

Electrochemical Oxidation of Textile Industry Wastewater Using DSA[®] In Tubular Reactor

E.Kavitha*

*(Assistant Professor, Department of Chemical Engineering, SRM University, Kattankulathur-603203, Kancheepuram District, Tamilnadu)

ABSTRACT

This paper presents the treatment of Acid green V by an electrochemical oxidation using Ti/RuO₂ IrO₂ TiO₂ as anode and cathode and NaCl as supporting electrolyte in a tubular flow reactor under continuous single pass process. During the electrolysis, COD reduction, color removal, and energy consumption were investigated under different flow rates and current densities. The experimental results showed that at 10 l/h flow rate and 2.5 A/dm² current density for an initial COD 960 mg/l (3000ppm), COD reduction, color removal and power consumption were found to be 87.5%, 100% and 3.2545 kWh/kg COD respectively. At the same flow rate and current density for an initial COD 480 mg/l (1500ppm), COD reduction, color removal and power consumption were found to be 100 %, 100% and 6.0417 kWh/kg COD respectively.

Keywords- Advanced oxidation, COD reduction, Color removal, Electro chemical oxidation, Textile wastewater

1. INTRODUCTION

Water is one of the abundantly available resources in nature and is essential for animal and plant life. Pollution of water bodies is increasing steadily due to industrial proliferation and urbanization. Nowadays, the worldwide production and use of chemical compounds have increased tremendously which find their way into the environment and many of these compounds are biologically non-degradable [1]. Many industries like textile, refineries, chemical, plastic and food-processing plants produce wastewater characterized by a perceptible content of organics (e.g. phenolic compounds) with strong color. Color is one of the most obvious indicators of water pollution and the discharge of highly colored effluents containing dyes can be damaging to the receiving bodies.

Textile dye processes are among the major industrial water users in many areas. This industrial wastes are the most difficult to treat satisfactorily [2]. The main cause of generation of this effluent is the use of huge volume of water either in the actual chemical processing or during re-processing in preparatory, dyeing, printing and finishing. In fact, in a practical estimate, it has been found that 45%

material in preparatory processing, 33% in dyeing and 22% are re-processed in finishing [3]. The fact is that the effluent generated in different steps is well beyond the standard and thus it is highly polluted and dangerous.

The establishment and enforcement of limits for the discharge and disposal of toxic and hazardous materials has required the development of advanced technologies to effectively treat a variety of gaseous and liquid effluents, solid waste and sludge. Conventionally effluents containing organics are treated with adsorption, biological oxidation, coagulation, etc. Though the conventional methods have individual advantages, they are lacking of effectiveness if applied individually. Due to the large variability of the composition of textile wastewater, most of the traditional methods are becoming inadequate. As environmental regulations become stringent, new and novel processes for efficient treatment of various kinds of wastewater at relatively low operating cost are needed. In this context, researchers are trying various alternative processes, such as electrochemical technique, wet oxidation, ionization, photo catalytic method for the degradation of organic compounds. Among these advanced oxidation processes, the electrochemical treatment has been receiving greater attention in recent years due to its unique features, such as versatility, energy efficiency, automation and cost effectiveness .

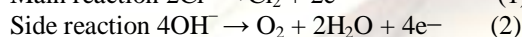
The electrochemical technique offers high removal efficiencies and has lower temperature requirements compared to non-electrochemical treatment. The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode. On anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where they are generated continuously (indirect electrolysis). In direct electrolysis, the rate of oxidation depends on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium

or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions [4].

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 1% 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 are assumed to take place [5]:

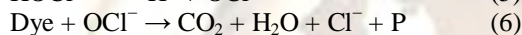
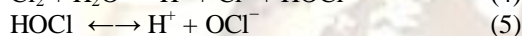
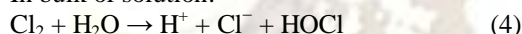
At anode:



At cathode:



In bulk of solution:



Since dye molecules of the effluent are electrochemically inactive, the primary reaction occurs at the anode is chloride ion oxidation (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 (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 (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 (4). The rate of reaction is less in acidic solution due to OH^- instability and considerably more in basic solution due to ready formation of OCl^- ion in (5) implying that the basic or neutral pH conditions are more favorable for conducting reactions involving Cl_2 [6]. 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^- .

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 Schematic diagram of indirect oxidation of pollutant is shown in Fig. 1 and 2. It shows a generalized scheme of the electrochemical conversion/combustion of organics on noble oxide coated catalytic anode (MO_x) [7].

3. MATERIALS AND METHODS

All the reagents used were of AR grade. NaCl was used as a supporting electrolyte and the synthetic effluent was prepared from Acid green V. The color index of the dye is 61570. The structure of dye is shown in Fig.3 and the characteristics of effluent before and after treatment is presented in TABLE 1 and 2.

3.1 Analytical measurements

The COD of all samples were determined by the dichromate reflux method [8]. The pH values of the untreated dye effluent and treated dye effluent were measured by using pH meter {LI 120}. The changes in absorbance characteristics of dye effluent were investigated over a large wavelength interval during the electrochemical decolorization process. UV-vis Spectra of untreated dye effluent and treated effluent were measured by using a UV-vis spectrophotometer {SL 159}. From the absorbance values the reduction in dye concentration or the color removal was calculated by following formula:

$$\% \text{ color removal} = 100 \times \frac{[\text{ABS}_0^{\text{M}} - \text{ABS}^{\text{M}}]}{\text{ABS}_0^{\text{M}}} \quad (7)$$

where ABS^{M} is the average of absorbance values at its maximum absorbency visible wavelength. ABS_0^{M} the value before electrolysis, ABS^{M} the value after electrolysis [5].

