

# Recovery of metals from an acid leachate of spent hydrodesulphurization catalyst using molecular recognition technology



Isabel S.S. Pinto<sup>a</sup>, S. Maryam Sadeghi<sup>a</sup>, Neil E. Izatt<sup>b</sup>, Helena M.V.M. Soares<sup>a,\*</sup>

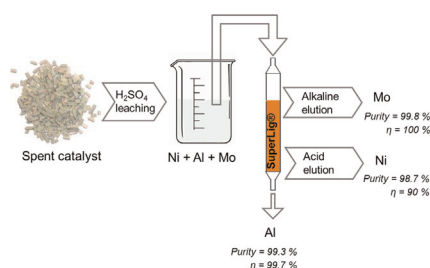
<sup>a</sup> REQUIMTE/LAQV, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Portugal

<sup>b</sup> IBC Advanced Technologies, Inc., American Fork, UT 84003, USA

## HIGHLIGHTS

- Recovery of Ni, Al and Mo from an H<sub>2</sub>SO<sub>4</sub> leaching solution of spent catalyst.
- Use of SuperLig<sup>®</sup> 167 based on molecular recognition technology.
- Ni and Mo retained by the resin and separated from Al efficiently.
- Two-step elution separates Ni from Mo with high purity and yield.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Acid leaching of spent hydrodesulphurization (HDS) catalysts solubilizes efficiently all metals present in the catalyst; however, this methodology poses subsequent difficulties in achieving metals separation with high purity. In the present work, molecular recognition technology, using SuperLig<sup>®</sup> 167 resin, was applied to recover Ni, Mo and Al from H<sub>2</sub>SO<sub>4</sub> leachate of spent HDS catalyst.

Batch tests showed a good resin affinity to Ni, in acid, with a maximum capacity of 1.35 mmol/g. The separation of Al, which was in excess, was efficient, but Mo was also retained by the resin.

Column studies, using 6 g of resin and performed at three flow rates (1.0, 1.5 and 2.1 mL/min), showed that the lower flow rate was better to treat a higher volume of solution. At 1.0 mL/min, each gram of resin treated almost 40 mL of solution with 97% and 100% of Ni and Mo retention, respectively. Elution with NaOH 0.25 mol/L, followed by HNO<sub>3</sub> 4 mol/L, both at 2.1 mL/min, led to efficient separation of Mo and Ni.

The use of SuperLig<sup>®</sup> 167 resin to treat the leaching solution enabled an easy and efficient separation of the metals present in the acid leachate into mono-metal solutions (Al in the raffinate, Mo and Ni in the alkaline and acid eluates, respectively) with high yield (99.7%, 100% and 87%, respectively) and purity (99.3%, 99.8% and 98.7%, respectively).

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## 1. Introduction

Catalysts are widely used in the petroleum refining industry for hydrodesulphurization (HDS) operations; after the end of their life-time, which occurs after continuous activity and regenerations, they become hazardous wastes that cannot be disposed of. About 120,000 tons (dry basis) of spent HDS catalysts are

\* Correspondence to: Departamento de Engenharia Química, Faculdade de Engenharia do Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal.

Tel.: +351 225081650; fax: +351 225081449.

E-mail address: [hsoares@fe.up.pt](mailto:hsoares@fe.up.pt) (H.M.V.M. Soares).

produced every year (Dufresne, 2007). These catalysts have valuable metals, such as Mo, Co and Ni supported in an alumina base, that make the recycling of used catalysts an economically and environmentally attractive option.

Hydrometallurgical processes, based on the extraction of metals through aqueous solutions, have some advantages over traditional pyrometallurgical operations (Ghosh and Ray, 1991; Kim et al., 2009). Dissolution of metals from spent HDS catalysts through hydrometallurgical operations usually consists of an acid or an alkaline leaching or even a combination of both at atmospheric pressure and below 100 °C.

The extraction of metals performed under concentrated acid solutions solubilizes all the metals present in the catalyst (Ildris et al., 2010; Kim et al., 2009; Pinto and Soares, 2013a; Valverde et al., 2008). This procedure requires further separation of the metals to obtain pure products suitable for being used in other industries. The separation and recovery of metals from the spent HDS catalyst leachate is frequently based on a combination of solvent extraction and precipitation methods. In the case of the recovery of Ni from an Al solution, several examples can be found in the literature (Kim and Cho, 1997; Park et al., 2012, 2007; Rao et al., 2012; Zhang et al., 1995). Extraction using Cyanex 272 proved to be more effective than precipitation at pH 12.5, as the second led to a solid of Ni with significant amount of Al (Orive et al., 1992). In the case of precipitation of Al at pH around 5, some Ni was lost to the solid due to its co-precipitation; so, this method is only suitable if Ni is in great excess (Lee et al., 2010). The synergy between solvent extraction and precipitation allows great recoveries of the metal salts with high purity; however, several stages and reagents are involved, including organic extractant, solvent and strong acid stripping solution. The application of adsorption with activated carbon to separate Mo from Ni and Al from the leaching solutions of spent HDS catalysts is possible and efficient under very acidic conditions; however, both Al and Ni remain in solution (Mohapatra and Park, 2007; Pagnanelli et al., 2011; Park et al., 2006). A chelating resin was studied to retain Ni in the presence of a large quantity of Al from a solution obtained after H<sub>2</sub>SO<sub>4</sub> leaching of HDS catalyst (Nagib et al., 1999).

