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Electrochemical Treatment of Acid Green V dye solution in a tubular flow reactor

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Abstract—Electrochemical oxidation of synthetic aqueous Acid Green V dye solution was investigated in a tubular flow reactor using $Ti/RuO_2IrO_2TiO_2$ as electrodes in NaCl electrolyte medium. The influence of effluent flow rate, initial dye concentration and the current density on COD reduction and color removal were studied and the power consumption computed. Percentage reduction in COD and color removal were found to be maximum(80% to 100%) at the minimum flow rate of 10 lph and the maximum current density of 2.5 A/dm^2 for all the effluent solutions of different initial concentrations. A flow rate of 30 lph and current density of 1.5 A/dm^2 was found to be optimal for lower power consumption.

Keywords: Electrochemical oxidation; Acid Green V; Decolorization; COD; Current density; Effluent flow rate.

I. INTRODUCTION

Dyes are used extensively in textile industries for imparting colors. These industries discharge wastewaters containing a variety of pollutants such as lost dyes, dissolved inorganic salts, organics and suspended material into public water bodies, thus often causing harmful and undesirable water pollution. Removal of color and organic matter from the textile industry wastewater has become a challenge especially in view of the stringent pollution control regulations.

Biological oxidation [1], adsorption [2], coagulation by aluminum or iron salts [3] are some of the traditional methods employed in the treatment of industrial wastewater before their disposal or reuse. These physicochemical methods have many disadvantages in terms of efficiency, cost, regeneration or secondary pollution [4-7]. In order to overcome these disadvantages, attempts have been made to find new methods which are more efficient and economical. Among them electrochemical oxidation seems to be more promising as it offers many advantages such as environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation and cost effectiveness [8-11]. Lin and Peng [12] has applied this method for textile wastewater and achieved good removal of organic matter. Chatzisymeon et al [13] investigated the electrochemical oxidation of a highly colored synthetic effluent containing 16 textile dyes in a flow through cell. Mohan et al [14] treated a textile effluent using the electrochemical technique and reported effective reuse of treated water in dying operations. Sakalis et al [15] studied the electrochemical treatment of synthetic and real wastewater samples in a pilot scale reactor for the removal of azo dyes. Parsa et al16] reported complete decolorization when they treated simulated wastewater containing Direct blue 71 azo dye in laboratory and pilot scale reactors. Electrochemical oxidation was found to be very effective [17] in the degradation of organics in the textile industry effluent water.

The current density and the effluent flow rate are two of the main parameters that influence the electrochemical oxidation process of textile wastewater. In the work reported in this paper, the electrochemical treatment of simulated wastewater containing a stable dye Acid Green V was investigated using $Ti/RuO_2IrO_2TiO_2$ electrodes in a tubular flow reactor. The influence of effluent flow rate and current density on chemical oxygen demand (COD) and color removal were studied along with energy consumption.

II. MATERIALS AND METHODS

The effluent to be treated was prepared synthetically from Acid green V, using NaCl as supporting electrolyte. The structure of the dye with its properties and the characteristics of the effluent prepared are shown in Fig.1 and Table 1 respectively.

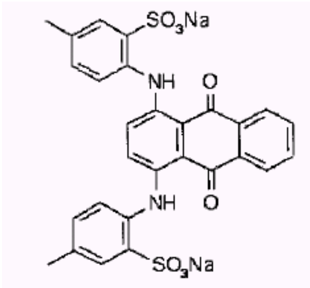

FIG. 1. MOLECULAR STRUCTURE OF ACID GREEN V DYE

Molecular weight	622.58
Molecular formula	$C_{28}H_{22}N_2O_8S_2.2Na$
Colour index	61570 CI

TABLE 1. CHARACTERISTICS OF THE EFFLUENT

Property	**Effluent characteristics**	
	Dye concentration 3000 mg/l	**Dye concentration 1500 mg/l**
COD (mg/l)	960	480
pH	4.55	6.49
Density (kg/m^3)	1003.29	980.74
Viscosity at 30°C (kg/m s)	9.9661×10^{-4}	8.664×10^{-4}

