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Research Article

Electrochemical Degradation of Remazol Black B Dye Effluent

This study focused on the electrochemical degradation of hydrolyzed Remazol Black B (CI Reactive Black 5), a common diazo reactive dye, in aqueous solution. In the presence of various auxiliary dye chemicals, a typical Remazol Black simulated exhausted dyebath liquor was treated electrochemically in various basic electrochemical reactor configurations such as batch, batch recirculation and single pass systems. The effect of current density, supporting electrolyte concentration, electrolysis duration, specific electrode surface and fluid flow rate on pollutant removal and energy consumption performance of the systems was critically evaluated. Batch studies show the following operating parameters, current density: 2.5 A/dm^2, electrolysis duration: 6 h, and supporting electrolyte concentration: 3 g/L, were optimal for good overall performance of the system. Color removal was complete by 3 h of treatment for all combinations of parameters studied. The pollutant removal performance of the batch recirculation system was found to have improved considerably by increasing the flow rate. Performance of the batch recirculation system was comparatively better than the other rector configurations studied, with respect to capacity utilization and energy consumption.

1 Introduction

Azo dyes are widely used in a number of industrial processes such as textile dyeing, paper and printing, food, pharmaceutical, color photography, leather, cosmetics, etc. The textile industry is the predominant consumer of azo dyes. The development of synthetic fabrics such as nylon, rayon, and polyester required the production of new dyes that can effectively bond to these materials. Azo dyes have been continually updated to produce colors that reflect the trends dictated by changing social ideas and styles. Brighter, longer lasting colors are often necessary to satisfy this demand. This resulted in a drastic increase in the production and types of dyes. More than 10 000 different textile dyes with an estimated annual production of $7 \cdot 10^5$ metric tonnes are commercially available worldwide, of which reactive dyes are the leading class because of their wide applicability [1]. Many of these dyes find their way into the environment via wastewater facilities. 2% of these dyes are directly discharged as aqueous effluents and 10% are lost during the coloration process [2]. These compounds retain their color and structural integrity under exposure to sunlight, soil, bacteria and sweat, and exhibit a high resistance to microbial degradation in wastewater

treatment systems. They remain in the environment for longer periods if discharged without adequate treatment. Hydrolyzed Reactive Blue-19 has a half life of about 46 years at pH 7 and 25°C [3]. The release of these colored compounds into water bodies is undesirable not only because of their impact on photosynthesis in aquatic plants but also due to the carcinogenic nature of many of these dyes and their breakdown products [4].

Effective and economic treatment of azo dye effluents has become a serious concern over the past few decades. No single conventional treatment system is adequate for degrading the dye structure. Currently, much research has focused on chemically and physically degrading azo dyes in wastewater. These methods include advanced oxidation techniques which use strong oxidizers such as hydrogen peroxide [5], ozone [6], etc. These techniques are sometimes coupled with UV light/sound wave exposure to increase the color removal [7–10]. Other techniques involve adsorption [11], reverse osmosis [12], coagulation/flocculation [13] or high energy irradiation [14]. Many of these technologies are still questionable in regards to their economic viability in large waste streams.

Azo dyes often pass through activated sludge facilities with little or no reduction in color [15]. Although some researchers have observed slight color reductions, their findings are largely outweighed by those who have not [16]. Reductions in the carbon content and oxygen demand of azo dye wastewater following aerobic treatment are well cited [15]. Even though anaerobic treatment of azo dyes shows color reduction by forming intermediates [17], this method is rarely preferred because of the fact that a higher percentage of these intermediates have been identified as carcinogens [18].

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Abbreviations: CE, Current efficiency; **COD**, Chemical oxygen demand; **EOD**, Electrochemical oxygen demand; **EOI**, Electrochemical oxidability index; **ICE**, Instantaneous current efficiency

InterScience

Over the past two decades there has been a growing interest in the use of electrochemical techniques such as electrocoagulation, electroflotation and electrooxidation for the treatment of organic effluents. The technical feasibility for the treatment of various industrial effluents such as textile wastewater [19], electroplating waste water [20], oil mill wastewater [21], heavy metal laden wastewater [22], nitrite effluent [23], defluoridation [24], arsenic removal [25], landfill leachate [26], restaurant wastewater [27], laundry wastewater [28], surfactants [29], agro industry wastewater [30], etc. has been studied. Mendez et al. [31] investigated the cathodic decolorization of Remazol black B (20 to 80 mg/L) using a Ni-polyvinyl-chloride composite and reported almost complete color removal and no organic contaminant removal after one hour of treatment at −3.0 V vs. SCE. Erdal et al. [32] studied the degradation of RB5 (Reactive black 5) at lower concentration levels (20 mg/L) using an electro-fenton method (carbon-platinum electrodes) in a batch setup and reported almost complete removal after 30 min of treatment. Rivera et al. [33] studied the electrochemical degradation of RB5 using diamond and metal alloys electrodes in a batch recirculation setup and reported 95% color removal and 65–67% COD (chemical oxygen demand) removal.

Electrochemical degradation of dye house effluent on noble metal oxide, being a non sacrificial anode process, eliminates the generation of chemical sludge and is thus attractive as regards operating costs and simplicity of operation. The economic viability of attempting complete mineralization of large volumes of such a heavily loaded organic effluent is questionable. But the possibility of integration of electrochemical methods with conventional methods for an improved, economically viable overall performance may be examined.

Electrochemical degradation of wastewater occurs by mediated oxidation. The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving the coupling of an electron transfer reaction with a dissociate chemisorption step. The type of oxidative mechanism may occur at the anode with a high electro catalytic activity, for example, in metal oxide electrodes oxidation occurs via the surface where mediators are generated continuously on the anodic surface [34–40]. For instance, the electrochemical oxidation of organics on noble oxide coated catalytic anode (MO_x) can be explained as follows.
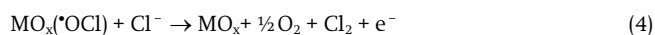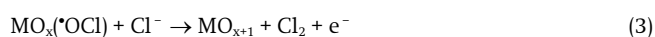
In the first step, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction:
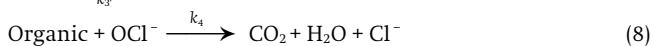
$$MO_x + H_2O \rightarrow MO_x(^{\bullet}OH) + H^+ + e^- \tag{1}$$
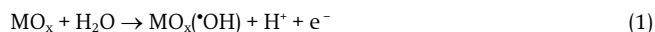
When NaCl is used as the supporting electrolyte, chloride ions may anodically react with $MO_x(^{\bullet}OH)$ to form adsorbed OCl radicals according to the following reaction:

$$MO_x(^{\bullet}OH) + Cl^- \rightarrow MO_x(^{\bullet}OCl) + H^+ + 2e^- \tag{2}$$
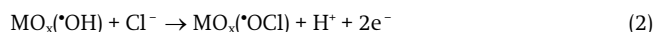
Further, in the presence of chloride ions, the adsorbed hypochlorite radicals may interact with the oxygen already present in the oxide anode with the possible transition of oxygen from the adsorbed hypochlorite radical to the oxide, to form the higher oxide MO_{x+1} according to the reaction given below. Simultaneously $MO_x(^{\bullet}OCl)$ can react with the chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:

$$MO_x(^{\bullet}OCl) + Cl^- \rightarrow MO_{x+1} + Cl_2 + e^- \tag{3}$$

$$MO_x(^{\bullet}OCl) + Cl^- \rightarrow MO_x + \tfrac{1}{2}O_2 + Cl_2 + e^- \tag{4}$$

