



Impedance spectra of anodic dissolution of iron in distillery vinasse



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ARTICLE INFO

Article history:

Received 13 December 2013
Received in revised form 14 July 2014
Accepted 15 July 2014
Available online 21 July 2014

Keywords:

Anodic dissolution
electrodissolution
distillery spent wash
vinasses
electrocoagulation
electrochemical impedance spectroscopy.

ABSTRACT

Electrocoagulation technique has a great application potential to treat distillery vinasse, a liquid effluent generated from alcohol distilleries. The anodic dissolution of carbon steel in this effluent in the potential range of -750 mV to -100 mV was investigated by potentiodynamic polarization; likewise, the electrochemical impedance spectroscopy spectra were registered over anodic potentials of -560 mV, -500 mV and -400 mV (overpotentials of 20 mV, 80 mV and 180 mV) corresponding to the active dissolution region in order to propose a mechanism for describing the behavior of the carbon steel electrodisolution. Were explored the effects of the flow regime (Reynolds number of 5,500 and 11,500) and the temperature (60°C and 80°C) over the behavior of the spectra. At low current densities the impedance behavior can be satisfactorily described by the combination of the catalytic and non-catalytic mechanism of iron dissolution. It was also found that the dissolution must be carry out at current densities closely to 1 mA cm^{-2} to prevent the possible formation of iron oxide layers on the anode. The anodic dissolution was favored by increasing the flow regime and temperature as well.

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1. Introduction

An average of 8–14 liters of distillery spent wash is generated by each liter of ethanol produced. This wastewater is characterized by an extremely high chemical oxygen demand (COD) ($80,000$ – $100,000\text{ mg L}^{-1}$) and a biochemical oxygen demand (BOD) ($40,000$ – $50,000\text{ mg L}^{-1}$), besides its low pH, strong odor, and dark brown color [1]. Despite that many alternatives have been studied for treating distillery spent wash, a successful treatment has not been found until now [2].

Recently, some researchers have proposed electrocoagulation (EC) as a possible alternative for treating spent wash, also known as vinasses. During the last decade, the EC technique has been recognized as an effective process for various water treatment applications [3], particularly, EC has been applied by some researchers in biologically pretreated vinasses. Gadd et al. (2010) used electrodes of iron and they reached decrease 99% in color and 80% on COD [4]. Ryan et al. (2008) obtained 90% of color removal and up to 50% of COD [5]; likewise, Thakur et al. (2009) diminished the COD in 62% and 98% color by using stainless steel electrodes [6].

Furthermore, Prasad et al. (2008) diminished 93.5% color by using iron anodes to treat raw vinasse [7]; and Kannan et al. (2006)

reached a removal of about 99% turbidity and 80% COD by adopting the EC technique with and without adding indigenously prepared activated areca nut carbon [8]. Dávila et al. (2011) studied electrocoagulation and electroflotation applied in raw vinasses and obtained a decrease of 89% turbidity and 61% COD [9]. Moreover, through a variation of the conventional electrocoagulation technique, it was possible to diminish 70% dissolved organic carbon and 90% color in raw vinasses by using anodic dissolution of iron and a second stage of flocculation by using slaked lime [10].

While many vinasse EC studies have been carried out to quantify the effect of the operating conditions on output responses through statistically planned experiments, the process of anodic dissolution of iron in this effluent has not been specifically investigated. Therefore, this study aimed to propose a mechanism that describes the behavior of the carbon steel electrodisolution in distillery vinasse by using potentiodynamic polarization and electrochemical impedance spectroscopy in order to explore some adequate operational conditions to carry out the electrocoagulation.

2. Experimental

The vinasse samples were taken from the bottom stream of the mash column in a local distillery. The temperature of this stream is typically 82 – 85°C , therefore, to carry out the study were chosen 60°C and 80°C ; the intention is to take advantage of the warm temperature of the vinasse in the industrial process. Part of the sample underwent a treatment immediately, and the rest of the

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Table 1
Vinasse characteristics.

Parameter	Magnitude
DQO, ppm	82,760-92,800
pH	4.3-4.5
Conductivity, mS cm^{-1}	15.4-16.0
Turbidity, NTU	8,828-11,132

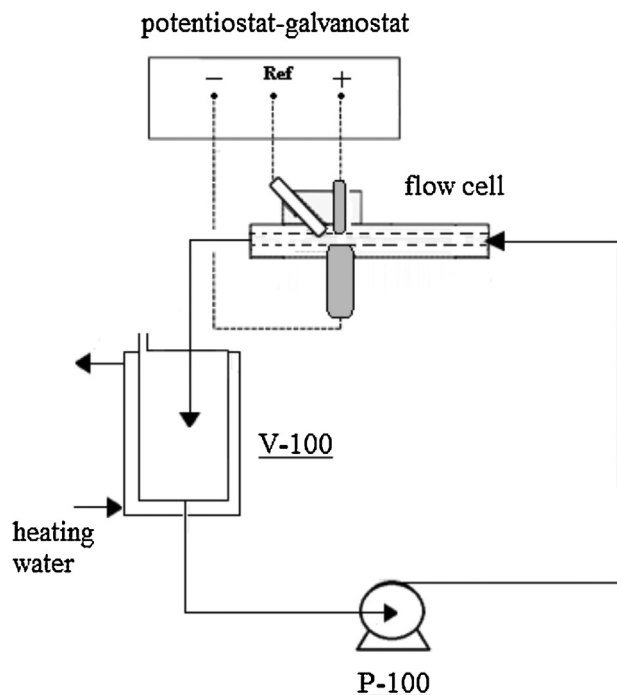


Fig. 1. Experimental set-up used in electrochemical tests.