II.A. Experimental set up:

Experiments were carried out in an electrochemical plug flow reactor. It consists of a cylindrical acrylic column of 5 cm diameter and 21.5 cm length, with three 20 cm x 3 cm x 0.15 cm cathodes and two 20cm x 3 cm x 0.15 cm anodes. The electrodes were made of mixture of metal oxides RuO_2, IrO_2, and TiO_2 coated to a thickness of 6μm on a titanium metal base. They were placed vertically, parallel to each other and the gap between them was maintained constant at 1 cm. The reactor hold up volume was 350 ml and it was provided with inlet and outlet for the flow of test sample, at the bottom and the top respectively. The electric power was provided using a 0 – 20A and 0 – 15 V, regulated DC power supply. Synthetic dye solution was pumped from a reservoir through the electrolytic flow reactor using a dosing pump. The schematic diagram of the experimental set up is shown in Fig.2.

Experiments were carried out at different current densities of 0.5, 1.0, 1.5, 2.0 and 2.5 A/dm^2 and with different effluent flow rates of 10, 20, 30, 40 liters per hour at each current density. The reactor outlet samples were collected after steady state is reached and were analyzed for COD, pH and color intensity.

II.B. Analysis:

The COD of treated samples were determined by the dichromate reflux method [18] and the pH was measured using pH meter (LI 120, ELICO, India). The extent of color removal was measured using spectrophotometer (UV–vis. SL 159, ELICO, India), at the maximum wavelength of 637 nm.

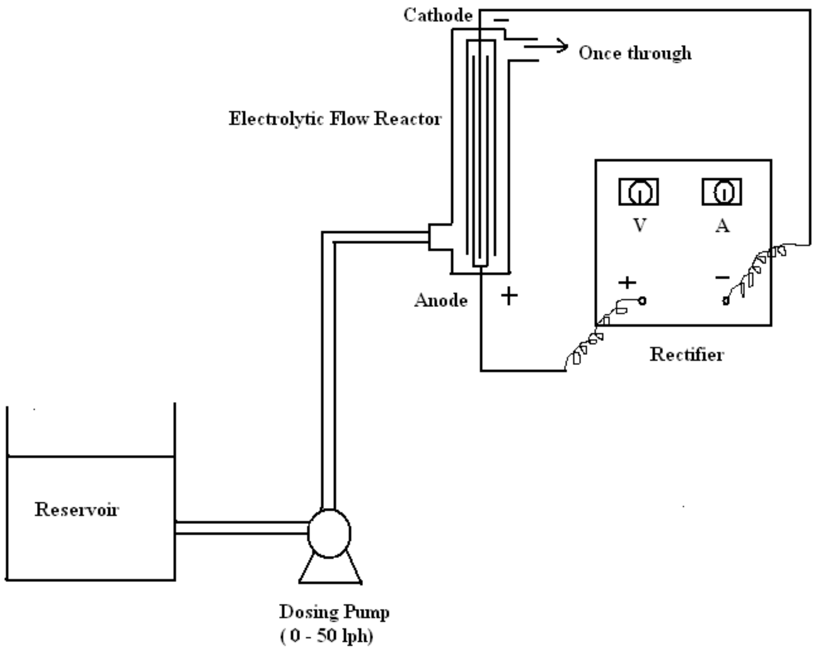

Fig. 2. Schematic diagram of Experimental Set Up

III. RESULTS AND DISCUSSION

Electrochemical oxidation destroys the organic pollutants in the wastewater and thereby causes the reduction in COD and decrease in the color. In this study the percentage COD reduction and percentage color removal were calculated using the following relations.

$$\frac{Original\ COD - COD\ after\ oxidation}{Original\ COD} X\ 100$$

$$\frac{Original\ color - Color\ after\ oxidation}{Original\ Color} X\ 100$$

III.A Effect of current density:

The current density is generally defined as the current applied divided by the projected area of the electrodes. In order to study the influence of current density and the effluent flow rate experiments were conducted at different current densities for different wastewater (of two different initial dye concentrations of 1500 mg/l and 3000 mg/l) flow rates and the data obtained are presented in tables 3 and 4.

