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Studies on various mode of electrochemical reactor operation for the treatment of distillery effluent

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ABSTRACT

The performance of different electrochemical reactor configurations of batch, batch with recirculation and single pass were investigated based on the COD removal, current efficiency and power consumption for the treatment of distillery effluent. The effect of various operating parameters such as current density, electrolysis time, supporting electrolyte concentration and recirculation flow rate on the oxidation of pollutant has been studied. The removal of COD was found to have increased with increase in current density and electrolyte concentration in the batch electrochemical reactor. The maximum percentage COD removal was found to be 83.2% with an energy consumption of 9.77 kWh/kg of COD. For the single-pass operation 52.94% COD removal with an energy consumption of 44.76 kWh/kg of COD has been observed. Continuous systems were found to be better than batch systems in terms of energy utilization with comparable COD removal and it was better to treat huge volume of the effluent. The single-pass operation shows less completion of the process due to the lower residence time. The kinetics of electrochemical reaction of various modes of operations has also been studied. The dispersed plug flow model value was compared with experimental value.

Introduction

Global industrialization and urbanization have led to the increasing pollution in water bodies, thereby requiring the need to treat the industrial wastewater before letting out to the environment. The large volume of hazardous effluents contains many bio-recalcitrant compounds generated due to industrial activity. Various organic pollutants create the colour and odour problem. These are responsible for being toxic and deteriorating to the environment. The different industrial effluents like distillery, agrochemical, kraft-bleaching, pulp and paper, textile dyehouse, oilfield and metal-plating wastes contain biologically recalcitrant organic pollutants and are not easily removed by biological treatment. So the conventional techniques of physical and/or chemical process are applied for the treatment of wastewaters to enhance their biodegradability and allow further applicability of biological treatment. The conventional treatment techniques such as coagulation, membrane separation, and adsorption result in phase transfer of pollutants and also result in secondary pollution. However, these processes are not yet completely adequate in treating effluents or because pollutants are refractory to chemical oxidation in aqueous medium or due to production of partially oxidized reaction products having greater toxicity [1].

One of the processes for treating such water containing toxic and persistent organic pollutants that has been increasingly used in recent years is the advanced oxidation process (AOP), a powerful tool applied to degrade this pollutant [2–5]. AOPs includes following processes such as treatment with H_2O_2, H_2O_2/UV, UV, photocatalysis, ozonation, ultrasound, wet air oxidation, electrochemical oxidation, Fenton and photo-Fenton. Electrochemical oxidation is one of the major and rapidly emerging AOPs and can be considered as an alternative treatment technology. Electrochemical techniques have been receiving greater attention in recent years due to their typical advantages such as environmental compatibility, selectivity, ease of automation, ease of scale-up and most importantly, versatility [6,7]. The mechanism and application of electrochemical process for the treatment of different industrial effluents have been reported by several investigators [8–11]. The electrochemical process using chloride as the supporting electrolyte was reported for the treatment of different industrial wastewaters such as electroplating [12], oil mill [13], heavy metal laden [14], nitrite effluent [15], defluoridation [16], arsenic removal [17], textile dyes [18], landfill leachate [19], restaurant [20], laundry [21], surfactants [22], agro-industry effluent [23], *etc.*

Electrochemical processes are based on the electrochemical reaction which occurs at the electrodes in the reactor. The design and development of an electrochemical cell is aimed at minimizing

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power losses due to poor current distribution and voltage drops and making the processes more competitive in energy consumption than the conventional techniques [24]. For an effective design of the electrochemical cell, understanding the various modes of its operation is crucial. The different possible reactor arrangements include batch, batch with recirculation, recycle and single-pass flow. The choice of batch or continuous operation for industrial application depends on the nature and toxicity of the effluent, simplicity of the process required, and the process economics [25]. In the present investigation, various modes of operation in the electrochemical cell have been tested for the treatment of industrial effluent to understand kinetics mechanism, pollutant removal and current efficiency.

Effluent originating from distilleries is densely coloured due to a dark brown pigment called melanoidin which is produced during the processing of sugarcane molasses for alcohol production, and this further ads to the bio-recalcitrance of the distillery effluent. Few investigators have studied the treatment of distillery effluent for the removal of colour and Chemical Oxygen Demand (COD) by different methods like biological [26–30] and electrochemical [31–34] methods. Krishna Prasad *et al.* have used electrochemical degradation and electrocoagulation for the treatment of spent wash from distilleries and observed the removal of COD and colour using ruthenium oxide coated titanium anode [31]. Manisankar *et al.* have studied treatment of distillery effluent in a static electrochemical cell employing two different kinds of anodes *viz.*, graphite and titanium anodes under varying operating conditions and they have observed a maximum COD and BOD removal of 92% and 98.1%, respectively, with complete decolourization.