In the same way, an indirect electrochemical oxidation mechanism has been proposed for metal oxide with chloride as the supporting electrolyte for wastewater treatment [40–42]. The anodic oxidation of chloride ions to form chlorine in the bulk solution, as given by Eqs. (3) and (4), proceeds as follows[1]:

$$2\,Cl^- \xrightarrow{k_1} Cl_2 + 2\,e^- \tag{5}$$

$$Cl_2 + H_2O \xrightarrow{k_2} H^+ + Cl^- + HOCl \tag{6}$$

$$HOCl \underset{k_{3'}}{\overset{k_3}{\rightleftharpoons}} H^+ + OCl^- \tag{7}$$

$$Organic + OCl^- \xrightarrow{k_4} CO_2 + H_2O + Cl^- \tag{8}$$

Since organic compounds in the effluent are electrochemically inactive, the primary reaction occurring at the anodes is chloride ion oxidation (see Eqs. (3) and (4)) with the liberation of Cl_2, which is a strong oxidizing agent. As regards the bulk reaction, gaseous Cl_2 dissolves in the aqueous solution due to ionization, as indicated in Eq. (6). The rate of bulk reaction is less in acidic solution due to OH^- instability, and considerably more in basic solution due to the ready formation of OCl^- (pK_a 7.44) ions in Eq. (7), implying that basic or neutral pH conditions are more favorable for conducting reactions involving chlorine. The indirect electrooxidation rate of organic pollutants depends on the diffusion rate of oxidants into the solution, the flow rate of the effluent, the temperature and pH. In moderately alkaline solutions, a cycle of chloride-chlorine-hypochlorite-chloride takes place, which produces OCl^-. The pseudo steady state theory can be applied to each of the intermediate products (HOCl and OCl^-) in the bulk solution. The rate of reaction of the components can be written as:

$$-r_{Cl_2} = k_2[Cl_2] \tag{9}$$

$$r_{HOCl} = k_2[Cl_2] - k_3[HOCl] + k_{3'}[H^+][OCl^-] = 0 \tag{10}$$

$$r_{OCl^-} = k_3[HOCl] - k_{3'}[H^+][OCl^-] - k_4[organic][OCl^-] = 0 \tag{11}$$

$$-r_{organic} = k_4[organic][OCl^-] \tag{12}$$

Using the above equations we can easily deduce the following expression:

$$-r_{Cl_2} = -r_{organic} = k_4[organic][OCl^-] \tag{13}$$

Finally as regards the bulk solution, it is also to be noted that $-r_{Cl_2} = r_{Cl^-}$ from Eq. (12), that is:

$$-r_{Cl_2} = r_{Cl^-} = k_2[Cl_2] = -r_{organic} = k_4[organic][OCl^-] \tag{14}$$

where the rate of reaction r_i and the rate constants k_i (i = 2, 3 and 4) are defined with respect to the bulk. The rate expression for the main electrode reaction, as per Eq. (5), can be written as:

$$-r'_{Cl^-} = r'_{Cl_2} = k_1[Cl^-] \tag{15}$$

where k_1 is the heterogeneous electrochemical rate constant.

In the following section an attempt is made to establish a relationship between the reacting species in the bulk solution and at the electrode surface. The basic relationship applicable to all elec-

[1] List of symbols at the end of the paper.

trochemical reactions is Faraday's law, which relates to the amount of substance reacted on the surface to the charge ($I_A\,t$) passed, $M_A I_A t/n F$ (assuming 100% current efficiency) and the characteristic measurable parameter, current density, i_A (defined as I_A/A_e). Thus, the electrochemical reaction rate (for the disappearance of reactant A) can be expressed as:

$$-\left(\frac{V_R}{A_e}\right)\frac{d[A]}{dt} = \frac{i_A}{nF} \tag{16}$$

where I_A is the current passed in time t, M_A is the molecular weight, n is the number of electrons transferred per mole of reaction, A_e electrode area, V_R reactor volume and F is the Faraday constant (96 485.3 Coulomb/mol). It has to be noted that $-r_A = -d[A]/dt = i_A a/n F$ where a is the specific electrode area (A_e/V_R). Assuming the main electrode reaction is governed by a simple Tafel type expression:

$$-\left(\frac{V_R}{A_e}\right)\frac{d[A]}{dt} = \frac{i_A}{nF} = k^\cdot [A]\exp(bE) \tag{17}$$

or

$$-r_{Cl^-}^\cdot = r_{Cl_2}^\cdot = k_1[Cl^-] = k_1^\cdot a[Cl^-]_s \exp(bE) \tag{18}$$

where b is the Tafel slope of the polarization curve obtained by plotting $\ln[i_A]$ against cell potential E.

The reaction may be assumed to be under diffusion control as the reacting species, Cl^- in the electrolyte is dilute. The reactant Cl^- is transported from the bulk to the electrode surface where it undergoes electrochemical oxidation to Cl_2 and it may be transported back to the bulk by diffusion reaction in the bulk. Then:

$$\frac{i_A}{zF} = k_L([Cl^-] - [Cl^-]_s) \tag{19}$$

Elimination of $[Cl^-]_s$ using Eqs. (18) and (19) gives:

$$\frac{i_A}{zF} = k_1[Cl^-] \tag{20}$$

where

$$\frac{1}{k_1} = \frac{1}{k_L} + \frac{1}{k'a\,\exp(bE)} \tag{21}$$

From a material balance of species Cl^- by taking note of Eqs. (7) and (8), one can write:

$$\frac{i_A}{zF} = k'[Cl_2] \tag{22}$$

$$\frac{i_A}{zF} = k[organic][OCl^-] \tag{23}$$

During electrolysis, if a constant current is applied, the rate of generation of $[OCl^-]$ will remain constant under a given set of experimental condition, but will vary if the applied current is altered. Then:

$$\frac{i_A}{zF} = k_{obs}[organic] = k[COD] = kC \tag{24}$$

The current efficiency of the process is studied in detail using the following performance terms. Instantaneous current efficiency (ICE), calculated from the values of depletion rate of COD of the solution, which is as follows:

$$ICE(t) = \frac{\left(\dfrac{d(COD)}{dt}\right)_t FV_1 \times 10^{-3}}{8I} \tag{25}$$

Where V_1 is the volume of the effluent in liters, I is the current (A) and F is the Faraday constant. If the parameter ICE is plotted as a function of time, the area under the curve divided by the total time (t) elapsed, an ‚average current efficiency' is obtained that is called the electrochemical oxidability index (EOI).

$$EOI = \frac{1}{\tau}\int_0^\tau ICE(t)dt \tag{26}$$

The parameter EOI gives a quantitative estimate of the ease of electrochemical oxidation of organic species; i.e., the larger this value, the more easily the species can be oxidized. The electron withdrawing groups such as $-SO_3H$ and $-COOH$ produce low EOI values (< 0.05) indicative of a low electron density available for oxidation, whereas electron donating groups such as $-NH_2$ produce high EOI values (0.56) due to the increased electron density available.

