Acid dye Degradation using electrochemical batch recirculation flow reactor

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ABSTRACT

Textile industries consume large volumes of fresh water and chemicals during wet processing of textiles. Among the various pollutants present in textile waste water, dye is the first contaminant to be recognized and has to be removed before discharging into water bodies or onto land. The release of colored effluents in to the environment is not desirable because of their color and their breakdown products. In this work, the electrochemical batch recirculation process is tried for acid dye degradation mainly focused on indirect anodic oxidation which involves application of an electric current on wastewater containing an acid dye Rose Bengal (Acid Red-94). The performance of electrochemical batch recirculation flow reactor in degrading the selected dye Rose Bengal was investigated using Ti/RuO$_2$-TiO$_2$ and stainless steel electrodes in presence of NaCl as supporting electrolyte. Due to strong oxidizing potential of chemicals produced, the effluent color and pollution load are reduced substantially in this treatment technique. The influences of current density, operating time and effluent recirculation rate on the reduction of COD were critically examined. It can be noticed that the rate of degradation of dye increases with applied current density. The cell voltage is increased with increasing applied current density in all the experiments. The results indicate that the electrochemical method is a viable and effective technique for the degradation of Rose Bengal dye from aqueous solution.

KEY WORDS: Acid dyes, Electrochemical reactors, Dye degradation, COD, Electrochemical oxidation.

1. INTRODUCTION

The major problem faced by human today is how to provide clean water to the entire population of the world. As fresh sources like rivers, lakes, canals etc., are limited and those available also are polluted by industries due to the discharge of their pollutants make water a precious commodity now a days. Textile industries consume large volumes of water and chemicals especially during wet processing of textiles. From the reports of Robinson (2001), and Parac-Ostermann (2004), there are over 100 000 commercially available dyes with about 700,000 tons being consumed in the textile industry. When dyeing textile materials, water serves two purposes. Water vapor acts as a heating agent for the dye baths, when liquid water ensures the transmission of the dyes onto the fiber. According to Hessel (2007), dyeing of one kg of cotton requires about 150 L of water, 0.6 kg of NaCl, and 40 g of dyes. As per the researchers Stolz (2001), Pearce (2003) and Moreira (2004), the process of delivering the color onto fabric is not an efficient process and about 40 % of the dyes are remain in water during dyeing process.

Among the various available classes of dyes, acid dye is a dye which is salt of a sulfuric, carboxylic or phenolic organic acid. The salts are usually sodium or ammonium salts. Acid dyes are normally soluble in water and possesses affinity with acid as well as base nature fibers which lacking direct dyes affinity for cellulose fibers. Acids are added to dye baths to increase the protonated amino-groups in fibers, which favors the dyeing ability of fibers. In textiles, acid dyes are effective on protein fibers like animal hair, wool and mohair. Acid dyes are also effective on silk fibers and synthetic fiber nylon, but not usually used in dyeing any other synthetic fibers.

The statements from the researchers Forgacs (2004) and Rai (2005), one of the important classes among the pollutants in textile industries are dyes, and once they entered into water bodies, it is difficult to treat because of the synthetic origin of dyes and a complex molecular structure makes them more stable and difficult to degrade. Further, as per the report of Moreira (2004), presence of very small amounts of dyes in polluted waste water is highly visible and it affects the light penetration capacity. In any further increase in temperature will greatly reduce the dissolved oxygen concentration in waste water. These will results, alteration of the aquatic ecosystem.

The acid dye, Rose Bengal (Acid Red 94) is extensively used in printing, insecticides and textile dyeing industries. It is a water soluble dye and exhibits a pink color. Rose Bengal dye has severe toxic effects on the human corneal epithelium. The dye is extremely hazardous when it comes in contact with skin and creates irritation, itching, scaling, reddening and even blistering. It also causes inflammation, redness, watering and itching in the eyes. On ingestion by inhalation, it affects mucous membranes, which leads to respiratory irritations in humans. The molecular structure of the selected dye Acid Red 94 is shown in Figure 1.
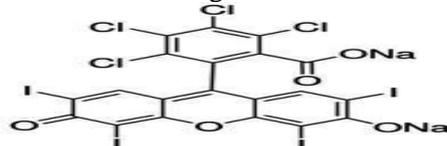

Figure.1. The molecular structure of the selected dye Acid Red 94

Among the various available dye degradation processes, electrochemical oxidation process has been receiving greater attention in recent past due to their distinctive advantages. As per Brillas (2003), the major advantage is environmental compatibility. This is because, in these techniques, the main reactant is the clean reagent electron. Further, versatility is an added advantage. A different type of reactors and electrode materials, designs, and configurations can be utilized. In addition, electrolytic processes can be scaled easily from the bench scale to commercial. Electrochemical methods are generally safe because of the mild operating conditions usually employed and the small amount and harmless nature of the added chemicals.

