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Research article

Oil refinery hazardous effluents minimization by membrane filtration: An on-site pilot plant study

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ABSTRACT

Experiments for treating two different types of hazardous oil refinery effluents were performed in order to avoid/minimize their adverse impacts on the environment. First, refinery wastewater was subjected to ultrafiltration using a ceramic membrane, treatment, which did not provide an adequate reduction of the polar oil and grease content below the maximal contaminant level allowed. Therefore the option of reducing the polar oil and grease contamination at its main emission source point in the refinery – the spent caustic originating from the refinery kerosene caustic washing unit – using an alkaline-resistant nanofiltration polymeric membrane treatment was tested. It was found that at a constant operating pressure and temperature, 99.9% of the oil and grease and 97.7% of the COD content were rejected at this emission point. Moreover, no noticeable membrane fouling or permeate flux decrease were registered until a spent caustic volume concentration factor of 3.

These results allow for a reuse of the purified permeate in the refinery operations, instead of a fresh caustic solution, which besides the improved safety and environmentally related benefits, can result in significant savings of 1.5 M€ per year at the current prices for the biggest Portuguese oil refinery. The capital investment needed for nanofiltration treatment of the spent caustic is estimated to be less than 10% of that associated with the conventional wet air oxidation treatment of the spent caustic that is greater than 9 M€. The payback period was estimated to be 1.1 years. The operating costs for the two treatment options are similar, but the reuse of the nanofiltration spent caustic concentrate for refinery pH control applications can further reduce the operating expenditures.

Overall, the pilot plant results obtained and the process economics evaluation data indicate a safer, environmentally friendly and highly competitive solution offered by the proposed nanofiltration treatment, thus representing a promising alternative to the use of conventional spent caustic treatment units.

1. Introduction

Aqueous effluents generated in a crude oil refinery, contain a diverse range of pollutants such as oil, phenols, sulfides, dissolved solids, suspended solids, toxic metals and BOD-bearing materials (Beychock, 1967). Among the different wastewater contaminants, oil is the most critical one since it is less biodegradable than other organic substances (Galil et al., 1988) and, if discharged to water bodies, may form undesirable surface films and shoreline deposits leading to severe environmental pollution (Clescer et al., 1999).

The parameter "oil and grease" refers to both non-polar material, which is insoluble in water and can be removed by oil/water separation, and polar compounds, such as aromatic, unsaturated, phenolic and heterocyclic compounds (U.S. EPA, 1999) that exhibit solubility in water, and therefore have a significant influence on water toxicity (Stanford et al., 2007; Lee et al., 1974; Lundegard and Knott, 2001).

In prior research, it was identified that the main contributor to the polar oil and grease contamination of the wastewater in the biggest Portuguese oil refinery, located in the town of Sines, is the spent caustic effluent originating from the kerosene caustic washing unit (Santos et al., 2013). On the other hand, the spent caustics poses very serious environmental management related issues for its use in the refinery operations in terms of its handling, treatment and disposal, because of its highly toxic nature, as indicated in Table 1.

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Table 1
Average composition of spent caustic effluents (Veerabhadraiah et al., 2011; Medel et al., 2015).

Parameter	Units	Range
Sodium hydroxide	wt%	1–15
Inorganic sulfides, as S	wt%	0–4
Mercaptide, as S	wt%	0–4
Cresylic acids	wt%	0–25
Naphthenic acids	wt%	2–15
Phenols	mg/l	0–2000
Total organic carbon (TOC)	mg/l	6000–20000
Chemical oxygen demand (COD)	mg/l	20000–60000
Biochemical oxygen demand (BOD)	mg/l	5000–15000
pH	Sorensen scale	12–14

The high concentrations of various pollutants, make this stream toxic to bacteria used in the wastewater treatment units, which can cause discharges of wastewater with pollutants levels above the limits defined by environmental legislations (Achaw and Danso-Boateng, 2013). Therefore, in order to mitigate the negative impacts of spent caustics, it is highly desirable to treat the respective streams at their source of origin in order to allow their reuse/recycle within the refineries (a preferred option) or at least to permit their safer disposal/abatement.

A certain reduction of the spent caustic volumes obtained can be accomplished by optimizing the procedure of caustic washing (minimizing the amount of fresh caustic used). However, there will be always a caustic-containing stream resulting from the washing process.

