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Dye Destruction and Simultaneous Generation of Sodium Hydroxide Using a Divided Electrochemical Reactor

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Textile dye bath effluent contains high concentrations of organic dye, sodium chloride, and other chemicals which inhibit the activity of microorganisms during biological oxidation. Hence high concentrations of organic dye and total dissolved solids have to be removed considerably before biological treatment. In this paper, degradation of dye effluent and simultaneous generation of caustic soda in an electrochemical membrane cell was investigated. Experiments were carried out at different current densities and different flow rates using Ti/RuO₂/IrO₂ as anode and stainless steel as cathode. In the present study of dye effluent treatment the results showed that the electrochemical process could effectively remove COD and color by anodic oxidation (92.16% and 100%) and concentrate caustic soda from 40 to 210.28 g L^{-1}.

1. Introduction

Textile processing industries are widespread sectors in developing countries. Among the various processes in the textile industry, the dyeing process uses large volumes of water for dyeing, fixing, and washing. Thus, the wastewaters generated from the textile processing industries contain suspended solids, high amounts of dissolved solids, unreacted dyestuffs (color), and other auxiliary chemicals that are used in the various stages of dyeing and processing. The conventional method of textile wastewater treatment consists of chemical coagulation, and biological treatment followed by activated carbon adsorption. The conventional coagulation process generates a huge volume of hazardous sludge and poses a problem of sludge disposal. The biological treatment of textile wastewater shows low degradation efficiency because of the presence of biologically inert high molecular weight dyestuffs.[1,2] Hence many investigators are studying alternative oxidation methods such as ozonation, photocatalytic oxidation, and electrochemical oxidation. The photocatalytic oxidation experiments were conducted for Acid Blue 80, Acid Orange 7, Brilliant Orange K-R, and Reactive Orange 16.[3–6] Electrochemically assisted photochemical degradation was also conducted to improve the degradation efficiency of the dye.[7] The ozonation process was studied for the removal of color and chemical oxygen demand (COD), however; this process showed less COD removal.[8,9] Researchers also investigated electrocoagulation methods for textile dye removal using aluminum or iron electrodes.[10–14] Several researchers have studied the feasibility of electrochemical degradation of textile dyes using various electrode materials for wastewater treatment. Electrochemical degradation of different dye compounds was studied using titanium-based DSA (dimensionally stable anodes) electrodes, platinum electrodes, diamond and metal alloy electrodes, and boron-doped diamond electrodes.[5–18] The membrane processes can meet the requirements of nanofiltration and reverse osmosis (RO), which retain not only relatively small organic molecules but also ions from dye wastewater. Removal of auxiliary chemicals, salt, and color from dye wastewater can thus be achieved in one step.[19] However, high osmotic

pressure differences limit the applicability of the RO process. RO membrane filtration has problems with fouling, which result in low fluxes and poor separation efficiency.[20,21] Nerini et al. studied the mediated electrochemical oxidation of organic pollutants in the presence of NaCl.[22] The electrochemical treatment of Procion Black 5B using a cylindrical flow reactor, a pilot plant, was studied earlier.[23] As all the above processes need pretreatment, they increase treatment costs. Considering the very stringent environmental regulations, there is an urgent need for development of alternative but cost-effective methods. This necessitates developing a laboratory-scale study of electrochemical membrane techniques for treatment purposes. Most investigators provided information on color and COD removal during the dye degradation and not provided for the recovery of chemicals (caustic soda) by an electrochemical-membrane process. Hence, in the present study, an attempt was made to generate sodium hydroxide (98−99%) as a byproduct during degradation of dye effluent, using a commercially available electrolytic divided cell.

2. Experimental Section

All the reagents used were of analytical grade. Procion Black 5B is a commercial azo dye whose color index is 20505 CI Reactive Black 5. It contains two chromogenic systems. The structure of the dye is shown in Figure 1, and the experimental setup is shown in Figure 2. Nafion 315 cation exchange membrane was used in the experiment. All the solutions were prepared with distilled water. Industrial dye effluent (dye bath) obtained from the Indian textile industry contains 54 g L^{-1} sodium chloride, 12.8 g L^{-1} sodium carbonate, 6.2 g L^{-1} sodium hydroxide, and other organic compounds (dye, surfactant). For investigations a synthetic dye effluent containing 1 g L^{-1} dye, 50 g L^{-1} sodium
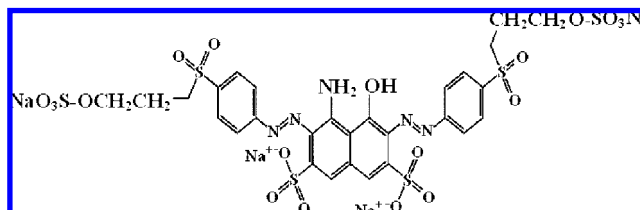

Figure 1. Structure of Procion Black 5B.