EOD is defined as the actual mass of oxygen evolved for unit mass of organic matter removed during the electrochemical treatment. Grams of oxygen actually evolved by passing I ampere for t seconds is given by:

$$g_{O_2} = \frac{8It}{F} EOI \tag{27}$$

The corresponding amount of organic matter removed is given by:

$$g_{org} = \Delta COD \times V_1 \times 10^{-3} \times \frac{992}{1024} \tag{28}$$

where ΔCOD is the COD removed due to the operation. 992 and 1024 stands for the molecular weight (g/mol) and theoretical oxygen demand (g/mol) of RB5 respectively.

$$EOD = \frac{g_{O_2}}{g_{org}} \tag{29}$$

The present study helps in comparing the performance of the most common electrochemical reactor arrangements. Since the lion's share of azo dye consumption is in textile dyeing, a simulated representative sample of one of the common diazo reactive dyes, Remazol Black B (CI Reactive Black 5) was tested by the use of electrochemical treatment; using a RuO_x-IrO_x-TiO_x coated anode in various types of reactor configurations such as batch, batch recirculation and once through reactors. The mechanism of the electrochemical degradation process and the effect of important operating parameters, such as current density, supporting electrolyte concentration and electrolysis time, on pollutant removal and energy consumption performance of these systems were studied.

2 Materials and Methods

All the chemicals used in the study were of analytical reagent (AR) grade. Remazol Black B (C.I. Reactive Black 5, RB5) was obtained from the dye manufacturer as a commercially available dye formulation [41]. This is a diazo type reactive dye containing vinyl sulfonate reactive groups, as represented by the chemical structure in Fig 1. Simulated dyebath effluent was prepared according to the composition commonly used in cotton dyeing with Remazol Black 5. In order to dye 100 g of fabric, 4 g of dye is needed. It was dissolved in 1L of double distilled water along with the auxiliary chemicals such as 3 g Na_2CO_3, 1 mL of 38°Bé NaOH and 10 g of Na_2SO_4. After the process of dyeing, the effluent was collected and characterized. The results are reported in Tab. 1. In reactive dyeing processes, sodium
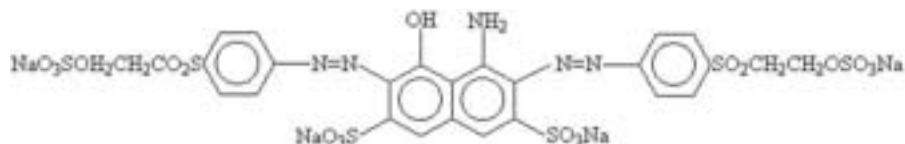
Figure 1. Schematic representation of the chemical structure of Reactive Black B dye.

Table 1. Characteristics of the Remazol Black 5 synthetic effluent.

Parameter	Value
pH	10.5 ± 0.5
COD (mg/L)	$1\,200 \pm 10$
Suspended solids (mg/L)	210 ± 10
Dissolved solids (mg/L)	$10\,500 \pm 100$

sulfate is the exhausting agent and sodium carbonate is the fixing agent. The effluent generated during this process could be used as the electrolyte [43, 38]. The study sample of required concentration was also prepared with a knowledge of the dye bath effluents density.

The COD of the samples was determined using the dichromatic open reflux method. All the experimental procedures of the study were conducted strictly following APHA methods [44]. The experiments were repeated until the absolute value of the difference between any two results was less than 3% of their average and if so, the average value was accepted.

Electrochemical experiments were carried out using a RuO_x-IrO_x-TiO_x coated [45] titanium substrate insoluble anode (TSIA) and stainless steel cathode.

2.1 Treatment in Batch Mode

The experimental setup of the batch reactor used for electrochemical degradation studies (see Fig. 2) consisted of a perspex cylinder of 350 mL capacity (diameter 6.3 cm, height 11.2 cm) with a PVC lid with provision for fitting a pair of electrodes. Provisions were also made in the lid for periodic sampling. A rectangular, stainless steel flat plate for use as the cathode and a rectangular flat expanded mesh of titanium (catalytic oxide coated) for use as the anode, each of dimensions 4 cm × 6.5 cm, were arranged parallel to each other with an inter electrode gap of 10 mm held inside the cell. The void fraction of the mesh type anode was 20% by area, which resulted in an effective area of 18.4 cm² (dipped area 4 cm × 5.75 cm). The electrodes were connected to a 5 A, 10 V DC regulated power supply, through an ammeter and a voltmeter. Preliminary batch experiments on COD removal were conducted to find the influencing parameters and their experimental domain. The wastewater was prepared by improvement of its ionic conductivity by adding the required amount of sodium chloride. Since the pH of the effluent was found to be less important in influencing the response, but was better at near neutral conditions during the preliminary runs, it was adjusted to neutral (pH 7). The electrode plates were cleaned manually by washing them in distilled water prior to every run. The electrodes were placed in the required volume of wastewater taken in the cell in such a way that 18.4 cm² of the active surface of the anode was immersed. The solution was constantly stirred at 200 rpm using a magnetic stirrer in order to maintain uniform concentration. DC power supply was given to the electrodes according to
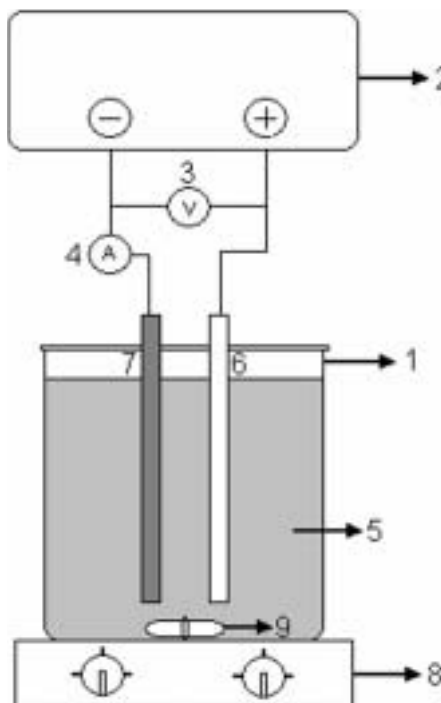

Figure 2. Experimental setup of the batch reactor: 1, electrochemical cell; 2, D.C. regulated power supply; 3, digital voltmeter; 4, digital ammeter; 5, wastewater; 6, anode; 7, cathode; 8, magnetic stirring controller; 9, magnetic stirring bar.

the required current density and the experiments were carried out under constant current conditions. The efficiency of the electrochemical reactor was studied at various conditions of current density and supporting electrolyte concentration. The effluent was treated at six different current densities, viz., 1.0, 1.5, 2.0, 2.5, 3 and 3.5 A/dm² and the holdup volume was 250 mL. The supporting electrolyte concentration was varied at 1, 2, 3 and 4 g/L. The progress of the pollutant removal was measured through COD at regular intervals for a duration of 6 h.