In this work, electrochemical batch recirculation flow reactor having the cell containing Ti/RuO$_2$-TiO$_2$ anode and stainless steel cathode is used to degrade the Acid Red 94 dye, which is present in synthetically prepared wastewater. Further, the influences of current density, operating time, effluent recirculation rate on dye degradation was critically examined.

2. MATERIALS AND METHODS

2.1. Materials: Analytical grade reagents are used for all the experiments and analysis. Textile dye Rose Bengal obtained from a textile industry near Tiruppur, Tamilnadu, India. Synthetic dye bath effluent is used in the present study and it was prepared according to the composition commonly used in dyeing the silk material with Rose Bengal. After the experiments, the treated effluent is collected and characterized. At initial condition, the characteristics of the dye bath effluent are shown in Table 1.

Table.1.Characteristics of the Rose Bengal synthetic effluent

Parameter	Value
pH	3.2
COD (mgL^{-1})	1280
Suspended solids (mgL^{-1})	200
Dissolved solids (mgL^{-1})	1050

2.2. Batch Recirculation Electro Chemical Oxidation System: The line diagram of the experimental set-up of the electrochemical batch-recirculation flow reactor operation is shown in Figure 2
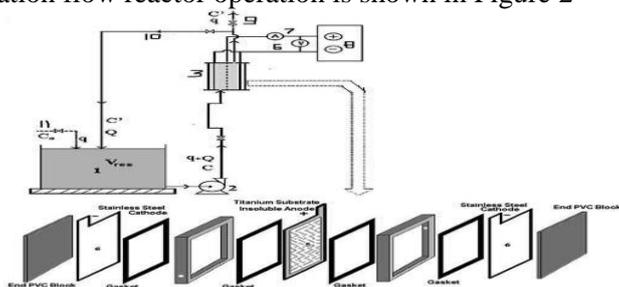
Figure.2.Schematic diagram of batch recirculation flow reactor (1. Reservoir, 2. Peristaltic Pump, 3. Filter press type flow cell, 4. Anode, 5. Cathode 6. Digital Voltmeter, 7.Digital Ammeter, 8.D.C. Regulated Power Supply, 9. Treated wastewater outlet, 10. Recirculation Stream, 11.Wastewater inlet to system)

By adjusting the appropriate valves, the set-up can be used for both batch recirculation and continuous mode operations (i.e. for batch recirculation mode, the streams 9 and 11 are closed). The electrochemical flow reactor consisted of a stainless steel flat plate cathode and a flat expanded mesh of titanium coated with RuO$_2$ anode. In the cell, the electrodes (0.07 m $\times$ 0.07 m) were parallel to each other with a 0.0125 m inter-electrode gap and immersed in dye solution in such a way to get an effective electrode area of 0.00392 m^2 for anodic reactions. The cell had one inlet in the bottom cover and an outlet in the top cover. The electrodes were connected to a 5 A, 30 V DC regulated power supply (Aplab L3210), an ammeter and a voltmeter. The DC power is supplied to electrodes by keeping a constant current corresponding to a current density. The other components of the set-up were a reservoir and a peristaltic pump, connected using silicone rubber tubes. The holdup volume of the reactor was 5.88 $\times$ 10^{-4} m^3.

2.3. Experimental Procedure for Electrochemical Batch Recirculation Flow Reactor: Electro oxidation studies were carried out in electrochemical batch recirculation flow reactor. All the experiments were carried out under galvanostatic conditions. In batch recirculation reactor the treated effluent in reactor is recirculated to the reservoir. Since the pH of the effluent was found to have less influence on the response during the preliminary runs, no adjustment was made. The untreated dye effluent (2 L having initial COD of 1200 mgL^{-1}) is taken in reservoir for studies and electrolysis experiments were carried out using different current densities (1.3 Adm^{-2}, 2.6 Adm^{-2}, 3.8 Adm^{-2} and 5.1 Adm^{-2}). Under these conditions experiments were repeated for four different flow rates viz. 20, 40, 60 and 80 mLmin^{-1}. In all current densities and re-circulation flow rates, the experiments were run for 5 h. The electrode plates were cleaned manually by washing using distilled water prior to every run. The cell voltage was noted down periodically and the samples were collected from reservoir before electrolysis, periodically during electrolysis and after electrolysis and subjected to COD analysis.