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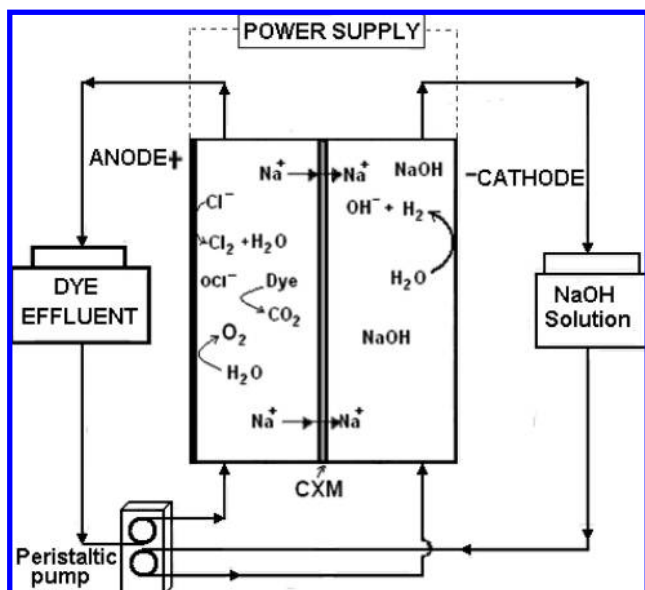
Figure 2. Experimental setup.

Table 1. Characteristics of the Dye Effluent Before and After Treatment

	Procion Black 5B dye bath effluent	
parameters	before treatment	after treatment[a]
pH	12	2
COD (mg L^{-1})	4080	320
TSS (mg L^{-1})	530	90
TDS (mg L^{-1})	680 200	59 280
chloride (mg L^{-1})	31 060	16 860
sodium chloride (mg L^{-1})	50 000	
molecular weight	992	
color index	20505 CI Reactive Black 5B	

[a] Current density 2.5 A dm^{-2} for 12 h.

chloride, 12 g L^{-1} sodium carbonate, and 5 g L^{-1} sodium hydroxide was prepared. The characteristics of the dye effluent before and after electrochemical treatment are shown in Table 1.

2.1. Instruments and Analysis Procedure. The analytical methods of determinations of the COD of all samples were by the dichromate reflux method.[24] The concentration of sodium hydroxide was determined by titration with HCl using phenolphthalein as indicator. The oxidized products and the reduction in dye concentration were measured by using a UV−visible spectrophotometer (Systronics 118). The color removal was calculated according to the following formula:

$$\% \text{ color removal} = 100\frac{\text{ABS}_o^M - \text{ABS}^M}{\text{ABS}_o^M} \quad (1)$$

where ABS^M is the average of absorbance values at its maximum absorbency value of visible wavelength (λ_{max}). ABS_o^M and ABS^M are the values before and after the degradation process.

Analysis of Procion Black 5B and its degradation products was also carried out on a high-performance liquid chromatograph (HPLC), consisting of a Waters Model 501 pump (flow rate 0.5−1.0 mL min^{-1}), Rheodyne injector containing a 20 μL sample loop, and Waters Model 440 UV absorbance detector operated at 254 nm. The detector output was processed with peak simple software. Separation was achieved on a reverse phase C18 (25 cm × 4.6 mm) stainless steel column, using 40:60 to 70:30 (v/v) methanol:sodium phos-
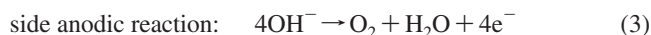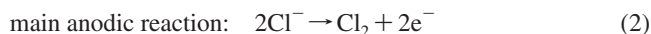
phate buffer (pH 2) as the mobile phase. All solvents used were Fisher Scientific HPLC grade.