Table 3. EFFECT OF CURRENT DENSITY AND FLOW RATE ON COLOR AND COD REDUCTION: DYE CONCENTRATION (3000 mg/l)

Current Density (A/dm^2)	Flow rate (l/h)	Voltage (V)	Residence Time (s)	COD (mg/l) Initial	COD (mg/l) Final	% COD Reduction	pH	% Color Removal	Power Consumption (kWh/kg COD)
0.5	10	2.75	126	960	720	25	8.21	82	1.375
	20		63	960	792	18	5.93	53	1.275
	30		42	960	874	9	5.51	30	1.183
	40		31.5	960	941	2	5.29	14	1.24
1	10	3.25	126	960	600	38	8.17	97	2.076
	20		63	960	702	27	8.09	74	1.447
	30		42	960	787	18	6.65	54	1.442
	40		31.5	960	840	13	6.56	43	1.557
1.5	10	3.75	126	960	480	50	8.06	99	2.734
	20		63	960	567	41	7.6	94	1.671
	30		42	960	674	30	6.78	90	1.529
	40		31.5	960	795	17	7.15	84	1.987
2	10	4.25	126	960	240	75	7.19	100	2.715

	20		63	960	420	56	7.79	99	1.809
	30		42	960	586	39	7.13	95	1.741
	40		31.5	960	726	24	7.07	90	2.087
2.5	10	5	126	960	120	87	6.97	100	3.452
	20		63	960	298	69	7.36	98	2.189
	30		42	960	461	52	6.83	97	1.936
	40		31.5	960	600	38	7.03	93	2.014

Table 4. EFFECT OF CURRENT DENSITY AND FLOW RATE ON COLOR AND COD REDUCTION: DYE CONCENTRATION (1500 mg/l)

Current Density (A/dm^2)	**Flow rate (l/h)**	**Voltage (V)**	**Residence Time (s)**	**COD (mg/l) Initial**	**COD (mg/l) Final**	**% COD Reduction**	**pH**	**% Color Removal**	**Power Consumption (kWh/kg COD)**
0.5	10	2.75	126	480	196	59	6.24	77	1.161
	20		63	480	245	49	6.86	49	0.702
	30		42	480	288	40	5.92	40	0.573
	40		31.5	480	349	27	4.65	27	0.630
1	10	3.25	126	480	134	72	7.52	97	2.163
	20		63	480	178	63	6.89	63	1.236
	30		42	480	211	56	7.52	56	0.927
	40		31.5	480	240	50	7.72	50	1.112
1.5	10	3.75	126	480	96	80	6.47	100	3.418
	20		63	480	125	74	7.12	74	1.848
	30		42	480	172	64	7.94	64	1.420
	40		31.5	480	216	55	7.73	55	1.543
2	10	4.25	126	480	61	87	6.23	100	4.671
	20		63	480	88	82	6.8	82	2.496
	30		42	480	120	75	7.75	75	1.810
	40		31.5	480	160	67	7.6	67	1.987
2.5	10	5	126	480	1	100	7.19	100	6.054
	20		63	480	5	99	6.56	99	3.051
	30		42	480	48	90	6.96	90	2.240
	40		31.5	480	79	84	6.82	84	2.807

The effect of current density and the flow rate on COD reduction are shown in figure 3 for effluent of initial dye concentration 3000 mg/l and in figure 4 for 1500 mg/l concentration.