2.2 Treatment in Batch Recirculation Mode

The experimental setup of the batch recirculation/once through mode of operation used for the electrochemical degradation studies is schematically represented in Fig. 3. By adjusting the valves the same setup can be operated either in batch recirculation and once through modes (i.e., for batch recirculation mode of operation, streams 10 and 12 were be closed). The electrolytic flow reactor consisted of a cylindrical stainless steel cathode (20 cm long and 7.8 cm diameter) and a catalytic expanded mesh cylindrical (surface void fraction: 0.2) anode, coated with RuO_x-IrO_x-TiO_x, measuring 15.2 cm long and 3.7 cm diameter (active anode area 141.3 cm²). The anode
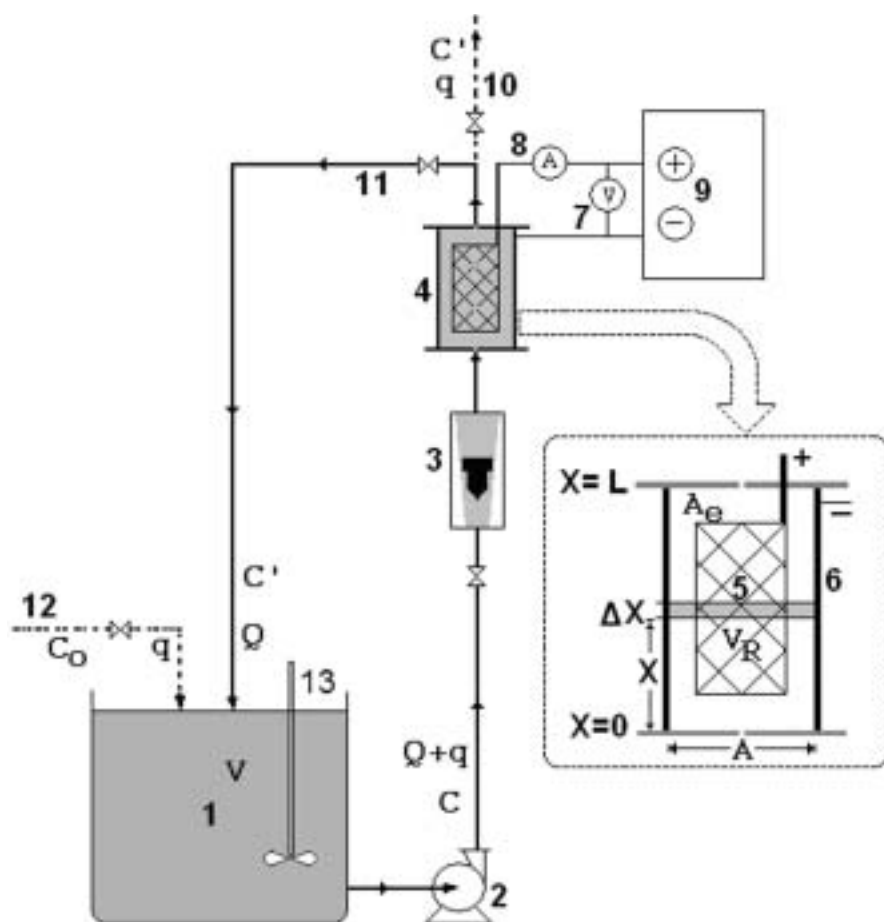
Figure 3. Experimental setup of the flow reactor: 1, reservoir; 2, pump; 3, rotameter; 4, cylindrical flow cell; 5, anode; 6, cathode; 7, digital voltmeter; 8, digital ammeter; 9, D. C. regulated power supply; 10, treated wastewater outlet; 11, recirculation stream; 12, wastewater inlet reactor; 13, mechanical agitator. For the batch recirculation system stream 10 and 12 will be absent and for once through operation stream 11 will be absent.

was held coaxially with the cathode with a constant inter electrode gap of 2.05 cm. Provisions were made for electrical connections so as to constitute an electrolytic cell. The cell had one inlet at the bottom cover and an outlet at the top cover. The electrodes were connected to a 5 A, 10 V DC regulated power supply, an ammeter and a voltmeter. The other components of the setup consisted of a 5.0 L capacity reservoir, a magnetically driven self priming centrifugal pump and a rotameter, connected using silicone rubber tubes. The required quantity of wastewater with 3 g/L of sodium chloride added was put into the reservoir. The contents of the reservoir were continuously stirred using a mechanical stirrer throughout the duration of experiment in order to ensure uniform concentration. The required flow rate through the reactor was established by pumping and adjusting the valves. The DC power supply of the required current density was given to the electrodes. Separate experiments were run for effluent volumes of 2.5 and 4.0 L. In each case the liquid flow rate into the reactor was varied (20, 40, 60, 80, 100 and 120 L/h). The flow rate of the effluent was measured using a calibrated rotameter. Every experimental case was run for a duration of 7 h. Samples were collected every hour from the reservoir for the estimation of COD.

2.3 Treatment in Once Through Mode

The reactor used in the investigation of the once through mode of operation was also of cylindrical type but dimensionally it was dif-

ferent from that of the reactor used in the batch recirculation system. The diameter and height of the reactor was 8 and 150 cm, respectively, and it functions as a cathode. The construction materials of the components were the same. The diameter and height of the anode measured 5 and 120 cm, respectively.

Wastewater with 3 g/L sodium chloride was put into the reservoir. The required flow rate through the reactor was established by pumping and adjusting the valves (i.e., stream 11 was closed). A 50 A and 20 V DC power supply was connected to the electrodes to keep the required level of current density. The liquid flow rate through the reactor (Q) was varied (2, 4, 6 and 8 L/h). A time duration of more than 3 times the residence time of the reactor was allowed before each sampling for COD estimation (i.e., for each experimental case, this time was allowed for the conditions to come to steady state in the new flow situation before sampling the outlet stream for COD estimation).

3 Design of the Reactor Model

Adopting the same classification for the reactors as for conventional reactors, to evaluate the electrochemical reaction rate (for removal of COD) in various basic electrochemical reactor configurations such as batch, batch recirculation and single pass systems, the following expressions were developed from first principles.

3.1 Batch Reactor

The batch reactor can be expressed as:

$$-\left(\frac{V_R}{A_e}\right)\frac{dC}{dt} = \frac{i_A}{zF} = kC \tag{30}$$

$$C = C_o \exp(-kat) \tag{31}$$

Or in integrated form one obtains:

$$-\ln\left[\frac{C}{C_o}\right] = kat$$

In electrochemical conversion, the high molecular weight aromatic compounds and aliphatic chains are broken down to intermediate products for further processing. In electrochemical reactions, the organics are completely oxidized to CO_2 and H_2O. The progress of the destruction of organic pollutants was monitored by COD estimation. The potentials required for oxidation of organic pollutants are generally high and the production of oxygen from the electrolysis of water molecules may determine the reaction yield.

3.2 Batch Reactor in Recirculation Mode

In the present flow reactor system, the flow was in the axial direction. For batch recirculation system streams 10 and 12 were absent. An approximate model which represented the given system in which the reactions take place can be described by a plug flow reactor (PFR). A dynamic material balance to each component or species in the reactor can be written as:

$$\left[\begin{array}{c}\text{rate of change mass of}\\\text{species in the reactor}\end{array}\right] = \left[\begin{array}{c}\text{rate of mass}\\\text{input}\end{array}\right] - \left[\begin{array}{c}\text{rate of mass}\\\text{output}\end{array}\right]$$

$$\pm \sum \left[\begin{array}{c}\text{rate of mass of species disappeared}\\\text{or generated physicochemicalphenomena}\end{array}\right]$$

The concentration variation of organics in the differential volume of the reactor (see Fig. 3) can be written as:

$$-A\Delta x\left(\frac{\partial C'}{\partial t}\right) = Q\left(\frac{\partial C'}{\partial x}\right)\Delta x + A\Delta x k_L a C' \tag{32}$$

The LHS represents the rate of change of COD in the differential volume of reactor, $A\,\Delta x$ where A is the cross section area of the reactor. The first term of the RHS is the net rate of change of COD due to the bulk flow in the differential volume, and Q is the volumetric flow rate through the reactor. The last term in the right hand side represents the rate of degradation of organic contaminants in the solution due to reaction.