Molecular recognition technology (MRT) has been gaining a lot of attention during the last decades. This technology started with the synthesis of crown ethers in the late of 1960s; this research evidenced promising results on the selective complexation of cations and culminated with the award of the Nobel Prize in chemistry in 1987 to Pedersen, Lehn and Cram, three of the main contributing scientists (Glennon, 2000; Izatt, 1997). Pedersen synthesized a large number of cyclic polyethers and observed that some of them had remarkable selectivity for specific alkali metal ions (Pedersen, 1967). This work eventually led to the development of SuperLig<sup>®</sup> resin systems in which a metal-selective ligand is attached by a chemical linker arm to a solid support particle, such as silica gel. An example of such a SuperLig<sup>®</sup> system is given in Fig. 1. The concept of this technology is basically “host-guest” chemistry: the design of macrocycle molecules with determined

cavity sizes and shapes that can suit the selected cation diameter and thus influence complexing properties (Bradshaw et al., 2000; Glennon, 2000; Izatt et al., 2000). The binding of such ligands to silica or polymeric supports for solid phase extraction (SPE) has the main advantages of forming a permanent bond; thus, the system can be used multiple times without loss of the macrocycle and allows the concentration of ions by eluting them with small solution volumes (Izatt, 1997). In addition, the product can be packed in fixed-bed columns for continuous operation at full-scale. Comparison with other traditional separation processes, like precipitation, ion-exchange and solvent extractions, SPE-MRT can overcome problems like low selectivity in the recovery and low purity of the products, organic contamination of streams, large space requirements, slow kinetics and treatment of low concentrated streams (Izatt et al., 2015, 2011). The high selectivity of MRT compared to other methods can be explained by the multiple parameters that affect the binding (ion radius, coordination chemistry, geometry, charge). Thanks to this specificity, several MRT products are commercially available that are adequate for different cations depending on the purpose of the process.

MRT can be useful for analytical purposes to concentrate solutions and eliminate interferences (Devol et al., 2009; O'Hara et al., 2009). Quite a few studies can be found in the literature and there are already implemented full-scale processes that use SPE-MRT to separate, recover or refine metal ions from different streams. Recovery of precious and toxic metals from electronic wastes, refining of platinum, rhodium and gold, uranium removal from mining solutions, cesium and technetium removal from wastewaters, removal of nickel, lead, bismuth or cobalt in the presence of other metal cations are examples of applications (with interest or already implemented) that use SPE-MRT (Adu-Wusu et al., 2006; Belanger et al., 2008; Hassan et al., 2002; Izatt et al., 2012, 2011; King et al., 2005; Navarro et al., 2012).

Since MRT has been showing encouraging results in the separation of metals from aqueous streams, the possibility of using such technology in the treatment of spent catalysts containing Ni, Mo and Al was assessed for the first time. In the present work, the separation and recovery of metals, obtained after H<sub>2</sub>SO<sub>4</sub> leaching of a spent HDS catalyst, was studied using MRT product SuperLig<sup>®</sup> 167 from IBC Advanced Technologies.

## 2. Experimental

### 2.1. Reagents and materials

Synthetic solutions of Ni, Al and Mo were prepared from Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·16H<sub>2</sub>O and Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, respectively. The initial pH was controlled through the addition of concentrated H<sub>2</sub>SO<sub>4</sub>. Aqueous solutions prepared from analytical grade HNO<sub>3</sub> (65%) and NaOH were used in the elution studies.

The real solution was obtained after the second leaching stage of a HDS spent Ni–Mo catalyst. Briefly, the catalyst was roasted in air, at 500 °C, and leached with NaOH 0.25 mol/L (Pinto and Soares, 2012); the remaining solid was then separated, dried and treated with H<sub>2</sub>SO<sub>4</sub> 0.8 mol/L in a thermostatic bath, at 80 °C, for 4 h (Pinto and Soares, 2013a). The solution, previously separated by filtration, had a final pH of 1.2 and contained  $2.3 \times 10^{-2}$  mol/L of Ni,  $4.2 \times 10^{-1}$  mol/L of Al and  $4.0 \times 10^{-3}$  mol/L of Mo.

The MRT product chosen was SuperLig<sup>®</sup> 167 from IBC Advanced Technologies, Inc. (American Fork, Utah, United States). The product is in the form of dark brown beads, 0.5 mm, made of polyacrylate, to which the ligand has been chemically attached. Chemical composition of the product is a trade secret, but a generic example of the ligand molecules is shown in Fig. 1.

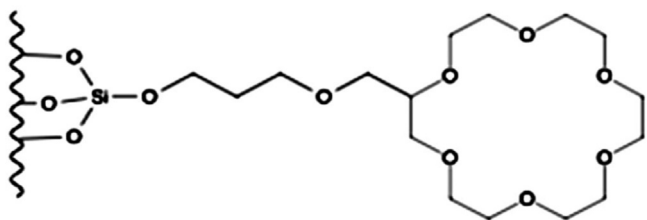


Fig. 1. Representative SuperLig<sup>®</sup> system consisting of a solid support particle, silica gel, to which a metal-selective ligand, 18-crown-6, is attached by a tether, which is chemically bound to both the ligand and the silica gel.

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