Reuse of spent caustics, within refineries, could be employed for pH regulation purposes in crude desalting units and/or in wastewater treatment units Nevertheless, any direct reuse of spent caustics in these operations is limited in its quantities and should be done in a strictly controlled manner in order to avoid possible adverse impacts (Ahmad, 2010).

Recycling of spent caustics has been so far reported in pulp and paper, tannery, mining and wood preservatives industries, for replacing some of the fresh caustic used in these industries. However, in what concerns refineries, such a recycling has either not been yet studied/performed or additional treatment, such as wet air oxidation, has been suggested for spent caustics conditioning inside the refinery (Veerabhadraiah et al., 2011). The possible spent caustic treatment options reported so far are summarized in Table 2. The most frequently applied treatment to handle with the problem of spent caustic is its oxidation at high temperatures in a reactor with air bubbling (Maugans et al., 2010; Al Jabari, 2012; Zhao et al., 2014). However, the capital investment costs for this treatment method can reach more than 9 million euros while the annual operation costs round about 1 million euros, mainly due to the high energy consumption needed for the hot air compressor (Al Jabari, 2012; Maloney, 2001).

So far, the use of ceramic membrane filtration has been applied in oil refineries for concentration and clarification of oily wastewater, as an alternative to its conventional treatment methods (Zhong et al., 2003). The relatively high degrees of oil and COD removal, elimination of chemical additives, comparatively lower energy costs and lower installation space requirements are the main drivers for membrane processes preference (Fakhru'l-Razi et al., 2009).

Target effluents reuse examples have been reported for the food and beverages industries. Dilute caustic solutions used for cleaning the process equipment, have been recovered with membranes with a primary objective of reducing the chemical disposal and reusing the caustic in the process (Mawson, 1997; Novalic et al., 1998; Räsänen et al., 2002; Gésan-Guiziou et al., 2007). Several commercial alkali-resistant nanofiltration membranes are available, amongst which SelRO® MPS-34 membrane manufactured by Koch Membrane Systems has demonstrated the highest alkali resistance and robust performance (Schlesinger et al., 2006). However, and despite the generation of much bigger amounts of highly contaminated spent caustics in oil refineries, to the best of our knowledge, there are still no reported studies dedicated to membrane treatment of refinery spent caustic.

Therefore, the main goal of this work, after identifying the inadequacy of purifying refinery wastewater streams by ultrafiltration, was to investigate the feasibility of solving the water contamination problem at its source of creation through dedicated spent caustic treatment by alkali-resistant nanofiltration. Process economics analysis was also performed and compared to that of wet air oxidation of spent caustic, which is the most common currently applied treatment option.

2. Materials and methods

2.1. Membranes and operation modes

The performance of two types of membrane-assisted treatment was studied with the objective of reducing the adverse impacts caused by spent caustic contamination of refinery wastewater.

A tubular ceramic UF membrane (Carbosep M2) with an inner diameter of 6 mm and a filtration area of 0.013 m^2 manufactured by Tech-Sep with a molecular weight cut-off 15 kDa (Rhône-Poulenc Group, Miribel, France), was used. This membrane is composed of a thin perm-selective skin layer of zirconium oxide and titanium dioxide spread on the interior (lumen) surface of a tubular porous carbon support.

The membrane performance was tested with refinery wastewater samples in cross-flow operation mode with permeate being collected and the concentrate recycled. The membrane performance was studied at different transmembrane pressures ranging

Table 2
Evaluation of available spent caustic treatment options (Veerabhadraiah et al., 2011; Medel et al., 2015).

Treatment method	Advantages	Limitations
Chemical oxidation	Low CAPEX	High OPEX
Fenton oxidation	Low CAPEX	High OPEX
Chemical precipitation	Can be applied in existing flotation units	High OPEX
	Low CAPEX	Large chemical sludge production
Electrochemical oxidation	Improvement of chemical oxidation efficiencies	High OPEX
Neutralization	Recovers valuable phenol/organic acid (when there is market)	High CAPEX and OPEX
Wet oxidation	Complete oxidation of sulfides and organics	High CAPEX and OPEX
Incineration (thermal oxidation)	Complete oxidation of sulfides and organics	High OPEX
	May allow for direct disposal	

CAPEX: CApital EXPense (i.e.: installation initial investment cost).
OPEX: OPerating EXPense (e.g.: energy; chemicals; …).