Since the reservoir is continuously mixed using a mechanical agitator, it can be assumed to be a perfectly back-mixed system. The mass balance for the effluent reservoir is:

$$V\left(\frac{dC}{dt}\right) = QC' - QC \tag{33}$$

Further, it can also be assumed that the reactor is under steady state condition as $\partial C'/\partial t = 0$, and Eq. (32) can be rewritten as:

$$C' = C\exp(-k_L a\tau_R) = C\exp\left(-\frac{k_L A_e}{Q}\right) \tag{34}$$

where a is the specific electrode area (A_e/V_R) and τ_R is the residence time (V_R/Q) in the reactor.

The mass balance equation can be solved after substitution of the expression for C'. Knowing the initial COD, the resultant equation can be written as:

$$\frac{C}{C_o} = \exp\left[-\frac{t}{\tau}(1 - \exp(-k_L a\tau_R))\right]$$

$$= \exp\left[-\frac{t}{\tau}\left\{1 - \exp\left(\frac{-k_L A_e}{Q}\right)\right\}\right] \tag{35}$$

where C_o is the initial value of COD of waste water and τ is the residence time (V/Q) in the reservoir. From Eq. (35), k_L, the mass transfer coefficient, may be determined.

3.3 Single Pass Flow Reactor

The expression for outlet concentration in the flow reactor (single pass or once through mode of operation) is:

$$C' = C_o\exp(-k_L a\tau_R) = C_o\exp\left(-\frac{k_L A_e}{Q}\right) \tag{36}$$

Hence,

$$k_L = -Q\frac{A_e}{\ln}\left(\frac{C'}{C_o}\right) = -\frac{Q}{A_e}\ln(1 - X) \tag{37}$$

It should be noted that the extent of degradation is defined as $X = (C_o - C')/C_o$. The unconverted species are denoted as $(1 - X)$, (or C'/C_o).

The current efficiency (CE) of the electrolysis can be calculated using the following expression.

For a batch reactor:

$$CE = \frac{V_R\Delta C}{\left(\frac{16It}{2F}\right)} \times 100$$

For a flow reactor:

$$CE = \frac{Q\Delta C}{\left(\frac{16I}{2F}\right)} \times 100 \tag{38}$$

where ΔC is the difference in COD in mg/L, due to treatment by passing I current for t seconds. V_R is volume of the reactor (L). Q represents the volumetric flow rate in L/h and F is Faraday's constant.

While current efficiency indicates the fraction of the total current passed for the targeted reaction, the term specific energy consumption (SEC), is the quantity of energy consumed in the process for a kg of COD to get digested. The term (in $kW\,h\,kg^{-1}$) for batch reactors can be obtained using the following equations:

For a batch reactor:

$$SEC = \frac{VIt}{3600 \times 10^3}\frac{1}{\Delta COD \times V_R \times 10^{-6}}$$

For a flow reactor:

$$SEC = \frac{VI}{3600 \times 10^3}\frac{1}{\Delta COD \times Q \times 10^{-6}} \tag{39}$$

where V represents the applied cell voltage in volts and the remaining terms are defined above.

Table 2. Effect of current density and supporting electrolyte concentration on COD removal, specific energy consumption, current efficiency and rate constant in the batch reactor. Initial COD: 1200 mg/L, pH: 7, volume of effluent treated: 250 mL, specific electrode surface: 0.0736 cm^{-1}, Duration: 6 h.

CD (A/dm^2)	Salt conc. (g/L)	Cell Voltage (V)	COD final (mg/L)	COD reduction (%)	SEC (kW h (kg COD)$^{-1}$)	CE (%)	Mass flux (kg COD m^{-2}h^{-1})	Rate constant · 10^4 (cm/s)
1	1	9.2	638	46.8	72.29	42.61	0.0127	3.97
	2	5	511	57.4	32.05	52.26	0.0156	5.37
	3	3.4	410	65.8	19.01	59.9	0.0179	6.75
	4	3.2	375	68.8	17.13	62.63	0.0187	7.33
1.5	1	10.2	600	50	112.61	30.35	0.0136	4.36
	2	5.8	455	62.1	51.57	37.69	0.0169	6.1
	3	4	332	72.3	30.53	43.88	0.0197	8.08
	4	3.7	309	74.3	27.51	45.09	0.0202	8.55
2	1	11.6	470	60.8	140.34	27.68	0.0165	5.89
	2	6.4	325	72.9	64.6	33.18	0.0198	8.21
	3	4.3	211	82.4	38.4	37.51	0.0224	10.93
	4	4.2	186	84.5	36.58	38.46	0.023	11.73
2.5	1	12.9	300	75	158.24	27.31	0.0204	8.72
	2	7.3	222	81.5	82.4	29.68	0.0221	10.61
	3	5.1	131	89.1	52.67	32.45	0.0242	13.94
	4	4.8	109	90.9	48.57	33.1	0.0247	15.08
3	1	14.2	243	79.8	196.57	24.22	0.0217	10.06
	2	9	208	82.7	120.19	25.1	0.0225	11.04
	3	6.4	122	89.8	78.65	27.25	0.0244	14.36
	4	6	103	91.4	72.46	27.74	0.0248	15.43
3.5	1	16.5	233	80.6	263.73	20.96	0.0219	10.32
	2	10.7	202	83.2	165.71	21.64	0.0226	11.22
	3	7.6	111	90.8	107.87	23.62	0.0247	15.01
	4	7.2	97	91.9	100.89	23.9	0.025	15.81

4 Results and Discussion

The results of the experiments carried out in various basic electrochemical reactor configurations such as batch, batch recirculation and single pass systems are presented below.

4.1 Treatment in Batch Mode

Preliminary batch experiments showed that the current density, electrolysis duration and supporting electrolyte concentration considerably influenced the performance of the process. Process performance is defined in two ways, one with respect to the extent of reaction (X or COD removal) of the process and the other with respect to the consumption of energy, E (kW h (kg COD)$^{-1}$) of the process. The rate of the process, controlled by current density (see Eq. (31)), was evaluated in terms of the heterogeneous rate constant k_L (cm/s) by monitoring the extent of COD removal. The energy consumption was also defined in two ways. Determination of the current efficiency (CE) indicates the path and course of the targeted reaction by monitoring the extent of COD removal (see Eq. (38)). The actual utilization of energy in fulfilling the unit quantity of the targeted reaction (power consumption, E (k W h (kg COD)$^{-1}$), was found by monitoring the cell voltage and extent of COD removal (see Eq. (39)).