2.2. Electrochemical Membrane Cell. The electrochemical reactor consisted of a titanium expanded mesh anode coated with TiO$_2$/RuO$_2$/IrO$_2$ and had an area of 0.4 dm^2; the stainless steel cathode of size 70 mm × 70 mm × 1 mm and the cation-selective membrane (Nafion 315) were fixed in a PVC frame with gaskets so that the cell was divided into two compartments. The distance between electrodes was 1.5 cm. The reactor was connected to a 2 A and 30 V dc APLAB regulated power supply. The anolyte compartment connected to a 6 L capacity effluent reservoir and catholyte compartment was connected to a 500 mL capacity sodium hydroxide reservoir. Both compartment reservoirs were connected to the peristaltic pump using silicone rubber tubes.
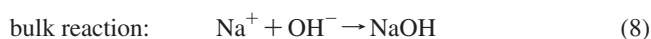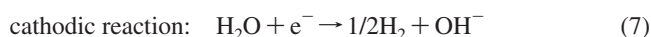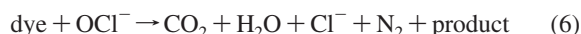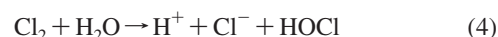
2.3. Experimental Procedure. About 5 L of dye effluent was passed through the anolyte compartment, and 200 mL of 40 g L^{-1} caustic soda solution was passed through the catholyte compartment using a double head peristaltic pump under batch recirculation mode at different flow rates of 25, 50, 75, 100, and 125 mL min^{-1}. The hardness of the effluent was automatically removed due to increasing pH (pH of the dye effluent was 12) and then filtered using a glass wool/micron filter to remove the suspended solids. This filtration significantly helped to avoid fouling of the membranes. Whenever the membrane becomes fouled, the cell voltages increases and the membrane needs cleaning. During the electrolysis at various current densities and various flow rates, recovery of caustic soda, COD reduction, color analysis, and HPLC data were measured. The various experimental conditions and parameters measured in the effluent are depicted in the respective figures and tables.

3. Results and Discussion

3.1. Mechanism of Dye Degradation and Recovery Of Caustic Soda. Most of the reactive dye effluents contain sodium chloride as the major constituent because in reactive dyeing of cotton process sodium chloride is used as exhausting agent. The method of treating of such solutions electrochemically is clean and easy as they involve no addition of chemicals for supporting the electrolysis in most cases. In the present study, the amount of sodium chloride present in the effluent is 50 000 mg L^{-1}, which is acts as a supporting electrolyte. The electrochemical reactions that take place during the electrolysis are complicated and are not entirely known. For the time being only assumptions can be made, based on the products that can be measured. Hence the following reactions are assumed to take place in the anodic and cathodic compartments along with bulk reactions:

main anodic reaction: $2Cl^- \rightarrow Cl_2 + 2e^-$ (2)

side anodic reaction: $4OH^- \rightarrow O_2 + H_2O + 4e^-$ (3)

bulk reactions in the anodic compartment:

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (4)$$

$$HOCl \leftrightarrow H^+ + OCl^- \quad (5)$$

$$\text{dye} + OCl^- \rightarrow CO_2 + H_2O + Cl^- + N_2 + \text{product} \quad (6)$$

cathodic reaction: $H_2O + e^- \rightarrow 1/2H_2 + OH^-$ (7)

bulk reaction: $Na^+ + OH^- \rightarrow NaOH$ (8)

Table 2. Destruction of Dye Effluent and Simultaneous Recovery of Sodium Hydroxide

| sample no.	current density (A dm^{-2})	cell voltage (V)	recovery of NaOH (g L^{-1})	energy consumption for NaOH generation (kWh kg^{-1})	energy consumption for COD removal (kWh kg^{-1})	overall energy consumption (kWh kg^{-1})
1	5	4.6	210.28	3.176	5.755	2.047
2	2.5	4.1	126.72	2.781	3.547	1.559
3	2	3.8	108.23	2.619	3.193	1.439
4	1.5	3.5	89.16	2.515	2.81	1.327
5	1	3.1	72.18	2.265	2.28	1.136

For textile industry effluents, the application of indirect electrochemical oxidation mediated by chlorine/hypochlorite was studied earlier.[25] Color removal and COD reduction occurred only in the presence of sodium chloride. Thus, decolorization occurs in the dye effluent because of the reaction between the generated chlorine/hypochlorite and the dye molecule. The indirect electrochemical treatment involves the application of an electrical current to the wastewater containing chloride to convert chloride to chlorine/hypochlorite which oxidizes the pollutants and is then reduced to chloride ion. In this process the dye effluent enters at the anolyte side of the cell. Sodium ions migrate across the membrane into the catholyte. Hydroxide forms at the cathode by the reduction of water. The catholyte product is thus sodium hydroxide or caustic soda. Chloride ions migrate to the anode. Hypochlorous acid (HOCl) which forms at the anolyte oxidizes the dye effluent.

