Electrochemical treatment of Procion Black 5B using cylindrical flow reactor—A pilot plant study

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Abstract

The paper presents the results of an efficient electrochemical treatment of Procion Black 5B—a pilot plant study. Experiments were conducted at different current densities and selected electrolyte medium using Ti/RuO$_2$ as anode, stainless-steel as cathode in a cylindrical flow reactor. By cyclic voltammetric analysis, the best condition for maximum redox reaction rate was found to be in NaCl medium. During the various stages of electrolysis, parameters such as COD, colour, FTIR, UV–vis spectra studies, energy consumption and mass transfer coefficient were computed and presented. The experimental results showed that the electrochemical oxidation process could effectively remove colour and the chemical oxygen demand (COD) from the synthetic dye effluent. The maximum COD reduction and colour removal efficiencies were 74.05% and 100%, respectively. Probable theory, reaction mechanism and modeling were proposed for the oxidation of dye effluent. The results obtained reveal the feasibilities of application of electrochemical treatment for the degradation of Procion Black 5B.
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Keywords: Advanced oxidation; Textile; Colour removal; Electro-oxidation; Ti/RuO$_2$ electrode

1. Introduction

Water is the best resources in nature and is essential for animal and plant life. Pollution of water bodies is gradually increasing due to industrial proliferation and urbanization. Nowadays, the worldwide production and use of chemical compounds have increased tremendously and many of them find their way into the environment. Many of these compounds are non-biodegradable. Therefore, the major concern is to treat the wastewater before it is discharged into environment [1]. The textile and dyeing industry has drawn the attention of environmentalist of worldwide because of its high resource consumption profile in terms of water, chemicals, energy and release of highly contaminated coloured effluent at the end of process leading to intense water pollution. The existing wastewater treatment technology is often inadequate to control the colour of effluent to minimize the toxicity of wastewater having impact on aquatic organisms [2,3]. Aerobic treatment of industrial effluents typically removes most of the biological oxygen demand (BOD) and 60–80% of COD in wastewater [4–6]. However, these treatments are ineffective for colour removals from the textile industry wastewater because most of the synthetic dyes that are non-biodegradable. In aerobic process, the azo bonds can be used as electron acceptor in the electron pathways. The products of the azo bond clevage are lower molecular weight aromatic amines. Although they are colourless, they cannot be further degraded under anaerobic conditions. Therefore, various combined processes, such as anaerobic/aerobic [5], chemical/biological [7], and electrochemical/biological [8], processes have been under intensive study to completely mineralize organic dyes.

Though all the above methods have been found to be fairly satisfactory, considering the very stringent environmental regulations, there is a need for more effective alternatives. Anodic oxidation of some benzene derivatives (model organic pollutants) at platinum and DSA (dimensionally stable anode) anode elucidate the possibilities of the electrochemical method [9]. Dimensionally stable anode (DSA) with Ru/TiO$_2$ as a catalytically active layer coated on a titanium substrate by the thermal decomposition method has been successfully used and caused a technological revolution in the chloro-alkali industry since its invention in 1960s [10]. The first fundamental research on the

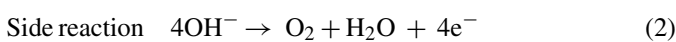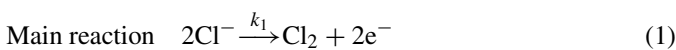* Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227779.
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properties of RuO_2, the main component of DSA, appeared in the open literature only in 1971 [11]. The Ti/RuO_2 electrode was prepared by thermal decomposition technique which consisted of the following steps: dissolution in isopropanol of $RuCl_3$; varnish application on the pre-treated titanium base; drying at $80\,^{\circ}C$; thermal decomposition at $500\,^{\circ}C$; cooling and repeating the above operation 10 times, finally post-heat treat for 2 h at $500\,^{\circ}C$ [9]. Earlier work has proposed electrochemical treatment of xylenol orange dye and dye effluents on bench scale [12]. Electrochemical oxidation of textile dye wastewater using Pt/Ti electrode was studied in a pilot plant under batch recirculation process [13]. This leads to develop a pilot plant study of electrochemical technique using Ti/RuO_2 electrode for the treatment purposes under continuous single pass process. Hence, this paper presents the treatment of Procion Black 5B by an electrochemical method using Ti/RuO_2 expanded mesh as anode, stainless-steel as cathode in a cylindrical flow reactor which is hitherto not reported on a pilot plant under continuous single pass process. It is to be pointed out that the Procion Black 5B (Remazol Reactive Black 5) dyes are considered because they work at temperature from 60 to $80\,^{\circ}C$. They are having excellent wash fastness and light fastness properties compared to other dyes. Use for dyeing high quality quilting fabrics, tie-dye, immersion dyeing, batik, airbrush, garment dyeing, screen-printing, and spatter painting. In reactive dyeing process, sodium chloride as exhausting agent and sodium carbonate as fixing agent. The effluent generated during this process could be used as the electrolyte. In this paper, the synthetic effluent was prepared from Procion Black 5B (a commercial Reactive Black 5B dye) and NaCl was used as supporting electrolyte. During the electrolysis on a continuous single pass process, COD reduction, colour removal; energy consumption and mass transfer coefficient were investigated on selected electrolyte medium under different flow rates and current densities.