3. RESULTS AND DISCUSSION

3.1. Mechanism of Electrochemical Oxidation: The mechanism which involved in electrochemical oxidation of wastewater is a complex one involving electron transfer reaction with a dissociate chemisorptions. Basically there are two different processes occur at the anode. First, due to high electro-catalytic activity of anode, oxidation occurs at the electrode surface (direct electrolysis); next, in metal oxide electrode, oxidation occurs via surface mediators, where mediators are generated continuously (indirect electrolysis). According to the reports of Basha (2009), Mohan (2007), Raghu and Ahmed Basha (2007), the electrochemical oxidation of organic dyes on oxide coated catalytic anode (RuO_2-TiO_2) is as follows:

During electrolysis, water reacts with noble metal oxide (NO) at anode will produce physically adsorbed hydroxyl radicals as mentioned in equation (1).

$$(NO) + H_2O \text{ (waste water)} \longrightarrow (NO)(^\bullet OH) + H^+ + e^- \tag{1}$$
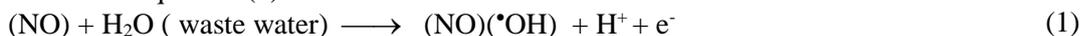
Next, thus formed hydroxyl radicals (NO) ($^\bullet OH$), further react with NO oxygen, the chemisorbed metal oxide, NO + O (CNO) is formed as indicated in equation (2).

$$(NO)(^\bullet OH) \longrightarrow (CNO) + H^+ + e^- \tag{2}$$

In anode surface, the active oxygen available as physorbed (NO) ($^\bullet OH$) and chemisorbed (CNO) forms. When sodium chloride is used as additional electrolyte in electrolysis, Cl^- ions may interact with physorbed oxygen (NO) ($^\bullet OH$), yield hypochlorite radicals as shown in equation (3).

$$(NO) (^\bullet OH) + Cl^- \rightarrow (NO)(^\bullet OCl) + H^+ + 2e^- \tag{3}$$

In presence of chloride ion, the adsorbed hypochlorite radicals again interact with oxygen, which present in NO yield again the higher oxide (CNO). Also, the adsorbed hypochlorite radicals (NO) ($^\bullet OCl$) simultaneously react with chloride ion, yield active dioxygen and chlorine as given in equations (4) and (5).

$$(NO)(^\bullet OCl) + Cl^- \rightarrow (CNO) + Cl_2 + e^- \tag{4}$$

$$(NO)(^\bullet OCl) + Cl^- \rightarrow (NO) + \tfrac{1}{2}O_2 + Cl_2 + e^- \tag{5}$$

Thus, the generated chlorine at anode surface, further react with water will give hypochlorus acid and further proceeds as shown in equations (6), (7) and (8).

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \tag{6}$$

$$HOCl \leftrightarrow H^+ + OCl^- \tag{7}$$

$$Dye + OCl^- \rightarrow CO_2 + H_2O + Cl^- \tag{8}$$

Since organic dyes present in the effluent are electrochemically not active, first oxidation reaction that occurs at the anode is due to the chloride ion oxidation with the production of Cl_2. As per the reactions in the bulk, gaseous Cl_2 dissolves in water as mentioned in equations (6) and (7).

3.2. Effect of time and Current density on % COD reduction: Experiments were conducted in batch recirculation reactor at four different current densities (1.3, 2.6, 3.8 and 5.1 Adm^{-2}), keeping other parameters such as circulation rate 20 $mLmin^{-1}$ and initial COD (1200 mgL^{-1}) constant for dye effluent. It can be ascertained from Figures 3, 4 and 5 that the percentage COD reduction increases as the electrolysis time increases.
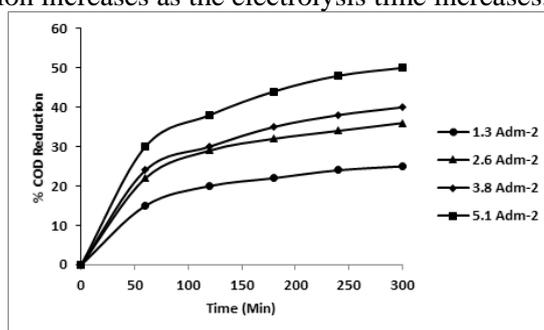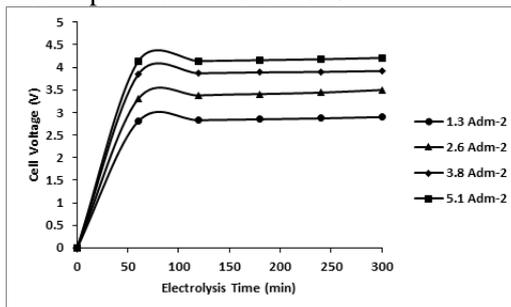

Figure.3.Effect of time and Current density on % COD reduction (circulation rate 80 mLmin^{-1} and initial COD = 1200 mgL^{-1})

The higher degradation rate was observed for dye bath effluent, in the initial hour of electrolysis, for all applied circulation rates and current densities. The rate of increase in percentage COD reduction is larger in the beginning of the process, and the same was decreases and approaches to zero in the later hours of electrolysis. The enhanced current density, not only increase the reduction of amount of pollutant removal (25% COD reduction for the current density 1.3 Adm^{-2}, 36% for the current density 2.6 Adm^{-2}, 40% for the current density 3.8 Adm^{-2} and 50% for the current density 5.1 Adm^{-2} in 5 h of operation) but also largely increases the specific energy consumption, because of the increased cell voltage.