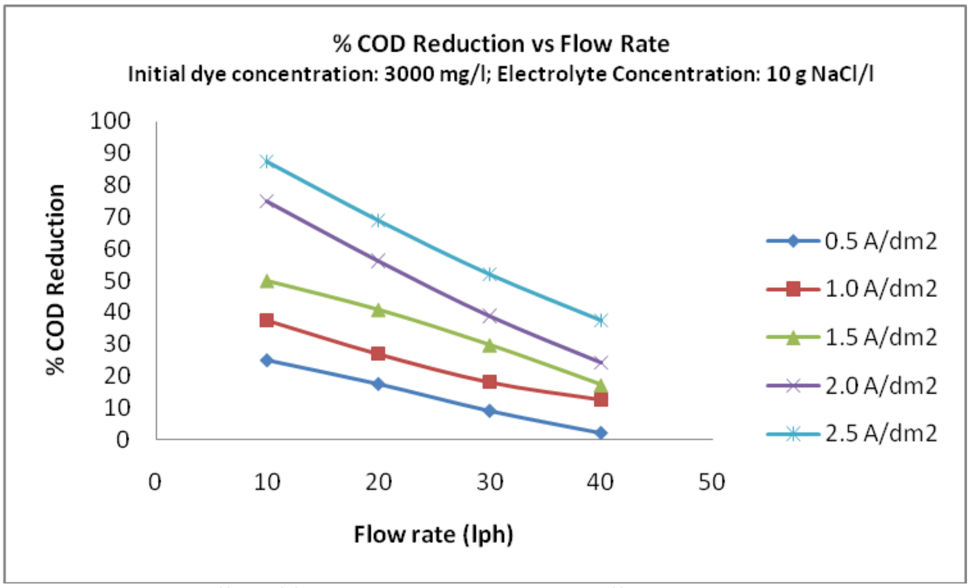

Fig. 3 Effect of flow rate on COD reduction at different current densities

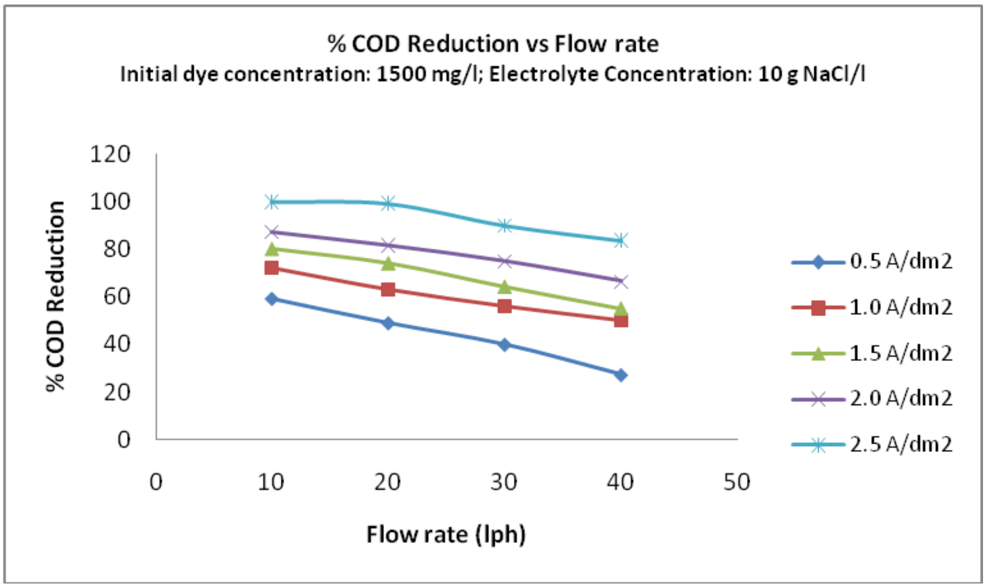

Fig. 4 Effect of flow rate on COD reduction at different current densities

Figures 5 and 6 depict the influence of current density and the flow rate on the color removal efficiency for 3000 mg/l and 1500 mg/l initial dye concentrations respectively.