The results of the detailed batch experiments are reported in Tabs. 2 and 3 and in Figs. 4a) and 4b). Batch studies were useful in determining the operating parameters, such as electrolysis duration, supporting electrolyte concentration and current density, which gave better reactor performance. Table 2 shows that the increase in COD removal was marginal for current densities more than 2.5 A/dm^2 and supporting electrolyte concentrations of more

Table 3. Effect of supporting electrolyte concentration on instantaneous current efficiency, electrochemical oxidability index and electrochemical oxygen demand in the batch reactor. Current density: 2.5 A/dm^2, Initial COD: 1200 mg/L, pH: 7, volume of effluent treated: 250 mL, specific electrode surface: 0.0736 cm^{-1}.

Time (h)	Salt concentration (g/L)			
	1	2	3	4
		ICE		
0.083	0.78	1.18	1.18	1.57
1	0.57	0.71	0.83	0.88
2	0.58	0.66	0.87	0.87
3	0.42	0.46	0.52	0.53
4	0.35	0.35	0.29	0.31
5	0.23	0.22	0.23	0.2
6	0.21	0.18	0.11	0.11
7	0.07	0.05	0.03	0.03
		EOI		
7	0.4	0.46	0.5	0.54
		EOD		
7	0.236	0.25	0.248	0.262

than 3 g/L over the entire domain of experiment. Since post treatment for the removal of dissolved inorganic substances is cumbersome, the salt level in the wastewater has to be limited. Moreover, the current density is a direct measure of the energy consumption of the process and thus, should be limited for better overall economy of the process.

Figures 4a) and 4b) show the variation in COD and color removal with electrolysis time for various supporting electrolyte concentrations at a current density of 2.5 A/dm^2. It can be seen from the figures that the rate of COD removal decreased as the process progressed. The increase in pollutant removal performance of the proc-
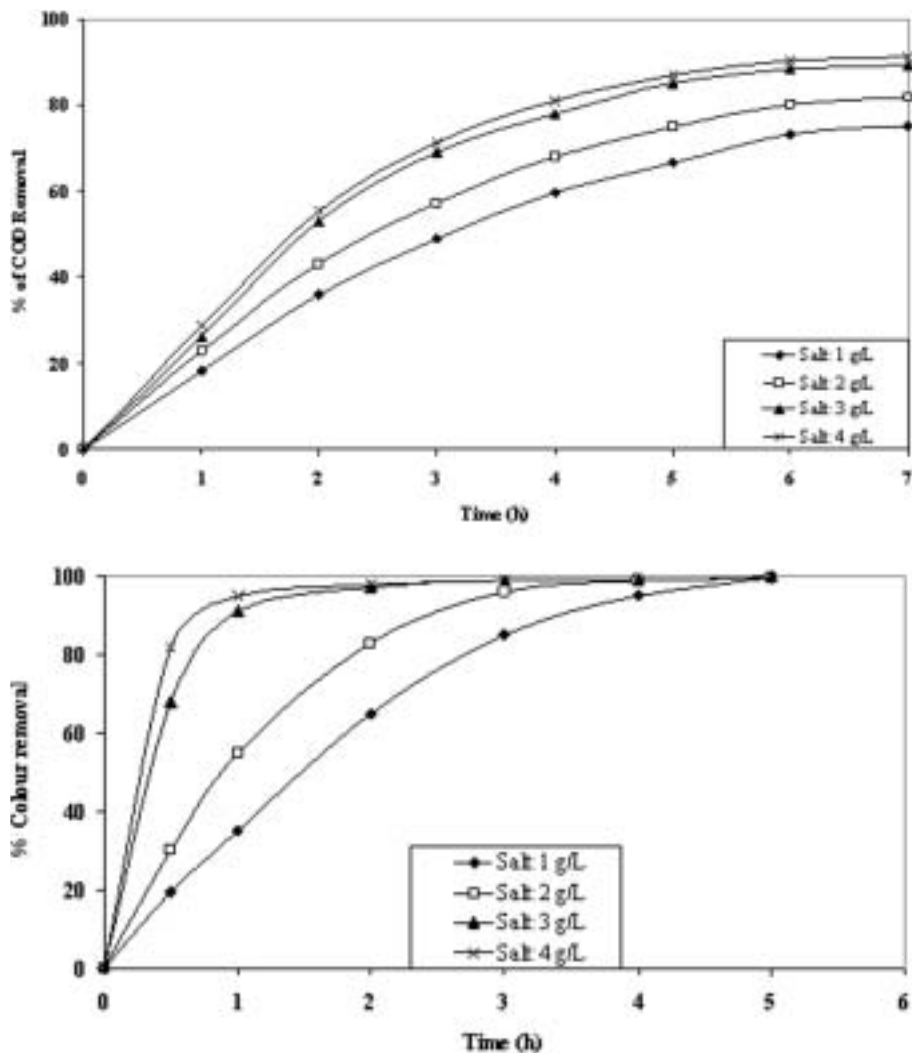
Figure 4. Effect of supporting electrolyte concentration in the batch reactor: a) COD removal and b) Color removal. Conditions: current density 2.5 A/dm^2, initial COD 1200 mg/L, pH 7, volume of effluent treated 250 mL, specific electrode surface 0.0736 cm^{-1}.

ess beyond 6 h of treatment was marginal. It can also be observed that the supporting electrolyte played a major role in the degradation of the organic matter present in the wastewater. Even though the pollutant removal performance of the system increased with an increase in salt levels, the change in the performance decreased monotonically as the salt concentration increased. From Tab. 2 it can be seen that an increase in supporting electrolyte concentration from 1 to 2 g/L resulted in an improvement from 73.2 to 80.2% in COD removal after 6 h of treatment at a current density of 2.5 A/dm^2. But the same improvement was less (from 88.3 to 90.3%) with an increase in supporting electrolyte concentrations at higher levels, i.e., from to 3 to 4 g/L. Removal of reactive dyes from real dyeing wastewater [46] reached 77% by electrooxidation using Ti/Pt as the anode, but unfortunately the potential value was not reported.

Trends in the heterogeneous rate constant k_L (cm/s), with respect to the variation in current density and supporting electrolyte concentration, were also studied in the batch mode of operation, and the results are presented in Tab. 2. There was a marked improvement in the value of k_L with an increase in salt concentration, especially at lower salt levels, probably due to the generation of more oxidizing agents from the additional amount of salt added in the effluent. With the addition of extra salt, the controlling step of the

process might have changed from a condition of oxidizing agents being limiting, to another limiting condition, such as limiting organic species.

Another important finding of the study was the current efficiency, CE (%) and the specific energy consumption, E (kWh kg^{-1}). As seen in Tab. 2, an increase in salt concentration improved the energy consumption of the process, especially at lower salt concentrations. This is because of the improved ionic conductance of the wastewater. Another noticeable result in Tab. 2 was the fact that an increase in current density decreased the current efficiency and increased the power consumption. The possibility of the loss of electrical energy in the form of heat and for unwanted reactions was greater at higher levels of current density. Thus, in general, a higher current density operation will improve the capacity utilization, at the expense of more energy loss. The mass flux reported in Tab. 2 was directly proportionality to both the current density and supporting electrolyte concentration in the experimental domain.

The instantaneous current efficiency (ICE), electrochemical oxidability index (EOI) and electrochemical oxygen demand (EOD) for the study are presented in Tab. 3. As seen in the table, the ICE decreased as the treatment proceeded. The values at a treatment duration of 5 min are reported. Values of ICE more than 1 indicate

Table 4: Effect of holdup volume and flow rate on COD and color removal, specific energy consumption, current efficiency and rate constant in the batch recirculation system. Current density: 2.5 A/dm^2, initial COD: 1200 mg/L, supporting electrolyte concentration: 3 g/L, pH: 7, area of anode: 141.3 cm^2, duration: 6 h.