3.3. Effect of Electrolysis time and Current density on Cell Voltage: From the Figure 4, it can be shown that, when the electrolysis time increases, the cell voltage is also increases up to 60 min, thereafter; there is no much

variation in cell voltage. However, the increase in current density considerably increases the cell voltage, thereby power consumption, under the specified experimental conditions.

Figure.4.Effect of Electrolysis time and Current Density on Cell Voltage (circulation rate 80 mLmin^{-1} and initial COD = 1200 mgL^{-1})

3.4. Effect of Recirculation rate on % COD reduction: Experiments were conducted for four circulation flow rates (20, 40, 60, and 80 mLmin^{-1}), keeping current density as 5.1 Adm^{-2} and initial COD (1200 mg L^{-1}) constant for dye effluent. It can be ascertained from Figure 5 that the percentage COD reduction increases as the electrolysis time increases, or in other words, the COD of the effluent exponentially decreases with electrolysis time. The higher degradation rate was observed for effluent in the initial hour of electrolysis for all the applied circulation flow rates. The rate of increase in percentage COD reduction is larger at the beginning of the process, and the same rate decreases in the later hours of electrolysis. Figure 5 shown that the increase in COD removal from 25 to 70 % in 5 h of operation as circulation flow rates increased from 20 to 80 mLmin^{-1}.
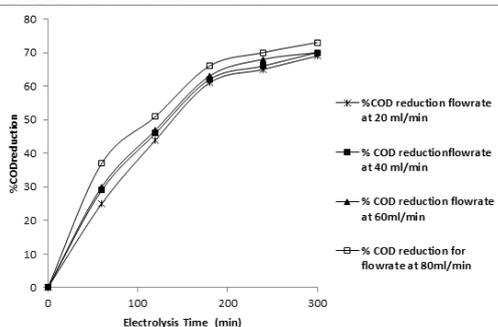
Figure.5.Variation of % COD Reduction with Electrolysis Time for Dye Effluent in Flow Reactor at Different Recirculation Rates

The cell voltages are not varying much with the circulation flow rates. The observed cell voltage is around 4 V for the current density 5.1 Adm^{-2} for the same initial COD concentration. The improvement in COD removal resulted when the circulation flow rate increased from 20 to 80ml min^{-1}. This may because of the improved ionic conductivity by bulk movement and reduction of resistance on the electrode surface results enhanced mass transfer coefficients at higher flow rates. In batch recirculation reactor, we found that to get complete removal of COD, we can prolong the electrolysis time, but the specific energy will be very large. In all cases, it can be seen that the % removal of the organic matter has increased exponentially with time. The increase in pollutant removal beyond 5 h of treatment is marginal when cell is operated at constant current densities. It can also be seen that with increase in current density, COD reduction is increased but the current efficiency is decreased. Thus, in general, a higher current density operation will give high capacity utilization, at the expense of higher energy loss.

4. CONCLUSIONS

Studies were made to degrade the hydrolyzed textile acid dye, Rose Bengal, using batch electrochemical recirculation process in order to reuse the treated effluent. It was observed that in dye degradation, the applied current density influence more in cell voltage in turn energy consumption. The maximum % COD reductions were observed at the flow rate of 80 mL/min and current density 5.1 Adm^{-2}. The higher degradation rates were observed for dye effluent in the initial hours of electrolysis for all applied circulation flow rates in batch recirculation flow reactor. In other words, the rate of increase in percentage COD reduction is larger in the beginning of the process, and the same rate decreases and approaches to zero in the later hours of electrolysis. In addition, it was observed that the rate of organic contaminant degradation is dependent on its bulk concentration. At the current densities 1.3, 2.6, 3.8, 5.1 Adm^{-2}, when initial COD is 1200 mgL^{-1}, the rate of degradation of organic contaminant increases as the electrolyte circulation rate increases, and the percentage COD reduction in the bulk of the reservoir increases and try to reaches a constant value. As the electrolyte circulation rate increases, the transport of the Cl$^-$ ion from the bulk to the electrode surfaces increases. This would facilitate Cl$_2$ generation, as well as the dissolution of Cl$_2$ to form OCl$^-$ for reaction with the organic contaminant.

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5. ACKNOWLEDGEMENT

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