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Research article

Evaluation of adsorbent and ion exchange resins for removal of organic matter from petroleum refinery wastewaters aiming to increase water reuse

Rodrigo de Abreu Domingos [a], Fabiana Valéria da Fonseca [b,*]

[a] PETROBRAS, School of Chemistry, Federal University of Rio de Janeiro, Av. Henrique Valadares, 28, Centro, Rio de Janeiro, RJ, 20231-030, Brazil
[b] School of Chemistry, UFRJ, Federal University of Rio de Janeiro, Av. Athos da Silveira Ramos 149, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ, 21941-909, Brazil

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A B S T R A C T

The oil refinery industry seeks solutions to reduce its water uptake and consumption by encouraging the reuse of internal streams and wastewater from treatment systems. After conventional treatment the petroleum refinery wastewater still contains a considerable quantity of recalcitrant organics and the adsorption on activated carbon is currently used in Brazilian refineries, although it is still expensive due to the difficulty of its regeneration. This study evaluated the use of adsorbent and ion exchange resins for the removal of organic matter from refinery wastewater after conventional treatment in order to verify its feasibility, applying successive resin regenerations and comparing the results with those obtained for activated carbon process. Adsorption isotherms experiments were used to evaluate commercial resins, and the most efficient was subjected to column experiments, where absorbance (ABS) and total organic carbon (TOC) removal were measured. The adsorption isotherm of the best resin showed an adsorptive capacity that was 55% lower than that of activated carbon. On the other hand, the column experiments indicated good removal efficiency, and the amount of TOC in the treated wastewater was as good as has been reported in the literature for activated carbon. The regeneration efficiency of the retained organics ranged from 57 to 94%, while regenerant consumption ranged from 12 to 79% above the amount recommended by the resin supplier for the removal of organic material from natural sources, showing the great resistance of these recalcitrant compounds to desorption. Finally, an estimate of the service life of the resin using intermediate regeneration conditions found it to be seven times higher than that of activated carbon when the latter is not regenerated.

1. Introduction

Water availability per capita in Brazil is higher than in many other countries in the world. However, this water is unevenly distributed throughout the territory, with about 80% of the water resources being in the Amazon basin, far from most industrial and more densely populated regions. These regions face critical water availability levels according to UN classification indexes (ANA, 2013). The recent water crisis faced by some Brazilian states worsens the situation and directly affects the industrial sector. The industries face increasing costs when purchasing water and spend more resources to treat it. Due to these factors, process optimization procedures and reuse actions are being increasingly applied in order to improve process efficiencies and water recovery.

The oil industry is included in this context since it is a major water consumer and, in many cases, is situated in water-scarce regions both in Brazil and worldwide. According to PETROBRAS (2015), a Brazilian petroleum refinery consumes an average of 0.9 m^3 water per m^3 of processed oil, with water-based cooling systems and steam generation being the largest consumers (Amorim, 2005; Pombo, 2011). As a result, a large amount of wastewater is also generated, which must be treated before disposal since tit contains high levels of pollutants such as oil, ammonia, phenols, sulfides, heavy metals, and organic compounds (Nacheva, 2011).

Wastewater treatment in refineries primarily consists of two steps: removal of contaminants (oil and suspended solids) by

* Corresponding author.
E-mail addresses: rodrigo.domingos@petrobras.com.br (R. de Abreu Domingos), fabiana@eq.ufrj.br (F.V. da Fonseca).

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physical and physical-chemical processes, followed by a biological step to remove organics and nitrogen compounds. As presented by IPIECA (2010) and Tchobanoglous et al. (2003), a third stage, usually called tertiary treatment, may be required to make the effluent suitable for disposal or reuse as cooling tower makeup water, process water or boiler feed water.

Tertiary treatment processes vary depending on the contaminants to be removed. In refineries, clarification, filtration, or membrane separation are commonly applied to remove suspended solids, which is then followed by one or more dissolved salt removal processes, such as electrodialysis reversal (EDR), reverse osmosis (RO), or ion exchange (IEX) resins. However, most dissolved salt removal processes require the reduction or elimination of residual organic compounds present in the wastewater, since these may foul membranes and IEX resins irreversibly. These recalcitrant compounds are difficult to remove using conventional wastewater treatment because they are poorly biodegradable, as indicated by Touma (2013a).