3.2. Effect of Current Density and Flow Rate. The results of the experiments that were conducted at the flow rate of 50 mL min^{-1} and at five different current densities of 1.0, 1.5, 2.0, 2.5, and 5.0 A dm^{-2} are presented in Tables 1 and 2 as well in Figures 3 and 4. The COD reduction was increased with increase in electrolysis time and current density (Figure 3). This might be due to the fact that the rate of generation of hypochlorite (OCl$^-$) increased with increase in current density, which eventually increased the pollutant degradation. The increase in hypochlorite (OCl$^-$) reaches equilibrium with the degradation of organics present in the effluent. For a given supporting electrolyte in the anolyte concentration, a pseudosteady state[23] between the generation of hypochlorite (OCl$^-$) and the degradation of pollutant may be arrived at when the current density increases. In 12 h of operation of the cell the maximum COD reduction was found to be 92.16% at 5 A dm^{-2}.

Figure 4 shows the residual dye concentration that was measured spectroscopically and associated with the decrease in the absorbance at the peak of maximum visible wavelength and expressed in terms of percentage. The decolorization efficiency was observed as 99.48% with a current density of 2.5 A/dm^2 for 12 h, and then it remained almost constant at higher current densities.

The initial and final pH values of the wastewater observed in the treatment process are presented in Table 1. The value of pH decreases gradually during the electrochemical reaction because of migration. The pH decrease is dependent on the operating conditions employed (e.g., current density, NaCl concentration, recirculation time). However, the final pH value was around ~2. This is due to the migration of Na$^+$ ions toward the cathode compartment and the formation of hypochlorous acid in the anolyte compartment. Increase in the current density and the electrolysis time was attributed to the increased formation of OCl$^-$ in the anolyte solution. In the case of an undivided cell system, the pH was increased from 10.6 to 13.6.[23] In both cases the current density degradation of dye increases linearly. In the case of the

undivided cell system COD reduction achieved was around 74%. However, in the divided cell system the COD reduction
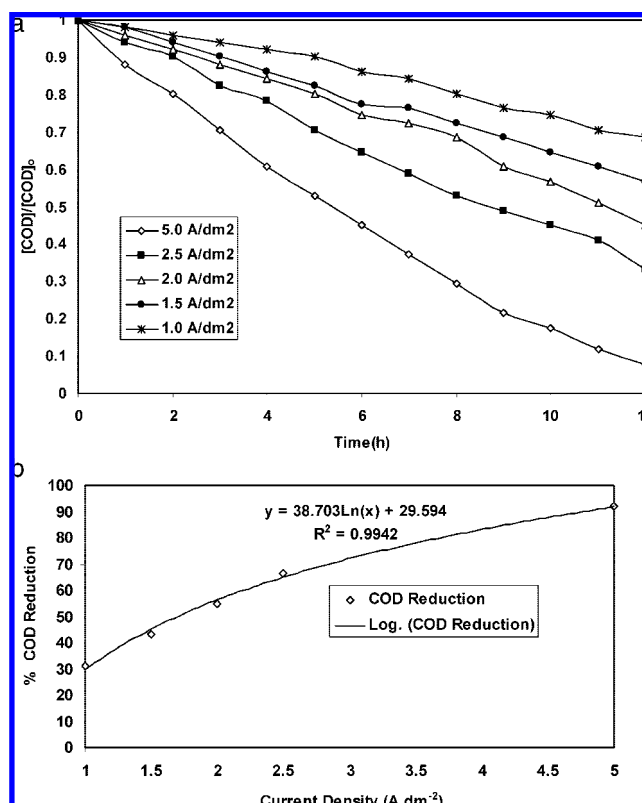