2. Theoretical approach

Most of dye effluents contain NaCl as the major constituent. The method of treating of such solutions electrochemically is clean and easy, as they involve no addition of chemicals for supporting the electrolysis in the most of the cases. In the present study, the effluent contains 4600 mg/l sodium chloride, which can be used as a supporting electrolyte. The electrochemical reactions that take place during the electrolysis are complicated and not entirely known. For time being assumptions can only be made, based on the products that can be measured. Hence the following reactions assume to take place:
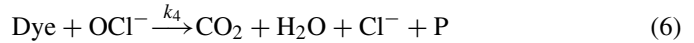
At anode:

$$\text{Main reaction} \quad 2Cl^- \xrightarrow{k_1} Cl_2 + 2e^- \tag{1}$$

$$\text{Side reaction} \quad 4OH^- \rightarrow O_2 + H_2O + 4e^- \tag{2}$$

At cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

In bulk of solution:

$$Cl_2 + H_2O \xrightarrow{k_2} H^+ + Cl^- + HOCl \tag{4}$$

$$HOCl \underset{k_{3'}}{\overset{k_3}{\longleftrightarrow}} H^+ + OCl^- \tag{5}$$

$$Dye + OCl^- \xrightarrow{k_4} CO_2 + H_2O + Cl^- + P \tag{6}$$

Since dye molecules of the effluent are electrochemically inactive, the primary reaction occurs at the anodes is chloride ion oxidation (Eq. (1)) with the liberation of Cl_2, which is a robust oxidizing agent. As the dye effluent is generally basic or neutral condition in which case the side reaction (Eq. (2)) takes place generating oxygen which is relatively weak oxidant and hence not useful in present context of effluent treatment and this leads to reduction of current efficiency. The counter reaction (Eq. (3)) at the cathode would be the reduction of the only water when no other reducible species are present. As regards to the reactions in the bulk, gaseous Cl_2 dissolves in the aqueous solutions due to ionization as indicated in Eq. (4). The rate reaction is less in acidic solution due to OH^- instability and considerably more in basic solution due to ready formation of OCl^- (pK_a 7.44) ion in Eq. (5) implying that the basic or neutral pH conditions are more favorable for conducting reactions involving Cl_2 [14]. The direct electro oxidation rate of organic pollutants depends on the catalytic activity of the anode, on the diffusion rate of the organic compounds in the active points of anode and applied current density. The indirect electro oxidation rate of organic pollutants depends on the diffusion rate of the oxidants into the solution, flow rate of the effluent, temperature and the pH. In moderate alkaline solution a cycle of chloride–chlorine–hypochlorite–chloride takes place, which produces OCl^-. The pseudo-steady-state theory can be applied to each of the intermediates products (HOCl and OCl^-) taking part in the bulk solution. Taking all other reactions are irreversible processes, the rates of reactions r_i for the sequence are:

$$-r_{Cl_2} = k_2[Cl_2] \tag{7}$$

$$r_{HOCl} = k_2[Cl_2] - k_3[HOCl] + k_3'[H^+][OCl^-] = 0 \tag{8}$$

$$r_{OCl^-} = k_3[HOCl] - k_3'[H^+][OCl^-] - k_4[Dye][OCl^-] = 0 \tag{9}$$

$$-r_{Dye} = k_4[Dye][OCl^-] \tag{10}$$

Then using Eqs. (8) and (9) we can easily deduce the following expression:

$$-r_{Cl_2} = -r_{Dye} = k_4[Dye][OCl^-] \tag{11}$$

Finally as regard to bulk solution it is also to be noted that $-r_{Cl_2} = r_{Cl^-}$ from material balance of Eq. (4), that is:

$$-r_{Cl_2} = r_{Cl^-} = k_2[Cl_2] = -r_{Dye} = k_4[Dye][OCl^-] \tag{12}$$

where the rate of reaction r_i and the rate constants k_i ($i = 2$, 3 and 4) are defined with respect to bulk and the rate expression

for main electrode reaction as per Eq. (1) can be written as:

$$-r'_{Cl^-} = r'_{Cl_2} = k_1[Cl^-] \tag{13}$$

where k_1 is heterogeneous electrochemical rate constant. Hence, in the following section an attempt has been made to establish a relation between the reacting species in bulk and at the electrode surfaces. The basic relationship applicable to all electrochemical reactions is Faraday's law that relates to the amount of substance reacted at the surface to the charge ($I_A t$) passed is $M_A I_A t/nF$ (assuming 100% current efficiency) and the characteristic measurable parameter is current density, i_A, which is I_A/A_e. Thus, the electrochemical reaction rate (for the disappearance of reactant A) can be expressed as:

$$-\left(\frac{V_R}{A_e}\right)\frac{d[A]}{dt} = \frac{i_A}{nF} \tag{14}$$

where I_A is the current passed in time t, M_A the molecular weight, n the number of electrons transferred per mole of reaction, A_e electrode area, V_R reactor volume and F is the Faraday (96,500 C or A s/mol). It has to be noted $-r_A = -d[A]/dt = i_A a/nF$, where a is specific electrode area (A_e/V_R). Assuming the main electrode reaction is governed by a simple Tafel type expression, then:

$$-\left(\frac{V_R}{A_e}\right)\frac{d[A]}{dt} = \frac{i_A}{zF} = k'[A]\exp(bE) \tag{15}$$

or

$$-r'_{Cl} = r'_{Cl_2} = k_1[Cl^-] = k_1' a[Cl^-]_s \exp(bE) \tag{16}$$

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 for the bulk to electrode surface where it under goes electrochemical oxidation to Cl_2 and it may be transported back to bulk by diffusion reaction in the bulk. Then:

$$\frac{i_A}{zF} = k_L([Cl^-] - [Cl^-]_s) \tag{17}$$

Elimination of $[Cl^-]_s$ using Eqs. (16) and (17) results as:

$$\frac{i_A}{zF} = k_1[Cl^-] \tag{18}$$

where

$$\frac{1}{k_1} = \frac{1}{k_L} + \frac{1}{k'a\exp(bE)} \tag{19}$$

From a material balance of species Cl^- by taking note of Eqs. (12) and (13) we can write:

$$\frac{i_A}{zF} = k'[Cl_2] \tag{20}$$

$$\frac{i_A}{zF} = k''[Dye][OCl^-] \tag{21}$$

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

$$\frac{i_A}{zF} = k_{obs}[Dye] \tag{22}$$

In electrochemical conversion the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing. In electrochemical combustion the organics are completely oxidized to CO_2 and H_2O. A brief explanation of reaction mechanism taking place at metal oxide electrode is enumerated below [15].

