and most of them use conventional pyrometallurgical processing techniques to produce metals to the reuse in the production of metals and alloys. Industrial pyrometallurgical processes are developed by Umicore, Dowa, Salesco Systems, Xstrata, Japan Recycle Center, Accurec, Aerc, DK, Afe Group and Citron for all batteries; Toxco for Li, Ni based batteries, Inmetco for Ni based batteries, Toho Zinc for Ni-Cd and NiMH batteries, Snam for Ni-Cd, NiMH and Li batteries, Nirec for Ni based batteries, Erachem for Mn based batteries.

Industrial hydrometallurgical processes are developed by Ipgna (Recupyl) and Euro Dieuze for all batteries, Ebs for zinc based batteries, TNO for alkaline and NiCd spent batteries. Other processes are developed in America, while Inmetco Recytec was developed in Switzerland, it combines hydro and pyrometallurgical processes (Espinosa et al., 2004; Ellis and Mirza, 2014).

The present paper is focused on the treatment of residual solutions coming from a hydrometallurgical process for the recycling of NiMH spent batteries. These accumulators, after collection, sorting and dismantling, are pretreated mechanically to remove paper, plastic and produce fine powders to send to pyro or hydrometallurgical processes for metal recovery.

Most of existing hydrometallurgical processes include a leaching stage, where the battery content is treated with a sulfuric solution (Zhang et al., 1998, 1999; Pietrelli et al., 2002, 2005; Li et al., 2009a,b; Bertoul et al., 2009, 2012; Nayl, 2010; Innocenzi and Vegliò, 2012a; Gasser and Aly, 2013) or using hydrochloric acid solution (Tzanetakis and Scott, 2004; Kanamori et al., 2009; Fernandes et al., 2013; Rodrigues and Mansur, 2010). These studies have demonstrated that it is possible to obtain dissolution of metals and rare earths. After leaching, rare earths can be selectively recovered by precipitation as double sulfate salts or processed by solvent extraction, precipitation and recovered as rare earth's oxides. Other metals remain in the residual leach liquors and can be separated by solvent extraction to product solutions concentrated of Mn, Zn, Co. and Ni. More details about the processes can be consulted in a recent review (Innocenzi et al., 2017a).

The hydrometallurgical treatments have the disadvantage to produce a large amount of residual solutions that shall be treated before its final disposal. These residual solutions must be treated before being discharged. The cost of the treatments or disposal have a relevant effect on operative costs of the plant that treats industrial or electronic waste (Innocenzi et al., 2017b), and ultrafiltration process could be a valid alternative to traditional treatments which require significant quantities of chemical reagents (as lime to precipitate the impurities). Heavy metal removal from these residual solutions or more generally from industrial wastewaters can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. These processes have significant disadvantages: incomplete removal, high-energy requirements, and production of toxic sludge (Eccles, 1999). Moreover, in the chemical precipitation processes it is not possible to recover the metals. Adsorption has become one of the alternative treatments. The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials (Kurniawan et al., 2005). The advantages of this treatment are low costs, easy operating conditions (wide pH range and high metal-binding capacities), while the disadvantages are low selectively and productions of wastes.

A recent technology is the photocatalytic process that allows to remove metals and pollutant simultaneously. The main disadvantages are its limited applications and the long duration time. Skubal et al., 2002.

Another alternative method to treat industrial wastewaters can be the membrane filtration. There are different types of membrane separation such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) Kurniawan et al., 2006. The main advantages of these processes are: small space requirement, high separation selectively and low pressure. Moreover, membrane separations allow to concentrate the metals in the retentate and after to recover them by further processes as for example selective precipitation or crystallization. Ultrafiltration process can be performed in presence of surfactant (micellar-enhanced ultrafiltration, MEUF). In this treatment a surfactant is added into the aqueous stream containing contaminants: when the surfactant concentration exceeding a critical value (critical micelle concentration), the surfactant monomers will assemble and aggregate to form large micelles having diameter higher than the UF membrane pore diameter. Micelles containing contaminants with a diameter larger than membrane pore size will be rejected during ultrafiltration process, while water, unsolubilized contaminants and surfactant monomers will pass in the permeate stream.

More details about this issue is reported in a review (Barakat, 2011). In the present paper, the ultrafiltration process in presence of surfactant, micellar-enhanced ultrafiltration (MEUF), is investigated in order to remove metals (Zn, Ni, Mn) from residual solutions obtained after hydrometallurgical process for the recovery of metals in NiMH spent batteries recycling. This technique was already efficiently tested for the removal of metals from leach liquors coming from the hydrometallurgical processes for the recovery of metals from cathode ray tubes (Innocenzi et al., 2018).