Figure 3. (a) Variation of the extent of unconverted COD with electrolysis time at various current densities. Conditions: [COD]$_0$ = 4080 mg L^{-1}; [NaCl] = 50 g L^{-1}; flow rate = 50 mL min^{-1}. (b) Effect of current density on COD reduction. Conditions: same as (a) and duration of electrolysis = 12 h.
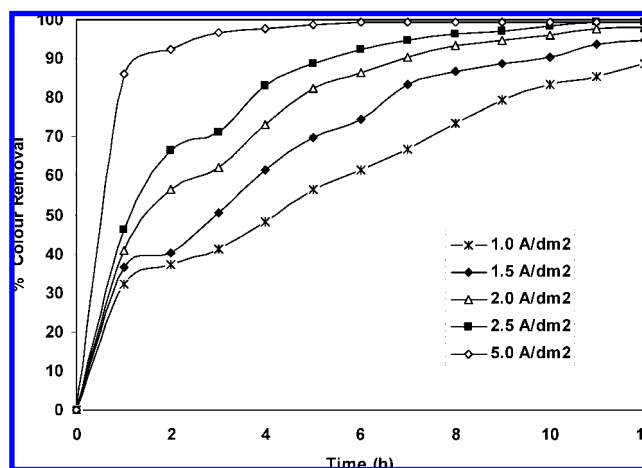
Figure 4. Color removal efficiency with time at various current densities. Conditions: same as Figure 3a.
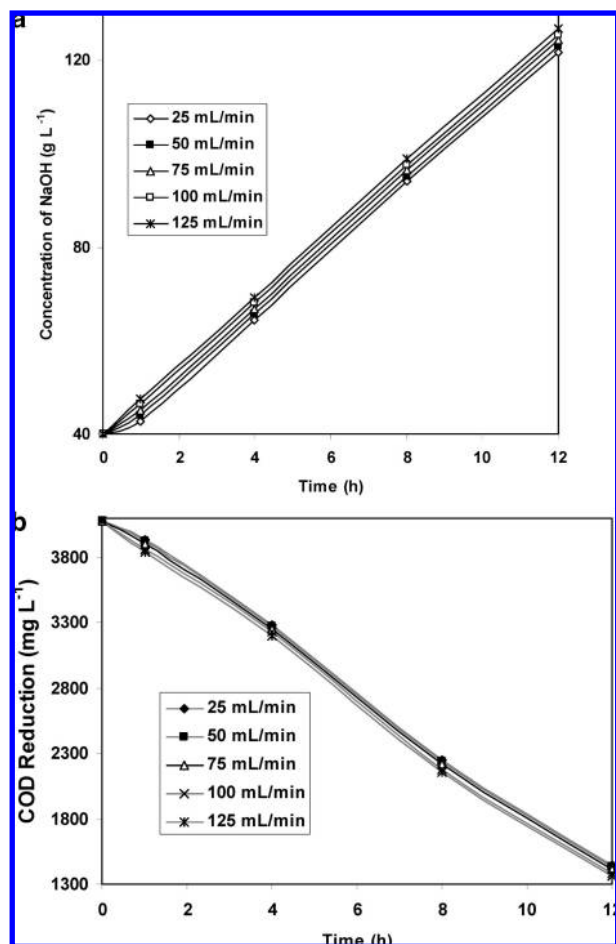
Figure 5. (a) NaOH buildup from 40 g L^{-1} with time at different flow rates at current density of 2.5 A dm^{-2}. (b) COD reduction from 4080 mg L^{-1} with time at different flow rates at current density of 2.5 A dm^{-2}.

achieved was 92.16% due to more generation of ClO$^-$ ions and HClO due to decrease in the pH from 12 to around 2.

The pH influences strongly the degradation process; in fact, in acid media (<2) the main active species is Cl$_2$, in neutral media HClO is the active species, and in alkaline media (>11) the active species is ClO$^-$. Furthermore, at pH close to neutrality a large amount of chlorate is formed. It should be noted that pH has a significant effect on the electrochemical degradation of organics over titanium catalytic coated anodes in the pH range 2−12.

Figure 5 shows the reduction of COD and recovery of NaOH with time at different flow rates of 25, 50, 75, 100, and 125 mL min^{-1}. As seen from the figure, the trend of the COD reduction and the recovery of NaOH were strongly influenced by the hydrodynamic conditions and, in particular, the degradation of dye and NaOH generation were favored by a high flow rate, indicating that oxidation and generation are mass transfer controlled processes.

3.3. Current Efficiency and NaOH Recovery. The theoretical amount of the cathodic generation of NaOH can be computed by Faraday's law. According to Faraday's law, 1 g-mol of products will be produced when 1 faraday of charge is applied. Since cathodic reduction of sodium is a one-electron-transfer reaction, the current efficiency (CE) can thus be calculated by eq 10:

$$m = \frac{ItM}{zF} \quad (9)$$

$$CE = \frac{m'}{m} \times 100 \quad (10)$$

where I is the current in amperes, t is the time in seconds, F is the Faraday constant (96 487 C mol^{-1}), M is the molecular weight of NaOH (g mol^{-1}), z is the number of electrons transferred in the reaction, m' is the experimental yield, and m is the theoretical quantity of NaOH. The percent current efficiency for recovery of NaOH is shown in Figure 6. In the first four current densities, the current efficiencies were found to be 91.64, 93.34, 97.15, and 99.26%, respectively; the current efficiency was found to increase linearly up to 2.5 A dm^{-2}. When the current density increased to 5.0 A dm^{-2}, the current efficiency fell to 96.98%. The current efficiency (CE) of dye degradation can be calculated from COD values using the following relation.[26]

