Separation and Purification Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Parameters of an electrokinetic reactor design for vanadium recovery from fluid catalytic cracking catalysts

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ARTICLE INFO

Keywords:
Catalyst
Fluid catalytic cracking
Vanadium
Electrokinetic remediation

ABSTRACT

The goal of this study was to evaluate the performance of electrokinetic remediation for vanadium removal from deactivated catalysts. In this study a fixed-bed reactor was used to lengthening the catalyst life cycle. Parameters such as the sulfuric acid electrolyte concentration and the applied electric potential were evaluated to determine a response function for the vanadium removal percentage. Because there are no mathematical models that fit the system and due to the complexity of such a system, the use of a 2^k factorial design statistical techniques with a center point, was chosen to obtain the desired responses. A 0.5 mol·L^{-1} sulfuric acid concentration and an electric potential of 5 V were found to provide the best operating conditions. In this study, 22.99% of catalyst vanadium content was removed within 48 h and 81.62 kWh/kg energy consumption.

1. Introduction

Petroleum refining processes have been developed with the goal of converting heavy petroleum fractions into lighter fractions with greater added value. Concerns regarding production cost optimization have encouraged petroleum refining industries to design fluid catalytic cracking (FCC) units using catalysts that increase the yield of the desired fractions of products [1–3]. Catalysts are acidic solids that accelerate the conversion of the cracking reaction, the acidity characterizes a heterogeneous catalyst with high selectivity and possibility of regeneration [4] FCC catalysts are composed of an inert matrix (usually kaolin), an active matrix (alumina), a binder (silica or silica-alumina) and a zeolite Y [5]. Among the main characteristics of the catalyst are: high selectivity; stability in operating conditions; mechanical strength and activity [6].

The use of crude oil in the process has several consequences, such as catalyst poisoning, which is caused by metals present in the petroleum [1,2]. Metals such as nickel, iron and vanadium are found in small amounts in petroleum and are removed during the separation process. However, residues of arsenic, vanadium and nickel can poison and clog the porous structure of catalysts. Vanadium concentrations in crude oil tend to range from 10 ppm (Middle East) to 1400 ppm (Central America) [7].

These contaminant metals oxides deposit at the catalyst surface, reducing its activity along the riser caused by coke formation on catalyst surface, blocking its active sites [7]. Catalyst deactivation may be caused by a decrease in the number and quality of active sites and by increasingly poor access to the pore space [8–12]. Interactions between vanadium and nickel adhered to the zeolite structure are complex, and have also been discussed in the literature. Studies with these two artificially impregnated elements resulted in smaller surface areas when compared to the effect of nickel and vanadium alone [13–16]. Specifically, vanadium acts on the FCC catalyst by neutralizing its acidic sites or by destroying its zeolitic components. Both mechanisms are responsible for negative effects on catalyst performance [14].

The amount of catalyst required to maintain the activity of FCC units worldwide corresponds to approximately 1400 tons per day, making the FCC process the most important market for catalyst production [15]. Production of synthetic zeolites occurs on a large scale, with production currently estimated at more than 1.39 million tonnes per year [17], with a third of this production being devoted to the catalytic cracking of petroleum. Thus, the use of deactivated catalysts to

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http://dx.doi.org/10.1016/j.seppur.2017.10.057
Received 26 December 2016; Received in revised form 4 October 2017; Accepted 27 October 2017

Please cite this article as: Broska da Cruz Deniz, A., Separation and Purification Technology (2017), http://dx.doi.org/10.1016/j.seppur.2017.10.057

form other products of commercial value is attractive from environmental and economic perspectives [16,18].

According the Brazilian National Environment Council (Conselho Nacional do Meio Ambiente – CONAMA) resolution N.313 of October 29, 2002, a deactivated catalyst is Class I (hazardous residues). Currently, cumulative amounts of deactivated catalyst are disposed of in chemical landfills, thus producing an environmental hazard, or are supplied to the cement industry [19]. Therefore, studies of new technologies that increase the length of a catalyst's life cycle are justified to prevent catalysts from becoming contaminants to the environment and humans.

This study presents an electrokinetic remediation technique as an alternative to catalyst treatment. This technique is based on applying a direct current of low intensity or a low electrical potential difference through electrodes and was used originally by Yeung and Accar [20,21] to treat soils contaminated with metals. This technique can also be applied in sediments because electrokinetic techniques may be applied in any permeable medium that is ionically conductive [21,22]. New and promising contributions using electrokinetic remediation have been studied, an example is the study of the use of innovative surfactants for the removal of organic and inorganic contaminants from polluted sediments, which presented good results, showing the efficiency of the technology and motivation for further studies [23,24]

In this study electrokinetic remediation is advantageous because it consumes little energy and preserves the catalyst structure for future use [21/25,22/26].