The present study focuses on the electrochemical reactor in various mode of operation such as batch, batch with recirculation and single-pass flow reactors. The effect of various experimental parameters such as current density, electrolysis time, supporting electrolyte concentration and recirculation flow rate on the percentage COD removal, current efficiency and power consumption of these systems have been studied. The batch with recirculation mode has been suitably modeled to represent a dispersed plug flow behavior.

Experimental details

Materials

The effluent was collected from a nearby distillery industry. The physicochemical characteristics of the effluent were determined before treatment. The main characteristics of the effluent are shown in the Table 1: and the effluent characteristics were determined according to the standard methods [35]. The dilution of effluent was carried out with deionised water from a Millipore purification system. The initial pH of the solution was measured using pH meter (Elico; Model LI120 and the accuracy is ±0.01). The pH of the solution was adjusted using NaOH and H_2SO_4 solutions.

All the chemicals were analytical reagent (AR) grade obtained from Merck and used without further purification. Electrochemical experiments were carried out using Mixed Metal Oxide (MMO) and stainless steel (SS) as an anode and a cathode mesh type electrode respectively. The MMO anode ($Ti/Ti_{0.7}O_2$-$Ru_{0.05}O_2$-$Ir_{0.25}O_2$) has the composition of 70% TiO_2, 5% RuO_2 and 25% IrO_2 (wt%). The electrodes were obtained from Titan Anode Fabricators Private Limited, Chennai. The MMO electrodes are having good electronic conductor at anode potential, high surface roughness and a large number of electro-active sites. Hence, these exhibit a high electrocatalytic activity for the oxygen per geometrical oxide [36].

Table 1
Characteristics of the distillery effluent.

Parameters	Range
pH	4.1–4.3
Chemical Oxygen Demand (COD)	80,000–90,000 ($mg\,L^{-1}$)
Biological Oxygen Demand (BOD)	7000–8000 ($mg\,L^{-1}$)
Total Suspended Solids (TSS)	15.44 ($g\,L^{-1}$)
Total Dissolved Solids (TDS)	5550–5750 ($mg\,L^{-1}$)
Colour	Dark brown
Odour	Burnt sugar

Experimental method

Batch operation

The experimental set-up of the electrochemical reactor operated in a lab-scale batch mode of operation is shown in Fig. 1a. It consists of a glass beaker with a volume of 700 ml a pair of electrodes and DC regulated power supply. The anode and cathode has the dimensions of 7.25 cm × 6.0 cm were placed vertically and parallel to each other with an inter-electrode distance of 2 cm. The void fraction of the mesh type anode accounts 20% by area. Hence, the available effective electrode area is 34.8 cm^2 for anodic reactions. The electrode plates were cleaned manually by washing in distilled water prior to every run. The volume of effluent taken was 500 ml in the electrochemical reactor and the electrodes were connected to DC power supply (APLAB Ltd; Model L1606). The ionic conductivity of the wastewater was increased by adding 2–10 $g\,L^{-1}$ supporting electrolyte concentration of NaCl. The temperature of the reactor was maintained constant ±2 °C by external cooling system with recirculation of water. The solution was continuously stirred at a constant speed using a magnetic stirrer. The cell voltage was periodically noted. The samples were collected at regular interval of time from the reactor and filtered using Whatmann 42 filter paper. The COD was determined to investigate the behaviour of electrochemical oxidation of distillery effluent in the batch reactor. The sample COD was determined using the dichromatic closed reflux method strictly following the APHA [35].

The performance of the batch electrochemical reactor was studied under various conditions of current density and electrolyte concentration of NaCl. The percentage COD removal, current efficiency (CE) and power consumption (EC) were studied at different current densities ranging from 1 to 5 $A\,dm^{-2}$ and NaCl concentration was varied from 2 to 10 $g\,L^{-1}$.

The CE and EC of batch operation can be calculated using following equations [37]:

$$CE = \frac{V_R \times \Delta COD}{\frac{16It}{2F}} \times 100 \quad (1)$$

$$EC = \frac{VIt}{\Delta COD \times V_R} \quad (2)$$

where difference in Chemical Oxygen Demand ($\Delta COD = COD_{initial} - COD_{final}$) is in $g\,L^{-1}$; applied current (I) in Ampere; electrolysis time (t) in hr; applied cell voltage (V) in volts, volume of the reactor (V_R) in liters and Faraday's constant (F) in C/mol.

Batch recirculation operation

A schematic representation of the experimental set-up of the lab-scale batch recirculation and single-pass mode of operation is represented in Fig. 1b. The electrochemical reactor is made of filter press type having a volume of 250 ml with an inlet at one side at the bottom and an outlet in the other side at the top. The electrolytic flow reactor consisted of an anode and cathode with inter-electrode distance of 2 cm. The DC power supply was used for electrical connections to constitute an electrolytic cell with