A Schematic diagram of indirect oxidation of pollutant [16] is shown in Figs. 1 and 2 shows a generalized scheme of the electrochemical conversion/combustion of organics on noble oxide coated catalytic anode (MO_x). In the first step, H_2O is discharged at the anode to produce adsorbed hydroxyl radicals according to the reaction:

$$MO_x + H_2O \rightarrow MO_x(^\bullet OH) + H^+ + e^- \tag{23}$$
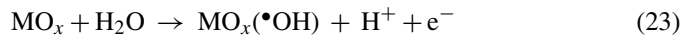
In the second step, generally the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the oxide forming the higher oxide MO_{x+1}:

$$MO_x(^\bullet OH) \rightarrow MO_{x+1} + H^+ + e^- \tag{24}$$
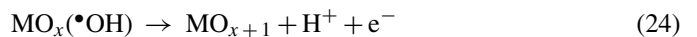
At the anode surface the "active oxygen" can be present in two states. Either as physisorbed (adsorbed hydroxyl radicals ($^\bullet OH$) or /and as chemisorbed (oxygen in the lattice, MO_{x+1})). In the

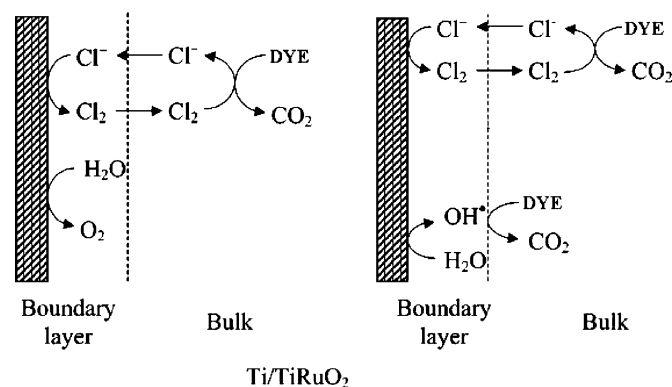

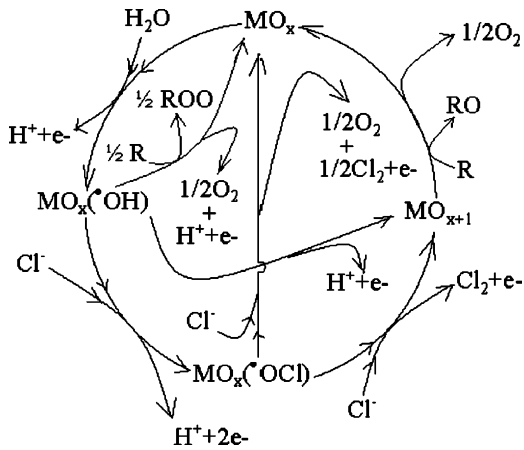Fig. 1. Scheme of the reactions and processes involved in the dye oxidation.
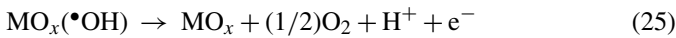
Fig. 2. Scheme of electrochemical oxidation of organic pollutants in presence of chloride ion.
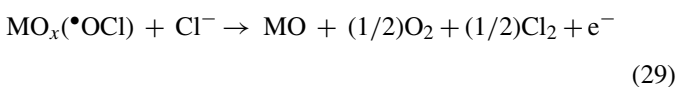
absence of any oxidizable organics, the "active oxygen" produces dioxygen according to the following reactions:

$$MO_x(^\bullet OH) \rightarrow MO_x + (1/2)O_2 + H^+ + e^- \tag{25}$$

$$MO_{x+1} \rightarrow MO_x + (1/2)O_2 \tag{26}$$

when NaCl is used as supporting electrolyte Cl ion may react with $MO_x(^\bullet OH)$ to form adsorbed OCl radicals according to the following:

$$MO_x(^\bullet OH) + Cl^- \rightarrow MO_x(^\bullet OCl) + H^+ + 2e^- \tag{27}$$
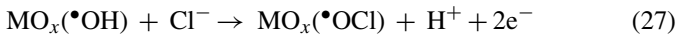
Further, in presence of Cl ion, the adsorbed hypochorite radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hypochorite radical to the oxide forming the higher oxide MO_{x+1} according to the following reaction and also $MO_x(^\bullet OCl)$ simultaneously react with chloride ion to generate active oxygen (dioxygen) and chlorine according to the following reactions:

$$MO_x(^\bullet OCl) + Cl^- \rightarrow MO_{x+1} + H^+ + e^- \tag{28}$$

$$MO_x(^\bullet OCl) + Cl^- \rightarrow MO + (1/2)O_2 + (1/2)Cl_2 + e^- \tag{29}$$
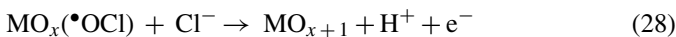
In the presence of oxidizable organics the physisorbed "active oxygen" ($^\bullet OH$) should cause predominantly the complete combustion of organics and chemisorbed will participate in the formation of selective oxidation products [17] according to the following reactions:

$$(1/2)R + MO_x(^\bullet OH) \rightarrow (1/2)ROO + H^+ + e^- + MO_x \tag{30}$$

$$R + MO_{x+1} \rightarrow RO + MO_x \tag{31}$$
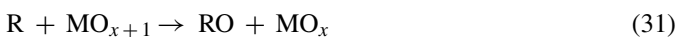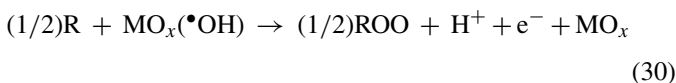
The physisorbed route of oxidation is the preferable way for waste treatment. It is probable that dioxygen participates also in the combustion of organics according to the following reaction schemes: (1) Formation of organic radicals by a hydrogen abstraction mechanism: $RH + ^\bullet OH \rightarrow R^\bullet + H_2O$; (2) reac-

tion of organic radical with dioxygen formed at the anode: $R^\bullet + O_2 \rightarrow ROO^\bullet$ and (3) further abstraction of a hydrogen atom with formation of an organic hydrogen peroxide (ROOH) and another radical; $ROO^\bullet + R'H \rightarrow ROOH + R'$. Since the organic hydrogen peroxides formed are relatively unstable, decomposition of such intermediates leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These sequential reactions continue until the formation of carbon dioxide and water. In this case the diffusion rate of organics on the anode area controls the combustion rate [18,19]. In the same way indirect electrochemical oxidation mechanism has been proposed for metal oxide with chloride as supporting electrolyte for wastewater treatment [20,21]. We have already described in detail the role of chlorine in electrochemical treatment of dye effluent via hypochlorite generation in the beginning of this section. Now let us consider the reactor.