$$CE = \frac{COD_t - COD_{t+\Delta t}}{8 I \Delta t} F V \times 100 \quad (11)$$

where t and Δt denote the time in seconds, I is the current (amperes), F is the Faraday constant (96 487 C mol^{-1}), V is the volume of the electrolyte (dm^3), and 8 is the equivalent weight of oxygen. In the electrochemical degradation of pulp and paper mill wastewater, Mishra et al.[27] had reported current efficiencies ranging from 400 to 500% and others[28] reported current efficiency increases above 100%. In this investigation, too, for indirect electrochemical degradation of dye effluent the current efficiencies increased above 100%. Here formation of such as chlorine (Cl$_2$), hypochlorite (OCl$^-$), and chlorate (ClO$_3^-$) may occur and these intermediate products may chemically oxidize dye effluent in a long period of electrolysis. The current efficiency depends on the current density as well as the types of anions and residence time. Significantly enhanced current efficiency, up to 455.87%, was obtained. The current efficiency decreases with an increase in the current density. During the electrolysis, the increase in the current density decreases the
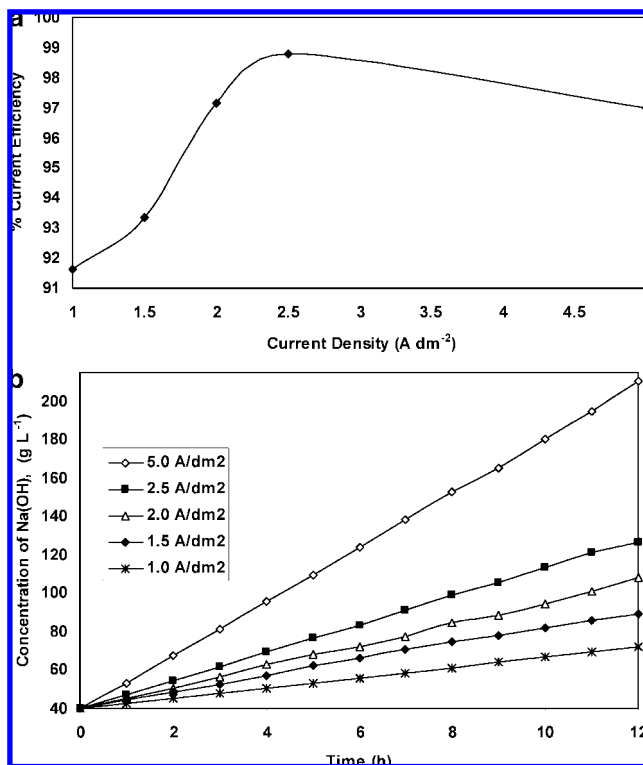
Figure 6. Effect of current efficiency on NaOH production at different current densities.
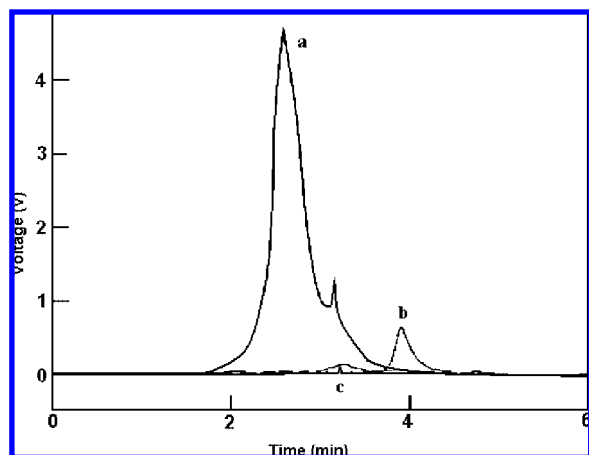
Figure 7. HPLC data for initial Procion Black 5B (a) and Procion Black 5B at 2.5 (b) and 5.0 A dm^{-2} (c) for 12 h electrolysis time.

current efficiency from 455.87% to 267.83%. Again it should be noted that COD is not a chemical compound to follow Faraday's law in a thermodynamic sense. These higher value efficiencies may only indicate that there exists a large chemical reaction to contribute to COD reduction. During the electrolysis, the higher current efficiency value is obtained due to an initial period of electrolysis, when the effluent contains more sodium chloride (50 g L^{-1}) and oxidized products of sodium chloride enhance the high CE. Also indirect oxidation of the process is dependent on the operating conditions employed (e.g., electrode, current density, NaCl concentration, recirculation time). At higher current density, the size of the bubble was large, which leads to an increase in resistance and hence an increase in the cell voltage (3.1 to 4.6 V).