Volume of effluent (L)	Flow (L/h)	Voltage (V)	COD		Absorbance		SEC (kW h (kg COD)$^{-1}$)	CE (%)	Mass flux (kg COD m^{-2}h^{-1})	Rate constant $\cdot 10^4$ (cm/s)
			COD (mg/L)	Rem. (%)	Ab. fin.	Rem. (%)				
2.5	20	5.3	505	57.9	0.029	99.9	64.67	27.46	0.0205	7.15
	40	5.2	433	63.9	0.026	99.91	57.49	30.3	0.0226	8.39
	60	5.1	382	68.2	0.0252	99.91	52.83	32.34	0.0241	9.42
	80	5.1	347	71.1	0.041	99.86	50.68	33.72	0.0252	10.2
	100	4.9	337	71.9	0.0584	99.8	48.15	34.09	0.0254	10.43
	120	4.9	325	72.9	0.02888	99.9	47.49	34.57	0.0258	10.72
4	20	5.3	636	47	0.02875	99.9	49.79	35.66	0.0266	8.41
	40	5.2	581	51.6	0.0468	99.84	44.5	39.15	0.0292	9.57
	60	5.1	523	56.4	0.05547	99.81	39.93	42.79	0.0319	10.93
	80	5.1	469	60.9	0.06439	99.78	36.98	46.21	0.0345	12.36
	100	4.9	457	61.9	0.08775	99.7	34.95	46.96	0.035	12.69
	120	4.9	456	62	0.11722	99.6	34.9	47.04	0.0351	12.72

the involvement of mechanisms other than electrochemical, e.g., chemical, in reducing the COD of the effluent. Lower ICE values towards the completion of the process indicated more energy wastage. The time average ICE reported as EOI increased with an increase in the supporting electrolyte concentration. But the rate of change of EOI decreased with an increase in the concentration of salt. The magnitude of EOI showed that the effluent was relatively easy to treat by electrochemical means. The relatively lower average EOD value of 0.25 (the weight of oxygen evolved per unit weight of organic matter removed) confirmed the attractive average energy efficiency of the process.

Fig. 4b) shows that the removal of color was relatively fast. Reactive dyes were removed with 87 – 100% efficiency in terms of color removal [47] by using an electrode made of carbon fiber and a piece of iron after 60 min treatment applying a high potential of 25 V. Moreover, the supporting electrolyte played a significant role in the color removal ability of the technique. More than 99% color was found to be removed when operated with a salt concentration of 3 g/L for 3 h.

The batch study showed that the voltage decreased almost exponentially from 12.9 to 4.8 V as the supporting electrolyte concentration varied from 1 to 4 mg/L at the end of 6 h of treatment at a current density of 2.5 A/dm^2. The effect of influent COD variation from 1190 to 1210 mg/L (i.e., 1200 ± 10 mg/L) on system performance was studied, and the variation was found to be less than 2% on all four performance terms. Interference from Cl$^-$ in the range of its concentration in the investigation (up to 4 mg/L) was noticed during the estimation of COD. To overcome this, HgSO$_4$ was added in addition to AgSO$_4$, as recommended in [44].

4.2 Batch Reactor in Recirculation Mode

The dynamic response of COD removal performance of the system was studied at various flow rates, Q at constant conditions of current density (2.5 A/dm^2), supporting electrolyte concentration (3 g/L) and initial COD (1200 ± 10 mg/L); and the results are presented in Fig. 5a). There was an increase in percentage COD removal of the process with respect to time as shown in Fig. 5a). The improvement in the process performance after 6 h of operation was marginal. It can also be seen that the pollutant removal performance of the system

improved considerably with an increase in the flow rate. As seen in Tab. 4, the COD removal of the system after 6 h of operation was found to be 57.9 and 72.9% at circulation flow rates of 20 and 120 L/h, respectively, when 2.5 L of the effluent was treated. This may be due to the enhancement of the transfer coefficient at higher flow rates. Pollutant removal performance and energy consumption performance of the system was studied with respect to the variation in flow rates for a treatment duration of 6 h at constant conditions as explained above. The results are presented in Tab. 4.

As seen in Tab. 4, the improvement in voltage (5.3 to 4.9 V) and in COD removal (57.9 to 72.9%) resulted in a considerable improvement in CE (27.46 to 34.57%) and specific power consumption, E (64.67 to 47.49 kW h kg^{-1}) of the system when the flow rate (Q, L/h) increased from 20 to 120 L/h for 2.5 L of effluent treated. This may be due to improved ionic conductivity by bulk movement and the reduction of resistance on the electrode surface. The quantity of pollutant removed was increased by a factor of 1.5 by this change in flow rate, as indicated by the values of the heterogeneous rate constant, k_L (7.15 · 10^{-4} to 10.72 · 10^{-4} cm/s).

The effect of the specific electrode surface on COD removal was studied by a batch recirculation process with various treatment volumes, but with the same electrode area. The results presented in Tab. 4 show that the COD removal decreased as the specific electrode area decreased. The percentage of COD removal reduced by an average of 1.2 times due to a decrease in the specific electrode surface, A_e/V_R (from 0.056 to 0.035 cm^{-1}). A decrease in the specific electrode surface caused a major increase in the value of k_L (cm/s). This may be due to the increase of the dye/oxidant ratio when the specific electrode surface is low. Even though the amount of reaction was greater, the extent of reaction was poor. The table also shows that the operation was more energy efficient when the specific electrode surface was low. As reported above, this may be due to the availability of relatively greater amounts of dye at these conditions. In general, the operation with a smaller value for specific electrode surface was advantageous because of the high capacity of operation or degradation of more amounts of pollutants at better energy figures, but with a poor extent of completion of the process. Color is found to be removed by more than 99% at all the conditions studied in the batch recirculation for 6 h of operation.

Correlating the mass transfer coefficient with the velocity of effluent flowing through the reactor was attempted:

Table 5. Effect of current density and flow rate on completion of COD removal, specific energy consumption, current efficiency and rate constant in the once through reactor. pH: 7, supporting electrolyte concentration: 3 g/L, initial COD: 1200 mg/L, volume of effluent treated: 2500 mL, specific electrode surface: 0.0565 cm^{-1}.