Since the electrochemical reactors are heterogeneous system by nature as they mostly involve a solid electrodes a liquid electrolyte and evolving gases at the electrodes. Electrodes come in many forms from large sized plate fixed in the cell to fluidizable shape and sizes. Further, the total reaction system consists of a reaction (or a set of reaction) at one electrode and another reaction (or set of reactions) at the other electrode in addition to the bulk as discussed above. The two electrode reactions are necessary to complete the electrical circuit. Thus, although these reactors can, in principle, be treated in the same manner as conventional catalytic reactors; detailed analysis of their behavior is considerably more complex. Adopting the same classification for the reactors as for conventional reactors, the cylindrical electrochemical flow reactor can be considered as plug flow reactor (PFR) and the material balance equation for PFR is given by:

$$U \frac{d[Dye]}{dx} + (-r_{Dye}) = 0 \tag{32}$$

where U is the average velocity of trough the reactor at a distance x from the leading edge and $-r_{Dye} = k_{obs}a[Dye]$ and in the integrated form:

$$[Dye]_x = [Dye]_0 \exp\left(\frac{-k_{obs}ax}{U}\right) \tag{33}$$

The rate of colour removal and COD reduction in the dye effluent depends upon the dye concentration. In addition only chromophoric compounds (azo, nitrazo, etc.) mainly influence the colour removal.

$$Dye + (O) \rightarrow colourless\ intermediates + (O) \rightarrow CO_2 + H_2O \tag{34}$$
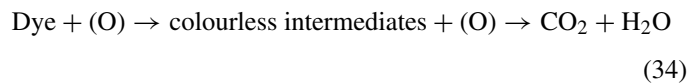
For this reaction kinetics by assuming steady-state condition in cylindrical flow cell the expression can be derived assuming plug flow:

$$[COD]_L = [COD]_0 \exp\left(\frac{-k_{obs}aL}{U}\right) \tag{35}$$

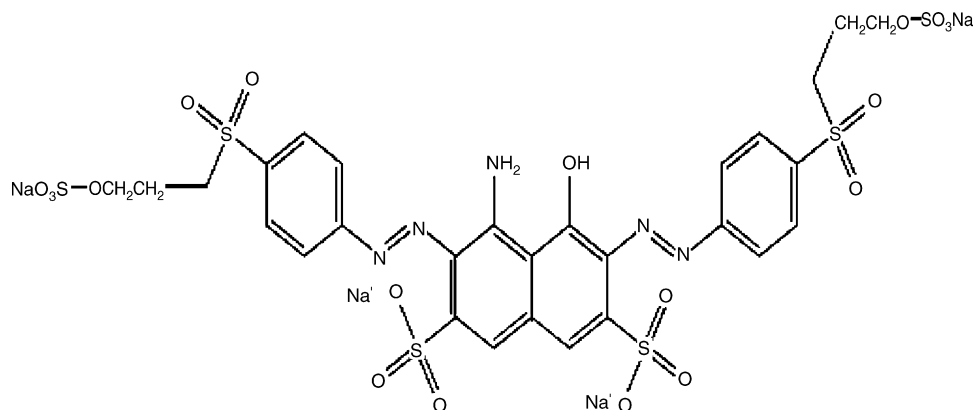$$[COLOR]_L = [COLOR]_0 \exp\left(\frac{-k'_{obs}aL}{U}\right) \tag{36}$$

Fig. 3. Molecular structure of Procion Black 5B.

where k_{obs} is the mass transfer coefficient, with respect to COD removal where as k'_{obs} corresponds to colour removal, $a = A_e/V_R$, a the specific electrode area, L length of the electrode area, U the superficial velocity $[COD]_0$ the concentration of dyestuff in terms of COD at the reactor inlet $[COD]_L$ at the reactor exit, A_e the area of electrode and V_R the volume of the reactor. If q the volumetric flow rate then U the superficial velocity, defined as q/A, where A is cross sectional flow area.

3. Materials and methods

All the reagents used were of AR grade. HCl, H_2SO_4, Na_2SO_4, NaCl, and KOH were used as supporting electrolyte and the synthetic effluent was prepared from Procion Black 5B (a commercial Reactive Black 5B dye). The colour index of the dye was 20505 CI Reactive Black 5. It contains two chromogenic systems. The structure of dye is shown in Fig. 3 and the characteristics of effluent before and after treatment (current density—2 A/dm^2 and 10 l/h) is presented in Table 1.

3.1. Cyclic voltammetry analysis

Cyclic voltammetry analyses were carried out by Potentioscan (Wenking model POS 88) and X-Y/t recorder (Rikadenki

model RW-201t). The simulated dye wastewater containing Procion Black 5B (of different concentration in the range 10–40 mg/l in different electrolyte medium HCl, H_2SO_4, Na_2SO_4, NaCl, and KOH.) were prepared and 10 ml of wastewater was taken in a three-electrode electrochemical cell. The working electrode for the controlled potential was a platinum foil of surface area of 1 cm^2 and the reference electrode was saturated calomel electrode and the counter electrode was a platinum wire. The electrodes were immersed in a Procion Black 5B dye solution. Cyclic voltammetry (CV) scans were taken in the direction of decreasing potential starting from 0.7 V to potential of −0.8 V and at a scan rate of 50 mV/s. The cyclic voltammetry studies were used to find out the medium (and its optimum conditions) in which the effective indirect oxidation of dye takes place. Hence readily available Pt electrode was used for the experiments and CV was studied in different electrolyte medium HCl, H_2SO_4, Na_2SO_4, NaCl and KOH.