Figure 6b shows the buildup of NaOH concentration with time for different current densities. At 5 A dm^{-2}, the recovery of NaOH maximum obtained was from 40 to 210.28 g L^{-1} and in the other four current densities (1, 1.5, 2 and 2.5 A dm^{-2}) recoveries of NaOH were found to be 72.18, 89.16, 108.23, and 126.72 g L^{-1}, respectively.

3.4. High-Performance Liquid Chromatography (HPLC). The HPLC samples were prepared from ether-extracted dried solution. The residue was dissolved in a small volume of HPLC-grade methanol, and the same sample was used for HPLC. Figure 7 shows the HPLC plots for the following three samples: the initial dye Procion Black 5B represented by plot a and the other two samples represented by graphs b and c for the residues obtained after 12 h of electrolysis time carried out at 2.5 and 5 A dm^{-2}, respectively. With respect to electrolyzed solutions of dye, no product information was available from the HPLC determination. From Figure 7, plot a indicates the two peaks at 2.6 and 3.2 min with 4.8 and 1.3 V, respectively. For the second sample (the residues obtained after 12 h of electrolysis time carried out at 2.5 A dm^{-2}), both peaks area were shifted 3.3 and 3.9 min with decreased 0 and 1.6 V, respectively, as represented by plot b. This indicates the existence of a very small amount of parent dye and correspondingly lower carbon atom number than the original dye molecule. Chemical reduction of azo linkage commonly results in the formation of lower molecular weight aromatic amine entities and products with the parallel elimination of color in the reduced solution of the dyes. Fourier transform infrared studies[23] indicated that the treated effluent contains very low concentrations of chlorinated organic compounds at low residence time. Hence, in this study, the electrolysis time and current density were increased
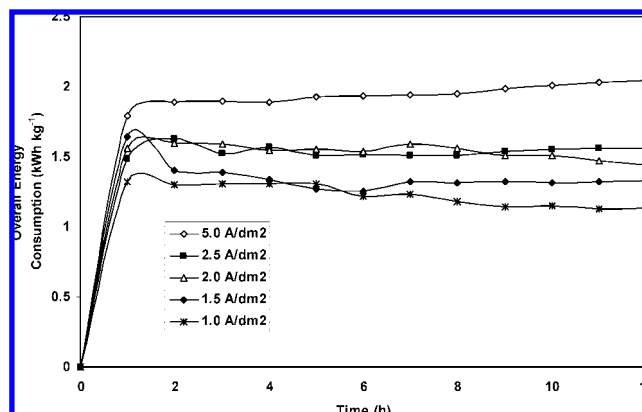
and experiments were conducted. No peaks were observed in curve c of Figure 7 which is due to increase of the current density (5 A dm^{-2}) and electrolysis time for 12 h. This result indicates the complete degradation of organic compounds and without formation of chlorinated organic compounds for long electrolysis time and high current density. It is clear that from increasing the time of electrolysis complete degradation of dye takes place.

3.5. Energy Consumption. The energy consumption was very important to study in the electrochemical process. The advantages claimed for Ti/RuO$_2$/IrO$_2$ (DSA) anodes over a graphite electrode are (i) lower cell voltage (3.90 V compared to 4.97 V for graphite), (ii) lower power consumption (2740 kWh per ton of Cl$_2$ compared to 3580 kWh per ton of Cl$_2$), and (iii) electrode erosion taking place only at graphite electrode, not in DSA.[29]

The results, which are presented in Figure 8 and Table 2, show that the operational current density significantly influences the power consumption. Only a few percent of the total energy requirement of the electrochemical step is needed for pumping the electrolyte around the electrolyte cycle and a small fraction of the energy is necessary to maintain a sufficiently fast flow through the electrodes.

The specific energy consumption for electrolysis, E, kWh kg^{-1}, is computed using the following expression:

$$E = \frac{V_{cell}It/10^3}{(C_o - C_t)V/10^3} \quad (12)$$

where the numerator represents the power input in kWh. V_{cell} is the cell voltage in volts, I is the current applied in amperes in the circuit, and t is the duration of electrolysis in hours for bringing the initial concentration, C_o (mg L^{-1}), of effluent to final concentration, C_t (mg L^{-1}), in the volume of the reservoir, V, in liters.