The most widely used process for removing these compounds in industry is adsorption on granular activated carbon (GAC) (Tchobanoglous et al., 2003; Yang, 2013), which is usually employed after a biological treatment step as the cost of GAC consumption without prior treatment would make the process economically unfeasible. Although GAC adsorption has been used for many years for water and wastewater treatment, it has some disadvantages when used in refineries. Due to the high levels of organic matter (OM) present after biological treatment, the GAC is quickly saturated and should be replaced with new inventory, or regenerated/reactivated. Thermal reactivation of GAC is not usually applied since it is not performed *in situ*, requiring GAC to be transported to reactivation sites that are not always close to the refineries. In addition, it requires a frequent labor force for handling, high capital expenditure, and has high GAC losses of 5–10% according to Sufnarski (1999). GAC regeneration also follows this trend and thus is not applied commonly either.

As an alternative to using GAC in refineries, polymeric IEX and adsorbent resins are based on adsorption and IEX mechanisms. They are more easily regenerated than GAC (Yang, 2013), as they can be regenerated *in situ* by pH adjustment, solvents, or water vapor, and they also result in lower losses than seen for GAC (Xu et al., 2003). This makes them good options for the capture of OM from oil refinery wastewaters even though their initial costs are higher than GAC, as noted by Yang (2013). The use of resins to capture some organic compounds, such as fulvic acids and tannins, is currently applied using upstream demineralization systems, usually to protect RO membranes and IEX resins.

The main objective of this work is to verify the applicability and feasibility of a residual OM removal process using adsorbent and IEX resins at the laboratory scale, in order to find an alternative to the use of GAC for tertiary water treatment in oil refineries aiming to reduce water consumption by reusing water. Initially, the adsorption capacities of resins were measured using isotherms and the best performing material was chosen for column tests. Column experiments were then performed to verify the performance of the resin when removing organics from wastewater and its ability to be regenerated by removing the OMs using regenerant chemicals. After the experiments, the service life of the resin when performing intermediate regenerations was estimated and compared with that of GAC under similar conditions as obtained from literature data (Touma, 2013a), with the latter not being regenerated.

2. Materials and methods

2.1. Effluent source

Effluents from the wastewater treatment plants of Brazilian refineries were used in this study. The samples were all collected after membrane bioreactors (MBR) in 20 L bottles after passing through ultrafiltration membranes, making them almost free of undissolved OM and microorganisms, which also ensured improved preservation of their original characteristics.

The effluents were sampled from two different refineries where MBR are installed, herein called A and B. Refinery A is an industrial-scale plant and provided the first samples for the initial isotherms. Refinery B, which contained a pilot-scale MBR, provided the rest of the samples for the adsorption/IEX isotherms and column experiments. The OM content varied between samples due to the use of different petroleum sources in the refinery feed and operational variations in the wastewater treatment steps. Because of the large effluent volume required, samples with the same characteristics could not be used in all the experiments. The initial TOC value for the refineries A and B was $14{,}2 \pm 1{,}1$ and $18{,}8 \pm 0{,}7$ mg/L, respectively.

2.2. Adsorbent and IEX resins

The macroporous adsorbent and IEX resins used in this study are listed in Table 1, along with their main characteristics as listed by their manufactures: matrices, functional groups, operational flow required (in bed volumes per hour), and possible regenerant chemicals. The resins were conditioned according to the manufacturer's recommendations by soaking them in water for half an hour in a mixer and then removing the air inside their pores with a vacuum pump before each experiment. The commercial names of the resins are not included in order to maintain manufacturer's confidentiality.

Since resin R8 was used throughout all experiments, its true and apparent densities were also obtained according to DOW (2014) and ASTM D2187-94 (2004), respectively. The true density was 1042 $kg\,m^{-3}$, whereas the apparent density was 621 $kg\,m^{-3}$. The calculated porosity based on these values was 0.40. The average particle diameter of these resins was 0.75 mm.

2.3. Granular activated carbon

NORIT 1240 W GAC was used in this study. GAC samples were prepared by grinding and sieving the commercial samples (Mesh 12×40). After this, GAC was washed several times to remove fine particles, dried at 100 °C in an incubator and had the air inside the pores removed using a vacuum pump.

2.4. Analytical methods

The source water and all samples were analyzed for total organic carbon (TOC) and UV254 absorbance. The concentration of TOC was utilized as the primary marker for performance. TOC testing was performed according to APHA (2005) 5310C method using a HiPerTOC TOC Analyzer. The UV absorbance was monitored following the APHA (2005) 5910 method using an UVmini 1240 Shimadzu UV–visible spectrophotometer.

2.5. Equilibrium isotherm experiments

Equilibrium isotherm experiments were conducted to investigate the capacities of the resins to remove the residual OM from refinery wastewater through adsorption and IEX mechanisms, allowing the most efficient resins to be identified and tested in columns. Data collected in these tests were also compared to GAC isotherm performances. The Langmuir and Freundlich models were also verified.

Sixteen experiments were conducted, as each resin had two isotherms, one for each refinery wastewater. They were performed