3.2. Analytical measurements

The COD of all samples were determined by the dichromate reflux method [22]. UV–vis Spectra of untreated dye effluent and treated effluent were measured by using a UV–visible spectrophotometer (Systronics 118). From the absorbance values the reduction in dye concentration or the colour removal was calculated by following formulae:

$$\%\text{Colour removal} = 100 \times \frac{[\text{ABS}_0^M - \text{ABS}^M]}{\text{ABS}_0^M} \tag{37}$$

where ABS^M is the average of absorbance values as it is maximum absorbency visible wavelength. ABS_0^M the value before electrolysis, ABS^M the value after electrolysis and the FTIR of the samples were obtained by Perkin-Elmer-Paragon 500 before and after electrolysis.

3.3. Electrolytic cylindrical flow reactor

A schematic view of the experimental set-up is shown in Fig. 4. The electrolytic flow reactor consist of the cathode, which was a stainless-steel pipe of 110 cm height and 7 cm diameter, and the catalytic anode, made of Ti/RuO$_2$ coated expanded mesh

Table 1
Characteristics of the effluent

Particulars	Procion Black 5B dye effluent before treatment	Procion Black 5B dye effluent after treatment (current density: 2.5 A/dm^2 at 10 l/h)
pH	10.6	13.6
COD (mg/l)	1264	328
TSS (mg/l)	460	240
TDS (mg/l)	9600	9280
Chloride (mg/l)	3860	3610
Molecular weight	992	–
Density of the effluent (kg/m^3)	989.04	–
Colour index	20505 CI Reactive Black 5B	–

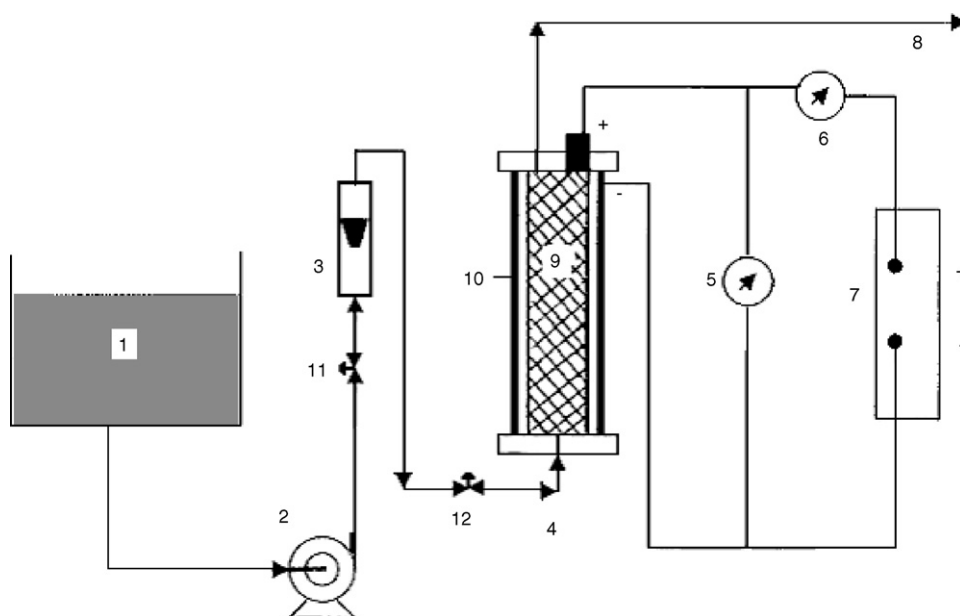Initial COD: 1264 ppm; λ_{Max}: 575 nm

Fig. 4. Experimental set-up of flow cell: (1) reservoir, (2) pump, (3) rotameter meter, (4) electrolytic cell, (5) voltmeter, (6) ammeter, (7) DC power supply (100A, 0–50 V), (8) treated effluent, (9) Ti/RuO$_2$ coated expanded mesh cylinder anode, (10) stainless-steel cathode, and (11) and (12) valves.

cylinder, measuring 100 cm long and 5 cm diameter which was held axially inside the cathode such that 1cm as inter-electrode distance. Provisions are made for electrical connections so as to constitute an electrolytic cell. The holdup of the cell is 4.5 l. Additionally, the cell had one inlet at the bottom cover and one outlet at the top cover. It is connected to 100 A and 50 V DC regulated power supply. Reservoir, pump, flow meter and electrolytic flow rector are connected using silicone rubber tubes.

3.4. Experimental procedure

The effluents were taken in the reservoir, which was passed to the cell. The flow rate was measured and adjusted by rotameter. The required current was passed using regulated power supply and cell voltage was noted for each flow rate. The effluent was allowed to flow at single pass from bottom of the cell using NaCl as electrolyte medium. After attaining steady-state, the outlet samples were collected and subjected to COD, FTIR, and colour (UV–vis spectra) analysis. The various experimental conditions and parameters were studied at different current densities such as 1, 1.5, 2 and 2.5 A/dm^2. For each current density the experiment was repeated for different flow rate of effluent to the reactor 10, 20, 30, 40 l/h (liter per hour).

4. Results and discussion

The effect of the parameters such as flow rate and current density on rate of COD removal as well colour removal were investigated in a pilot scale cylindrical flow electrolyzer in a single pass for Procion Black 5B in a NaCl electrolyte medium. The option for the above medium was based on CV scans as given in Fig. 5. The following data such as specific power consumption, mass flux and mass transfer coefficient were computed for various flow rate and current densities is given in Table 2. The COD

reduction and colour removal efficiencies shown in Figs. 6 and 7. The FTIR and UV–vis spectra obtained for the outlet samples are given in Figs. 8 and 9. All the above studies were carried out under ambient conditions.