sample remained cooled in 500 mL vessels to be used in the amount needed each day. Vinasse samples remained cooled for 72 hours maximum to avoid degradation to interfere with the results. Raw vinasse characteristics are presented in [Table 1](#).

2.1. Three-electrode flow cell

Vinasse was poured into a vessel (V-100) where temperature was controlled by means of a thermostatic bath ([Fig. 1](#)), and the flow regime was varied by means of a centrifugal pump at a variable speed (P-100). A three-electrode flow cell was built with two 2.54 cm thick acrylic blocks ([Fig. 2](#)) to register the potentiodynamic polarization curves and impedance spectra.

The working electrode consisted of a cylindrical carbon steel rod (ASTM A36) with a 0.64 cm^2 anodic area and the counter-electrode consisted of a cylindrical stainless steel rod (AISI 316) with a 1 cm^2

cathodic area. An Ag/AgCl electrode (Gamry 930-15), which used a KCl solution (3 M), was used as a reference electrode. The reference electrode was located at approximately 2 mm from the working electrode surface to minimize the ohmic losses.

The distance between the electrodes was 8 mm, and precautions in the cell design were taken to eliminate interference caused by edge effects or due to non-uniform flows on the electrode surfaces. Prior to each experiment, the working electrode and the counter-electrode were abraded using a 320 grade silicon carbide paper; then, with a 600 grade paper, and finally with a 1,200 grade paper to obtain a uniform and shiny surface. They were subsequently immersed in acetone for eliminate any trace of grease and then were rinsed with distilled water three times to eliminate any kind of contamination. All potential measures reported in this study took an Ag/AgCl electrode as reference. The electrodes were connected to a potentiostat/galvanostat (Gamry® series G750) and the open circuit potential (E_{oc}) was registered during a 300 second period.

Prior each test with vinasse the working electrode was anodically polarized at -450 mV (vs. Ag/AgCl) for 2 minutes and then cathodically at -850 mV (vs. Ag/AgCl) for 10 minutes in order to eliminate any oxide layer and to develop the surface morphology.

For the potentiodynamic polarization by using vinasse it was found out initially than, with a scanning rate of 5 mV s^{-1} , were not presented passivation trends over the anodic branches, according the methodology proposed by Ateya et al. [[11](#)].

2.2. Six-electrode assembly

To study the working electrode performance during the electrodisolution, an assembly with 6 carbon steel flat electrodes (ASTM A36) was placed into a V-100 vessel. The distance between electrodes was 5 mm and the anodic total area was 150 cm^2 . The assembly was operated simultaneously with the three-electrode flow cell and, in this way, was possible to reach the specific electric charge into the vinasse samples.

The electrochemical impedance spectroscopy (EIS) was conducted by disturbing the system with a 10 mV (rms) AC voltage, with a frequency range from 100 mHz to 300 kHz, using ten points per decade. EIS records, at different anodic potentials (-560 mV ; -500 mV ; -400 mV) corresponding to the active electrodisolution region, were obtained and, as an attempt to reach steady state during the electrodisolution, the EIS spectra were recorded after 60 minutes of beginning the anodic polarization. The consistency of experimental data was validated by applying *Kramers-Kronig* relations to ensure the principles of causality, linearity, and stability. On the other hand, the impedance data were adjusted to equivalent circuits with the *Echem Analyst* software (Gamry).

Anodic polarization curves, with scanning rate of 5.0 mV s^{-1} , were carried out on the working electrode of the three-electrode flow cell from E_{corr} up to -100 mV . Conversely, the cathodic polarization curves were carried out from -750 mV up to E_{corr} .

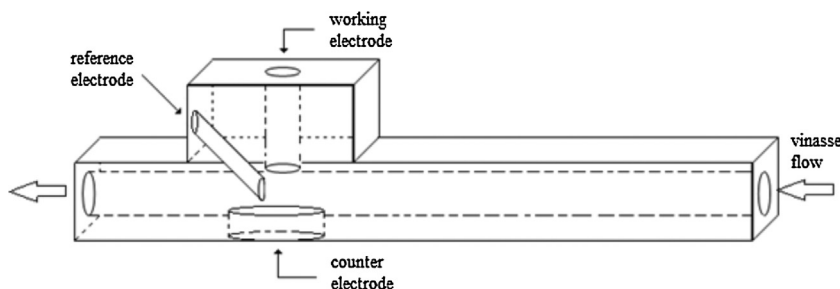


Fig. 2. Scheme of flow cell.

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