At 5.0 A dm^{-2} with the flow rate of 50 mL min^{-1} the energy consumption was 5.775 kWh kg^{-1} of COD for 12 h with 92.16% COD removal, whereas 31.37% COD reduction was obtained at 1.0 A dm^{-2} with the energy consumption about 2.28 kWh kg^{-1} of COD. The maximum recovery of NaOH was found to be 210.28 g L^{-1} at 5.0 A dm^{-2} with an energy consumption of 3.176 kWh kg^{-1} of NaOH. When the cell was operated at the lower current density (1.0 A dm^{-2}), the energy consumption was 2.265 kWh kg^{-1} of NaOH; the recovery of NaOH decreased to 72.18 g L^{-1}.

However, at 5 A dm^{-2} with the flow rate of 50 mL min^{-1}, the overall specific energy consumption was observed to be

Figure 8. Energy consumption for COD reduction and recovery of NaOH with time at various current densities. Condition: same as Figure 3a.

2.047 kWh kg^{-1} of COD removal with simultaneous buildup of NaOH. That, is at 5 A dm^{-2} with the flow rate of 50 mL min^{-1} the power consumption of 5.775 kWh kg^{-1}of COD removal was from 4080 to 320 mg L^{-1}, while at the same flow rate and current density, if the computation was done based on NaOH recovery the power consumption was 3.176 kWh kg^{-1} for simultaneous buildup of NaOH from 50 to 210.28 g L^{-1}. The overall energy consumption of the process was found to increase with increasing current density as shown in Table 2.

3.6. Cost Estimation. The cost of treatment of the waste generation from chemical production significantly contributes to the total production cost. In this study a process is developed for removal of organic matter and the generation of some chemicals. This process involves simple operation and the ability to generate byproduct sodium hydroxide. At the same time environmental advantages are realized such as reduced emission of gaseous species and reduced disposal of liquid effluent during the process development.

At the present levels, the caustic soda price is around rupees (Rs.) 24 per kg (May 2007), while the cost of electric energy paid by the industry in Tamilnadu, India, is about Rs.4.00 per kWh. With the specific energy consumption for the caustic, recovery was 2.781 kWh/kg of NaOH. From the experimental results, 5 dm^3 volume of effluent (92.16% COD reduction) energy consumption was obtained at 0.1082 kWh. Simultaneously, 200 mL of caustic soda (210 mg L^{-1} NaOH) was also recovered. The average value of 5 m^3 volume of effluent treatment gives roughly a treatment cost of Rs.433/ −. The quantity of caustic soda recovered is around 34 kg, and the cost is Rs.816/−. Also, recovery of chlorine and hydrogen gas are not studied and presented. On an industrial scale, "treatment of dye bath effluent and simultaneous generation of sodium hydroxide using electrochemical membrane process" favors the economic balance of the process. However, in this process there is a need for considerable capital investments. Then, besides the caustic recovery, significant savings in the purchase of chemicals used in the mercerization, dyeing, printing, and neutralization processes should be achieved, since most of the dyes are electrolytically destroyed, and additional savings due to the reduction of hazardous sludge handling and disposal costs is also accomplished.

4. Conclusion

In the present study an attempt was made to generation of sodium hydroxide as byproduct during degradation of dye effluent, using Ti/TiO$_2$−RuO$_2$−IrO$_2$ anode and stainless steel used as cathode.

The experimental results showed that the electrochemical process could effectively remove color, reduce COD, and recover caustic soda from the dye effluent. The maximum COD reduction, color removal, and caustic recovery were 92.16%, 100%, and 210.28 g L^{-1}, respectively. The optimization of simultaneous recovery of caustic (∼99% current efficiency) and COD removal (∼66.67%) could be achieved at a current density of about 2.5 A dm^{-2} during the electrolysis with minimum energy consumption.

In the present investigation completely degraded organic compounds, without formation of chlorinated intermediate compounds, were identified at high current density and increased electrolysis time. However, further investigation is necessary in order to identify lower molecular weight aliphatic compounds. Hence activated carbon polishing

treatment is recommended for the removal of other aliphatic/ organic compounds before the discharge of treated water.

The results of the study show that the electrochemical membrane process offers an interesting alternative economical method for the treatment of dye bath effluents.

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