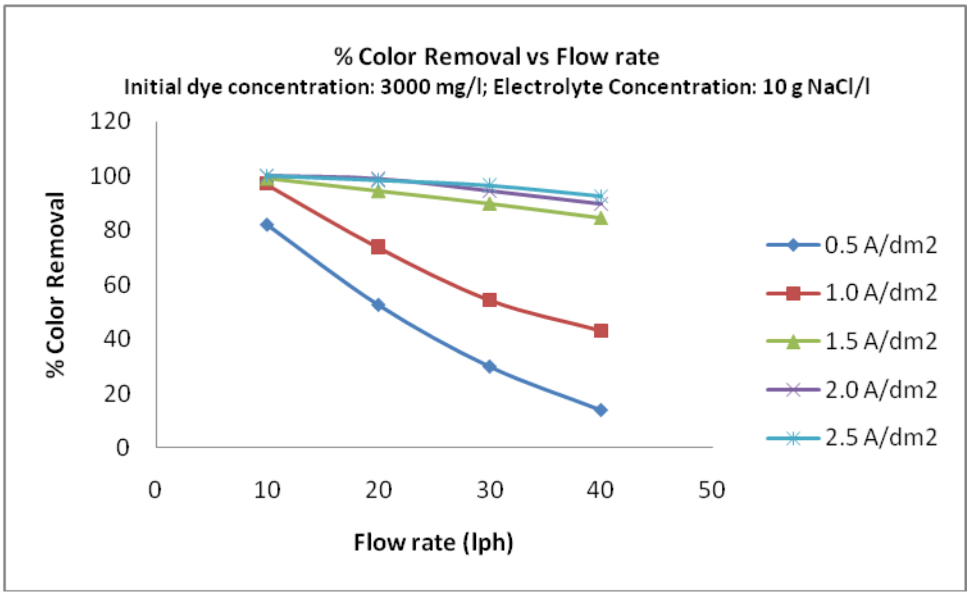

Fig. 5 Effect of flow rate on color removal at different current densities

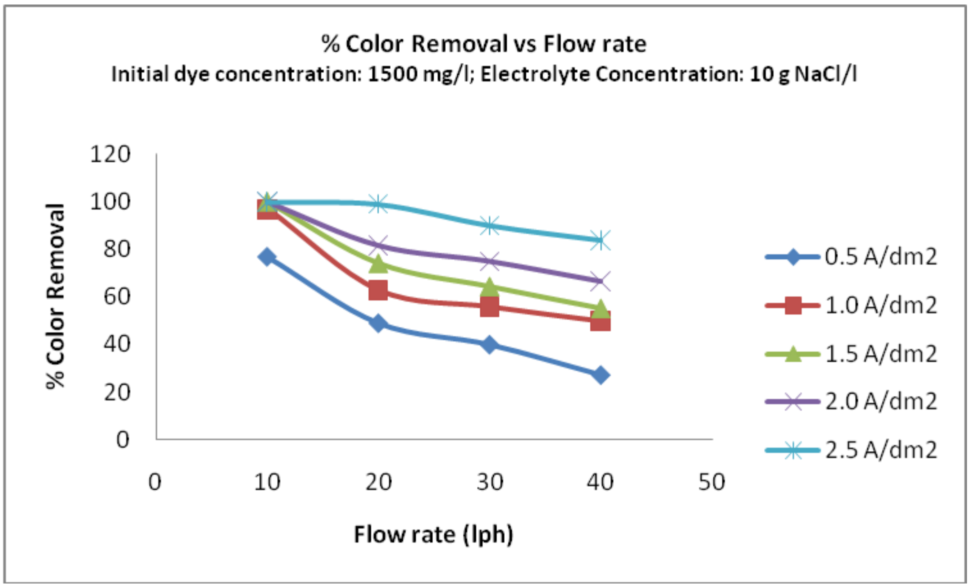

Fig. 6 Effect of flow rate on color removal at different current densities

As can be seen from the figures, the COD reduction and color removal efficiencies significantly increased with increase in current density and decrease in the flow rate. For example, percentage COD reduction increased from 25% to 87% for wastewater of 3000 mg/l initial dye concentration and from 59% to 100% for wastewater of 1500 mg/l dye concentration, when applied current density was increased from 0.5 A/dm^2 to 2.5 A/dm^2 and with the effluent flow rate being 10 lph in both situations. Percentage color removal also increased from 82% to 100% for 3000 mg/l feed and 77% to 100% for 1500 mg/l feed with current density increasing from 0.5 to 2.5 A/dm^2, at 10 lph feed rate. It is also seen that the percentage removal of COD and color decreases with increase in flow rate at every applied current density.

The electrochemical oxidation rate increases with current density if the pollutants are transported to the electrode surfaces efficiently; further the electrodes Ti/RuO_2 IrO_2 TiO_2 employed in this study catalytically liberate chlorine from the NaCl containing solution. Addition of NaCl to the wastewater increases the solution conductivity, and promotes indirect anodic oxidation by producing hypochlorite at the anode through the liberation of chlorine. It is the hypochlorites which reacts with the contaminants and remove them from the solution. Since the amount of hypochlorite produced increases with increase in current density, more hypochlorites are produced at higher values of current density, which react with more amounts of contaminants in the wastewater, resulting in better COD reduction and color removal.

It is seen that better results are obtained at the lower wastewater flow rate of 10 lph. The flow rate is related to the space or residence time and the residence time of the reactants in the reactor is the effective contact time during which the desired changes can occur. Generally more is the residence time; more would be the desired changes. Space or residence time is defined as the time required to process one reactor volume of feed measured at specified conditions or in other words is the ratio of reactor volume to volumetric flow rate. At low flow rates, residence times are high and COD reduction and color removal are more.