2. Materials and methods

2.1. Materials

A reactor with electrodes coupled to anode and cathode chambers was used in this study. The anode was a circular Ti/Ru-Ir plate, and the cathode was a circular lead plate. The electrokinetic reactor has as main characteristic the easy exchange of the anode and the cathode, in order to guarantee the execution of the proposed experimental part. The electrolyte is introduced into the reactor through the anodic chamber, runs through the entire bed of the reactor composed of the catalyst and is extracted by the cathodic chamber. The catalyst was fed in an acrylic tube 9 cm in diameter and 22 cm in length between electrodes, as shown in Fig. 1 [27,28].

The material investigated in this study was a fluid catalytic cracking (FCC) waste with low catalytic activity remaining, which is known as an equilibrium catalyst (E-cat). This catalyst was primarily composed of aluminum and silicon oxides and was saturated with vanadium (4277 ppm). The porosity of the fixed bed was calculated by the Eq. (1) which resulted approximately 0.23.

$$\varepsilon = \frac{V_T - V_A}{V_P} \tag{1}$$

where ε is the porosity of the fixed bed; V_T is the total volume of water placed in the measuring cylinder; V_A is the volume of water absorbed by the catalyst and V_P is the volume filled by water plus the catalyst. Granulometry tests were performed on the CILAS 1064 Granulometer and obtained an average diameter of particles of 65, 66 µm.

Approximately 600 g of E-cat were remediated in each experiment. A sulfuric acid solution was used as the electrolyte at concentrations of 0.5, 0.75 and 1.0 mol·L^{-1}. It was concluded that the use of sulfuric acid as electrolyte presented the best experimental condition by removing a larger amount of metal [24/28]. Remediation with sulfuric acid, in addition to removing a good percentage of vanadium, also results in an increase in the surface area of the catalyst [25/29]. A peristaltic pump at a flow rate of 60 mL·h^{-1} fed the electrolyte. The constant applied electric potentials were 5 V, 8 V and 11 V.

The remediation experiment time was 48 h, and samples collected at points 1 and 3 and, also, at the cathode chamber for pH measurement. After several studies varying the time of remediation, the time of 48 h was defined because it is where the apex of vanadium removal occurs. For longer periods, the vanadium removal percentage showed a small increase until it stabilized after several hours of remediation, therefore it is not advantageous to increase the remediation time due to energy and time expense [21/25,25/29]. Then, the E-cat was washed for 24 h with distilled water and dried in an oven at 50 °C for 48 h. The E-cat and the recovered E-cat were then characterized by X-ray fluorescence spectroscopy to determine their vanadium concentration.

2.2. Methods

2.2.1. Experimental design

The experimental design included three steps: statistical design of the experiments, calculation of coefficients using a mathematical model with response estimates and model applicability analysis.

Because there are no mathematical models fitting this complex system, statistical techniques were used to obtain responses as empirical functions of the chosen variables. The 2^k factorial design technique with a center point was chosen, which indicates the curvature of the response function when fitting a second-order model [26/30].

Two variables were chosen in this study to evaluate the effect of vanadium removal: the electrolyte concentration and the applied electric potential. The variables were coded based on the factorial design technique, and the values corresponding to levels −1, 0 and 1 are

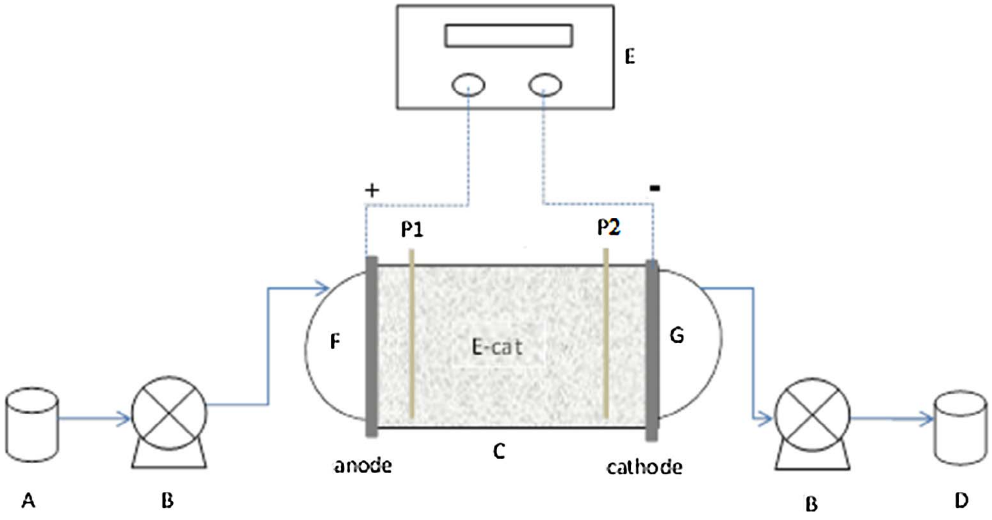

Fig. 1. Electrokinetic reactor used for electrokinetic remediation: (A) compartment with new electrolyte, (B) peristaltic pump, (C) electrokinetic reactor, (D) compartment of contaminated electrolyte, (E) power supply, (F) anodic chamber and (G) cathodic chamber, (P1) and (P2) collection points of the electrolyte [28].