Current Density (A/dm^2)	Flow rate (L/h)	Cell Volt. (V)	COD removal (%)	SEC (kWh/(kg COD)$^{-1}$)	CE (%)	Mass flux (kg COD m^{-2}h^{-1})	Rate constant · 10^4 (cm/s)
1	2	3.3	44.1	47.02	23.51	0.007	2.14
	4	3.3	38.4	27	40.95	0.0122	3.57
	6	3.2	30.9	21.69	49.43	0.0148	4.09
	8	3.2	28.8	17.45	61.42	0.0183	5.01
	10	3.2	23.5	17.11	62.65	0.0187	4.93
1.5	2	4	59	63.9	20.97	0.0094	3.28
	4	3.9	46.9	39.19	33.34	0.0149	4.66
	6	3.9	35.2	34.81	37.54	0.0168	4.8
	8	3.8	32	27.98	45.5	0.0204	5.68
	10	3.8	26.7	26.83	47.45	0.0212	5.72
2	2	4.3	70.7	76.43	18.85	0.0113	4.52
	4	4.3	53.6	50.41	28.58	0.0171	5.66
	6	4.2	38.6	45.58	30.87	0.0184	5.39
	8	4.1	33.5	38.45	35.72	0.0213	6.01
	10	4.1	27.5	37.47	36.66	0.0219	5.92
2.5	2	4.9	79.2	97.18	16.89	0.0126	5.78
	4	4.8	57.8	65.22	24.66	0.0184	6.36
	6	4.8	42	59.84	26.87	0.0201	6.02
	8	4.8	36.7	51.36	31.31	0.0234	6.74
	10	4.8	29.6	50.94	31.57	0.0236	6.47

$$k_L = a\, u^b \tag{40}$$

By graphically solving the above equation, the values of a and b were obtained as 0.0012 and 0.234, respectively, when 2.5 L of the effluent is treated. The R^2 value of the model (0.989) was quite good and shows the ability to predict the rate constant. The Reynolds Number was found to vary from 90.7 to 544.1 as the flow rate varied from 20 to 120 L/h, which indicated that the flow was laminar. The value of the exponent (0.234) of u in Eq. (40) supports this. This correlation indicated that there is scope for augmentation of the mass transfer of the system by improving turbulence.

4.3 Single Pass Flow Reactor

The pollutant removal and energy consumption performance of the single pass flow reactor were studied by varying the current density (1 to 2.5 A/dm^2) and flow rate (2 to 10 L/h), and the results are presented in Fig. 5b) and Tab. 5. As seen in Tab. 5, there was a marked increase in COD removal with increasing current density, especially at lower flow rate conditions. In other words, operation of the cell at a higher current density levels enabled more COD removal at an improved rate, at the expense of greater energy wastage and more unwanted side reactions.

An increase in the flow rate resulted in a decrease in COD removal, especially at lower flow rates. This may be due to the reduction in residence time. In general the performance terms of the system, such as specific energy consumption, current efficiency and rate constant, improved by an increase in the flow rate at the expense of lower process completion.

5 Conclusions

The electrochemical degradation of simulated RB5 dye effluent was investigated in various types of reactor configurations such as
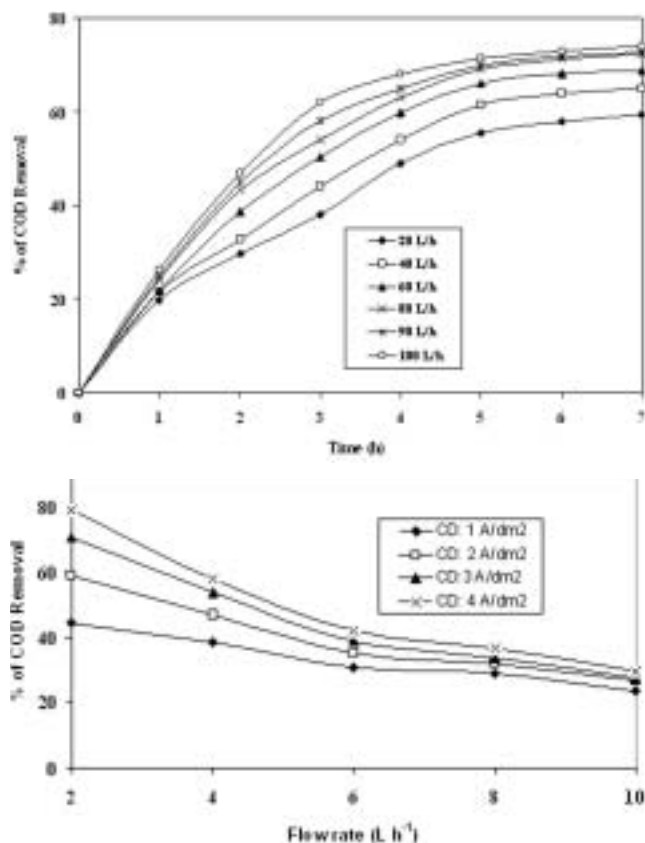
Figure 5. Effect of flow rate on COD removal: a) 2500 mL effluent treated in the batch recirculation system (specific electrode surface 0.0565 cm^{-1}) and b) 7540 mL effluent treated in the once through reactor (specific electrode surface 0.2 cm^{-1}). Conditions: current density 2.5 A/dm^2, initial COD 1200 mg/L, supporting electrolyte concentration 3 g/L, pH 7.

batch, batch recirculation and single pass systems. The effect of important operating parameters such as current density, electrolysis time, supporting electrolyte concentration and specific electrode surface on pollutant removal and energy consumption performance of these systems were critically examined. The results show that electrooxidation can be a viable treatment technique for RB5 effluent.

Batch studies show the operating parameters of; current density: 2.5 A/dm², electrolysis duration: 6 h, and supporting electrolyte concentration: 3 g/L, were optimal for better overall performance of the system. Color removal was almost complete after 3 h of treatment in all combinations of the parameters studied in the experimental domain. The heterogeneous rate constant (cm/s), instantaneous current efficiency, electrochemical oxidability index and electrochemical oxygen demand were also reported.

The pollutant removal performance of the batch recirculation system was found to improve considerably with an increase in the flow rate. The improvement in voltage (5.3 to 4.9 V) and in COD removal (57.9 to 72.9%) resulted in a considerable improvement in CE (27.46 to 34.57%) and E (64.67 to 47.49 kWh kg⁻¹) of the system when the flow rate (Q, L/h) increased from 20 to 120 L/h for 2.5 L of the effluent treated. Operation of the batch recirculation system at varied reactor holdup (specific electrode surface) showed that the capacity utilization and energy figures improved considerably with a decrease in the specific electrode surface, with little effect on the completion of the process.

A single pass operation was found to give a lower extent of process completion due to less residence time. In order to get a comparable residence time as the batch systems studied, the feed rate could be reduced, the reactor volume could be increased, or both of these. While the reduction in flow rate limits the process by a reduction in transfer coefficients, an increase in reactor volume needs greater capital investment. Performance of the batch recirculation system was found to be better comparatively, with respect to capacity utilization and energy figures.

Symbols Used

A_e	[dm²]	electrode area
A	[cm²]	cross sectional area of the reactor
a	[cm⁻¹]	specific electrode area A_e/V_R
b	[V⁻¹]	Tafel slope
C	[mg/L]	
C_o	[mg/L]	initial value of COD of waste water
C'	[mg/L]	
ΔC	[mg/L]	difference in COD due to treatment by passing I current for t seconds
E	[kWh/kg]	power consumption
E	[V]	cell potential
F	[Ah/mol]	Faradays constant
I_A	[A]	charge passed in time t
i_A	[A/dm²]	current density I_A/A_e
k_L	[cm/s]	heterogeneous rate constant
M_A	[g/mol]	molecular weight
n, z	[–]	number of electrons transferred per mole of reaction
Q	[L/h]	flow rate
t	[h]	time
r_i	[mol/L h]	rate of reaction
V	[V]	applied cell voltage
V_R	[L]	reactor volume
X	[–]	extent of reaction
Δx	[cm]	reactor axial differential distance
t	[h]	total time elapsed

t	[s]	residence time (V/Q) in the reservoir
τ_R	[s]	residence time (V_R/Q)

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