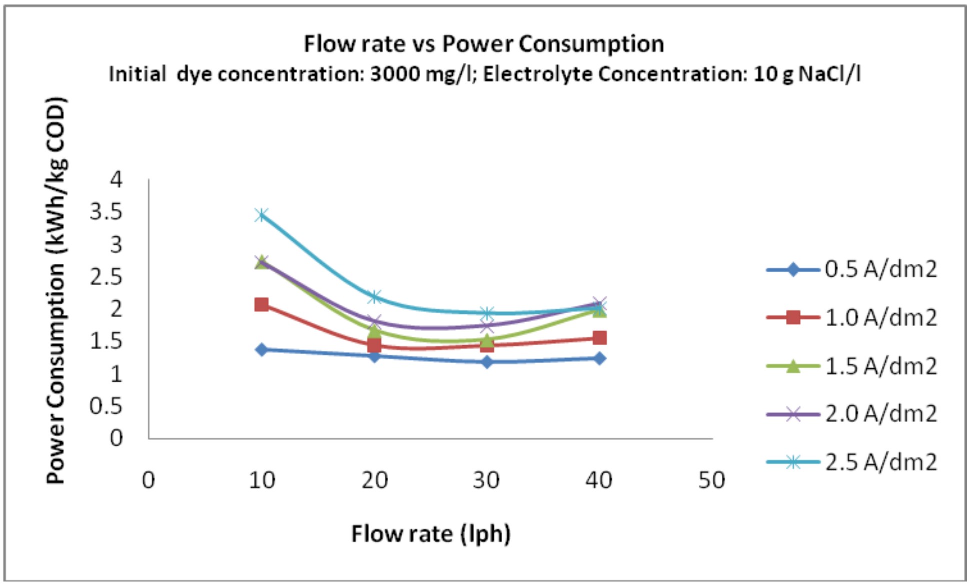

Fig. 7 Flow rate vs Power Consumption

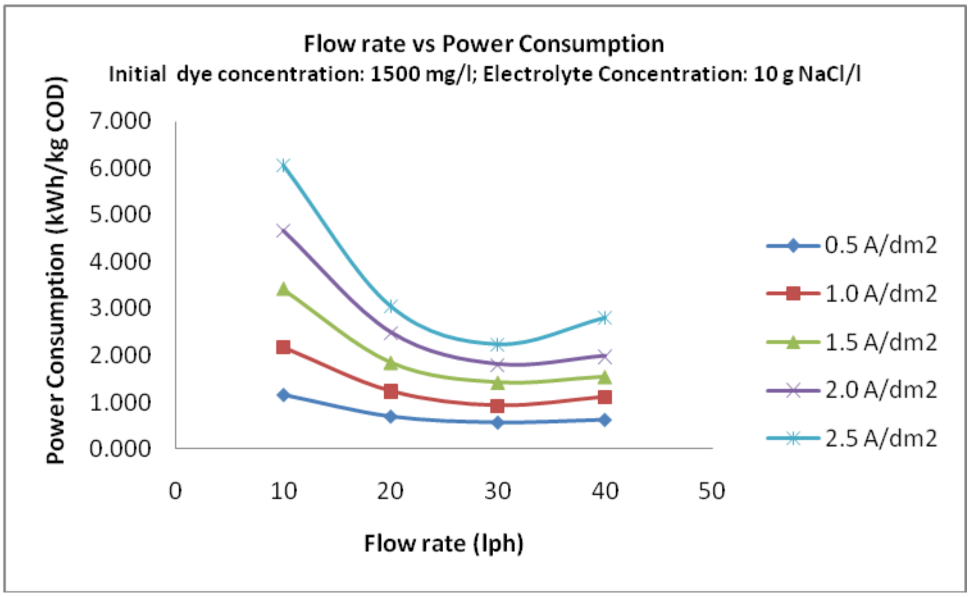

Fig. 8 Flow rate vs Power Consumption

The power consumption, calculated at various current densities and the flow rates as per the equation given by [19] are presented in Tables 2&3 and Fig. 7&8. 87% reduction in COD and 100% reduction in color were achieved at the current density of 2.5A/dm^2 and flow rate of 10 lph consuming 3.452 kWh/kg COD removed, when an effluent of 960 mg/l initial COD was treated. 100% removal of COD and color was possible under the same conditions with a power consumption of 6.054 kWh/Kg COD removed, when effluent of 480 mg/l initial COD was treated. The residence time and COD removed influence the value of power consumption along with the other variables. At lower flow rates, the residence time is more and more of easily oxidizable materials are quickly oxidized and kgs of COD removed is more. As the flow rate is increased both the residence time and the COD reduction are decreased. The decrease in residence time tends to increase the power consumption while the decrease in COD removal tends to increase the power consumption. Due to these two opposing tendencies, the power consumption reaches an optimum value at a fixed flow rate. Also increase in current density increases the power consumption by increasing the COD removal. The current density of 1.5 A/dm^2 and a flow rate of 10 lph can be taken as the optimum values for lower power consumption in the present investigation.

IV. CONCLUSIONS

The conclusions drawn from this study can be summarized as follows.

1. Electrochemical oxidation is effective in reducing the color and COD of simulated Acid green dye V textile effluent.
2. Percentage color removal increased with decrease in effluent flow rate and increased with increase in current density in both cases of initial dye concentrations. An effluent rate of 10 lph and a current density of 1.5 A/dm^2 were found to be optimum in the range of experimental conditions studied.
3. Energy consumption is affected by the operating conditions of flow rate, current density and initial dye concentration.
4. In conclusion, the application of electrochemical oxidation method employed in treating synthetically prepared Acid green V dye effluent resulted in almost colorless final wastewater with a considerably reduced value of COD.

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