4.1. Cyclic voltammetry studies

To understand the electrochemical behaviour of the electrolytic medium, cyclic voltammetry (CV) studies were carried
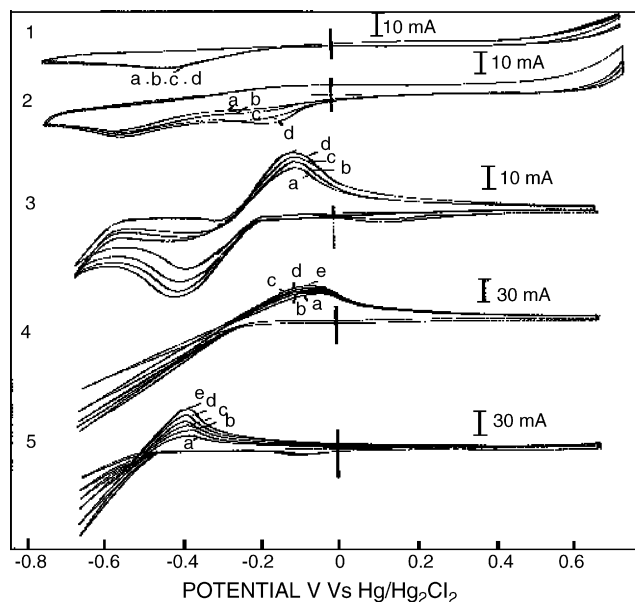

Fig. 5. Cyclic voltammogram (50 mV/s) studies for Procion Black 5B dye under different electrolytic conditions: (1) KOH (0.1 M) medium, (2) Na$_2$SO$_4$ (0.1 M) medium, (3) NaCl (0.1 M) medium, (4) C1 (0.01 M) medium, (5) H$_2$SO$_4$ (0.01 M) medium with increased concentrations of: (a) background of the electrolyte, (b) 10 ppm, (c) 20 ppm, and (d) 30 ppm, (e) 40 ppm, respectively.

Table 2
Effect of current density and flow rate on power consumption, mass flux and mass transfer coefficient

| Current density (A/dm²)	Flow rate (l/h)	Voltage (V)	Residence time (H)	COD (mg/l)		Power consumption (kWh/g COD)	Mass flux (g COD/h dm²)	Mass transfer coefficient (cm/s)
				Initial	Final			
	10		0.4500	1264	544	2.8190	0.1256	0.0018645
	20		0.2250	1264	600	0.7658	0.2349	0.0032957
1	30	3	0.1500	1264	666	0.3766	0.3185	0.0042712
	40		0.1125	1264	752	0.2480	0.3623	0.0045940
	10		0.4500	1264	448	6.2316	0.1444	0.0022940
	20		0.2250	1264	496	1.6549	0.2721	0.0041377
1.5	30	5	0.1500	1264	552	0.7935	0.3779	0.0055021
	40		0.1125	1264	616	0.4903	0.4586	0.0065387
	10		0.4500	1264	384	11.5340	0.1557	0.0026348
	20		0.2250	1264	440	3.0819	0.2916	0.0046676
2	30	7.5	0.1500	1264	504	1.4850	0.4034	0.0061005
	40		0.1125	1264	544	0.8815	0.5096	0.0074583
	10		0.4500	1264	328	16.3034	0.1656	0.0029835
	20		0.2250	1264	392	4.3750	0.3086	0.0051786
2.5	30	9	0.1500	1264	448	2.0776	0.4331	0.0068819
	40		0.1125	1264	504	1.2549	0.5379	0.0081339
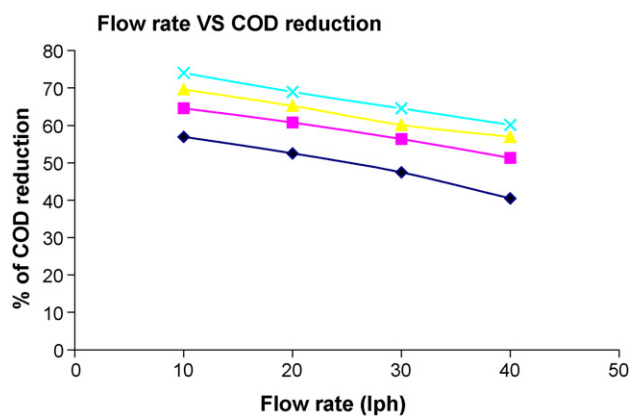
Fig. 6. Effect of COD reduction on flow rate at different current densities (♦) 1 A/dm², (■) 1.5 A/dm², (▲) 2 A/dm², (×) 2.5 A/dm².
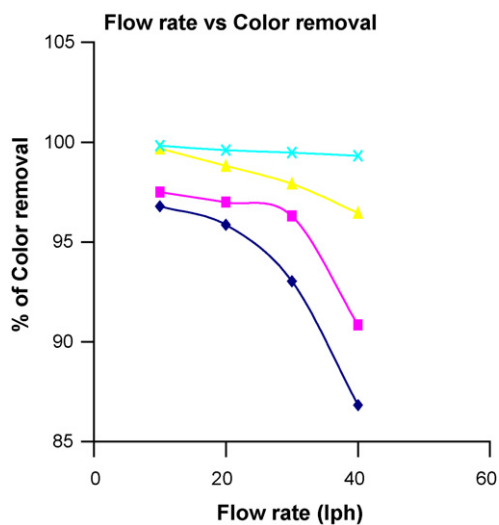

Fig. 7. Efficiency of colour removal on flow rate at different current densities (♦) 1 A/dm², (■) 1.5 A/dm², (▲) 2 A/dm², (×) 2.5 A/dm².

out. To know the actual behaviour of the real effluent it is always better to resort to study of the effect of cationic radicals such as Na^+, K^+, H^+ and anionic radicals SO_4^-, Cl^-, OH^-, CO_3^-, HCO_3^-, and HSO_4^- (that are generally present in the effluent) separately and their various combination with different ionic strengths. Since the main scope of this paper is limited to demonstrate the pilot scale reactor study, in NaCl medium, in which the behaviour of Cl^- ions plays a vital role in indirect oxidation. CV studies were carried out to compare the electro chemical behavior of Procion Black 5B at different electrolytes such as KOH, Na_2SO_4, NaCl, HCl and H_2SO_4. CV scans are shown in Fig. 5. In case of KOH, Fig. 5(1) the reduction of Procion Black 5B occurs at −0.57 V and in Fig. 5(2) in respect of Na_2SO_4 electrolytes, the reduction peak appears at −0.21 and −0.72 V. The absence of oxidation peaks indicate that the presence of either KOH or Na_2SO_4 will not help in reduction of COD but may help in the removal of colour. The oxidation peak observed
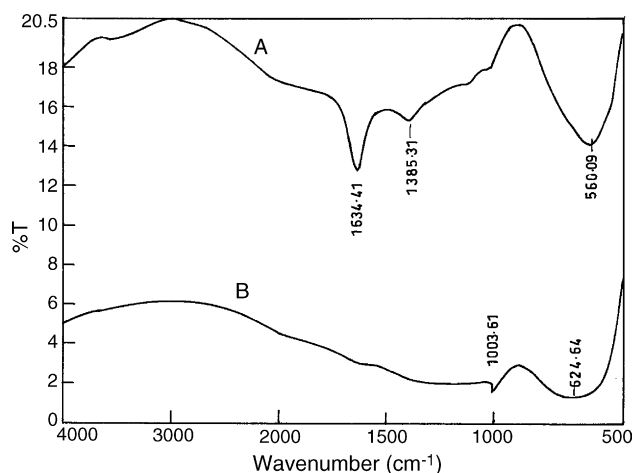

Fig. 8. Changes of infrared absorption bands of: untreated (A) and treated (B) dye effluent (operating condition: current density 2.5 A/dm² at 10 l/h).
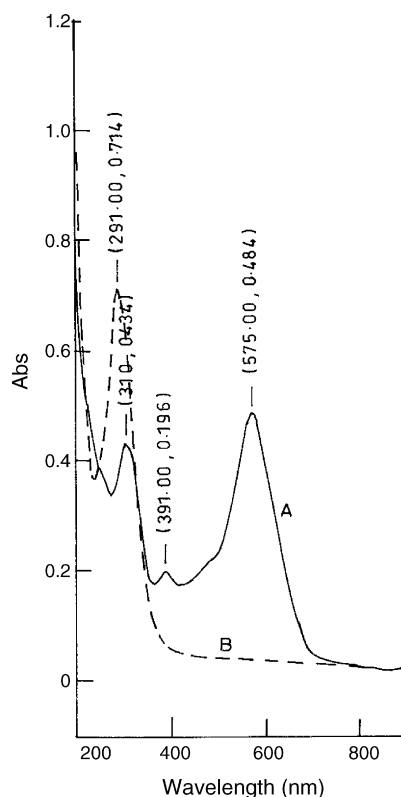
Fig. 9. UV–vis spectra of untreated dye effluent (A) and treated effluent (B) (operating condition: current density 2.5 A/dm^2 at 10 l/h).

at −0.04 V in Fig. 5(4) appear even in the volammograme for the background electrolyte (curve (a)). With increase in addition of Procion Balck 5B current increase is insignificant. This suggests that the electrochemical oxidation of dyes is not favorable in these media. Similar observation is made in Fig. 5(5). The curve (a) shows an anodic peak around −0.4 V, which is due to background electrolyte. Addition of dye was examined at various dye concentration from 10 to 40 ppm, which causes peak current increase to a small extent, compared to Fig. 5(4). In NaCl (Fig. 5(3)) electrolyte medium the redox behavior of Procion Black 5B occurs at cathodic peak −0.57 V and at anodic −0.14 V. A reversible electrochemical process for Procion Black 5B is observed in NaCl. In all the cases (Fig. 5(3–5)) peak currents increase, which will aid in the removal of colour and COD. In all the electrolytes, it is observed, that Procion Black 5B does not give any separate electrochemical response or it does not get oxidized directly on the electrode surface in all the electrolytes. The background electrolyte gives a peak on the anodic side in the case of Fig. 5(3–5). The dye under goes oxidation at the peak potential of background response, which indicates that the dye is indirectly oxidized by some reactive species in the background electrolyte. This suggest that the oxidation of Procion Black 5B occurs by indirect oxidation by hydroxyl or other oxidant reagent electro generated from the electrolyte (mainly ClO$^-$ ions in NaCl), Among all the results, the redox behavior of Procion Black 5B in NaCl was good when compared to other electrolytes.

4.2. Effect of COD and colour removal

The extents of COD removal at different reaction times under various conditions are shown in Fig. 6. During the present investigation the operating parameters such as flow rate and current densities were varied to explore the effect of such parameters on COD removal. Results showed (Table 2) higher COD reduction occurred at higher charge input and electrolysis (residence time) time. The residence time is defined as the ratio of volume of the reactor by volumetric flow rate; at low flow rate the residence time becomes high hence the COD reduction is more as well as higher current also COD reduction is more because the generation of large amount of OCl$^-$, when sufficient amount of chloride is available in the system. In this study, the increase in flow rate from 10 to 40 l/h leads to gradual decrease in the COD removal; at 40 l/h it was 20% less than that at 10 l/h because the residence time of the effluent at 10 l/h was 4 times higher than that at 40 l/h. The maximum possible COD reduction was 74.05% at 10 l/h and 2.5 A/dm^2.

Also, the samples were taken from outlet of the cell for analysis. The residual dye concentration was measured spectroscopically and associated with the decrease in the absorbance at the peak of maximum visible wavelength (575 nm) and expressed in terms of percentage. These results are shown in Fig. 7. The maximum colour removal (99.83%) was obtained at 10 l/h and 2.5 A/dm^2. At high flow rates (40 l/h) and lower current density (1 A/dm^2) the colour reduction was found to be low (86%).

4.3. IR-spectral studies

Fig. 8 shows the IR-spectra of the dried solution residue before and after the electrochemical treatment. It can be seen that some structural changes might have occurred during the electrochemical process. The appearance of peak at 1634 cm^{-1} indicates the presence of C=C conjugated diene group. The other peak at 1385 cm^{-1}, indicates the presence of CH def for CH$_3$. After electrolysis, there are two peaks appeared at 1003.6 and 624.64 cm^{-1}, while peaks at 1634.41 and 1385.31 cm^{-1} are completely disappeared and 560.09 cm^{-1} peaks shifted to 624.64 cm^{-1}. The appearance of peak at around 1003.6 cm^{-1} suggests the formation of ClO$_3^-$, which may generally be present in the hypochlorite solution. Presence of peak at about 624.64 cm^{-1} is thought to belong to C–Cl stretching. This variation in the IR-spectra can be explained by completely degradation of organic compounds and formation of chlorinated organics.

4.4. UV–vis spectrophotometer studies

The changes in absorbance characteristics of dye effluent were investigated over a large wavelength interval during the electrochemical decolourization process and the results are shown in Fig. 9. The spectra shows that there is a maximum absorbance at 575 nm in the visible region. This peak disappears gradually during the electrolysis. There are also two peaks observed at 391 and 310 nm, respectively in the UV region which become at 391 nm peak was disappeared and 310 nm

peak shifted to 291 nm as the electrolysis progresses. This result shows the cleavage of azoic group and total discolouration of the solution. The presence of the peak at 291 nm at the end of the electrolysis, shows that the mineralization of the Procion Black 5B it is not completely achieved. This peak can be attributed to carboxylic acids accumulated at the final stage of the oxidation. This is represents the residual COD present in the effluent. It is clear from Fig. 9 that the electrochemical oxidation process has effectively reduced the colour of the dye effluent.

4.5. Effect of flow rate and current density

To enumerate the effect of current density on power consumption, the current was varied from 1 to 2.5 A/dm^2. The values are given in Table 2. Shows, increase in the flow rate reduces the power consumption of the process. This is attributable to the preferential oxidation of easily oxidizable materials. At 1 A/dm^2, the power consumption at of 0.2480 kWh/kg of COD is found to be lower at 40 l/h and the power consumption of 2.8190 kWh/kg of COD is found to be highest at 10 l/h. Increase in the current density increases the power consumption. This is evident from the values given in Table 2. At 1 A/dm^2, flow rate of 10 l/h, the power consumption was found to be 2.8190 kWh/kg of COD. At 2 A/dm^2, at same flow rate the power consumption was increased to 11.5340 kWh/kg of COD.

Mass flux of the system decreases linearly with the decrease in flow rate. This is shown in Table 2 at 2.5 A/dm^2, the mass flux was found to be 0.1656 g COD/h dm^2 at flow rate of 10 l/h and mass flux of 0.5379 g COD/h dm^2 at flow rate of 40 l/h. As mass flux depends on the time of operation, the effect of residence time plays an important role in the process. The easily oxidizable parts present in the effluent contribute to the decrease in the COD at low flow rate. The current density is directly proportional to the mass flux. These results are shown in Table 2. At current density of 1 A/dm^2 and flow rate of 10 l/h, the mass flux was 0.1256 g COD/h dm^2, but high current density (2.5 A/dm^2) and same flow rate mass flux was increased to 0.1656 g COD/h dm^2.

From Table 2 shows the mass transfer coefficient increases with increase in flow rate as well as increase in current density. Mass transfer coefficient verses flow rate under various current densities. The mass transfer coefficient 0.0081339 cm/s was found to be high in the case of 40 l/h and 2.5 A/dm^2. The mass transfer coefficient of the process was indirectly related to the time of operation, as time of operation reduces, mass transfer coefficient increases steadily. It has a direct relation to the current density at 2.5 A/dm^2 was 0.0081339 cm/s and 1 A/dm^2 was 0.0045940 cm/s at 40 l/h. Hence to degrade Procion Black 5B having the initial absorbency and COD values are 30.6 and 1264 mg/l. It has to electrolyze in order to bring down below 250 mg/l to meet out the discharge standards. At 1 A/dm^2 and 10 l/h, the final absorbency and COD values are 0.981 and 544 mg/l (96.99% and 56.92% reduction) and 2.5 Am/dm^2 in 10 l/h charge to bring down the absorbency and COD value are 0.052 and 328 mg/l (99.83% and 74% reduction). This is due to rapid reaction that is followed by a slow reaction at high current density. Murphy et al. [23] reported that pollutant removal efficiency at same charge loading was independent upon the value

of current density in a direct electrochemical oxidation treatment process. Here the result shows that current density strongly influences the rate of reaction.

5. Conclusion

In the present work, dye effluents were treated using Ti/RuO$_2$ as anode and stainless-steel as cathode. The experiments were carried out in cylindrical flow cell (single pass) reactors under different conditions. Treatment using physico-chemical method produces more sludge, involves high cost and lower efficiency. In biological treatments the process takes longer time and gives lower efficiency. Hence this electro chemical treatment is best suited for treating the dye house effluent. From the results COD reduction was found to be 74.05% and colour removal was nearly 100% at 2.5 A/dm^2 for flow rate of 10 l/h, respectively. The flow rate of effluent in to the reactor is significantly affected by the reactor performance. The decrease in flow rate and increase in current density significantly increase the reduction of COD. Both mass flux and mass transfer coefficient are higher in the case of flow cell reactor method. This method is also economical. For the industrial application, flow cell method can be recommended with two or more reactors in series at a current density of 1–2.5 A/dm^2.

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