3.2 Electrolytic Tubular flow reactor

A schematic view of the experimental set-up is shown in Fig.4. The electrolytic flow reactor is a cylindrical glass column of 5cm diameter and 21.5cm length. The electrolytic flow reactor consists of parallel plate cathode (20cm x 3cm x 0.15cm; 3 Numbers) and anode (20cm x 3cm x 0.15cm; 2 Numbers). Both the electrodes were made of mixture of metal oxides (RuO_2 , IrO_2 , and TiO_2) of 6 μm thickness coated over titanium substrate. The electrodes were held vertically and positioned parallel to each other in the electrolytic reactors such that a 1cm inter electrode gap was maintained. Provisions are made for electrical connections so as to constitute an electrolytic cell. The holdup of the cell is 350ml. Additionally; the cell has one inlet at the bottom and one outlet at the top. It was connected to 0 – 20A and 0 – 15 V DC regulated power supply. Reservoir, dosing pump and electrolytic tubular reactor are connected using rubber tubes.

3.4 Experimental procedure

The effluents were taken in the reservoir, which was pumped to the cell using dosing pump. 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 with NaCl as electrolyte medium. After attaining steady-state, the outlet samples were collected and subjected to COD, pH and color {UV-vis spectra} analysis. The various experimental conditions and parameters were studied at different current densities such as 0.5, 1, 1.5, 2 and 2.5 A/dm². For the flow rates of effluent to the reactor such as 10, 20, 30, 40 l/h the experiment was repeated for different current densities 0.5, 1, 1.5, 2 and 2.5 A/dm².

4. RESULTS AND DISCUSSION

The effects of the parameters such as flow rate and current density on rate of COD removal as well as color removal were investigated in a electrolytic tubular reactor in a single pass for Acid green V in a NaCl electrolyte medium. The following data such as % COD reduction, pH, % color removal, power consumption is given in TABLE 3 & 4.

4.1 Effect of current density and flow rate on COD reduction

The extents of COD removal at different flow rates under different current densities were shown in Fig. 5 & 6. The Results showed that higher COD reduction occurred at higher current density and lower flow rate. 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 at higher current density 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 led to gradual decrease in the COD removal; at 40 l/h it was 50 % less than that at 10 l/h flow rate and 2.5A/dm² current density for 3000ppm concentration, and COD at 40 l/h was 25% less than that at 10 l/h flow rate and 2.5A/dm² current density for 1500ppm concentration 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 100% at 10 l/h flow rate and 2.5A/dm² current density for 1500ppm concentration. As the inlet flow rate was increased to 10, 20, 30 and 40 l/h, the residence time directly decreased to 126, 63, 42 and 31.5 sec. For the concentration of 3000ppm, if the flow rate was increased from 10 l/h to 40 l/h, correspondingly the COD reduction efficiency decreased from 87.5% to 37.5% for the maximum current density 2.5 A/dm². Similarly, for the concentration of 1500ppm, if the

flow rate was increased from 10 l/h to 40 l/h, correspondingly, the COD reduction efficiency decreased from 100% to 75% for the maximum current density 2.5 A/dm². It showed that the effects of inlet flow rate as well as current density affected the COD reduction. Therefore, the optimum operating conditions for maximum COD reduction by electrochemical oxidation were 2.5 A/dm² current density and 10 l/h flow rate.

4.2 Effect of current density and flow rate on Color removal

The extents of color removal at different flow rates under different current densities were shown in Fig.7 & 8. The Results showed that higher color removal obtained at higher current density and lower flow rate. The maximum color removal (100%) was obtained at 10 l/h flow rate and 2.5 A/dm² current density. At high flow rate (40 l/h) and lower current density (0.5 A/dm²) the color removal was found to be low. It showed that the flow rate and current density affected the color removal. Therefore, the optimum operating conditions for electrochemical oxidation were 2.5 A/dm² current density and 10 l/h flow rate.

5. CONCLUSION

In the present work, the experiments were carried out in a once through electrolytic tubular reactor under different flow rates and current densities for COD reduction and color removal of the synthetic dye effluent. The following conclusions can be arrived at:

Treatment using physico-chemical methods produce more sludge and involve high cost and lower efficiency. In biological treatments the process takes longer time and gives lower efficiency. Hence, this electrochemical treatment is best suited for treating the dye effluent.

At 10 l/h flow rate and 2.5 A/dm² current density for an initial COD 960 mg/l (3000ppm), COD reduction and color removal were found to be 87.5% and 100% respectively. Power consumption required for the above condition was 3.2545 kWh/kg COD. On the other hand, at 10 l/h flow rate and 2.5 A/dm² current density for an initial COD 480 mg/l (1500ppm), COD reduction and color removal were found to be 100 % and 100% respectively with the power consumption of 6.0417 kWh/kg COD. Hence, operating at high concentration reduces the power consumption.

6. FUTURE WORK

From this experiment, good positive results were obtained for synthetic dye effluent. So, it has been decided to use this technique to treat real textile industry effluent as well as other industrial wastewater.

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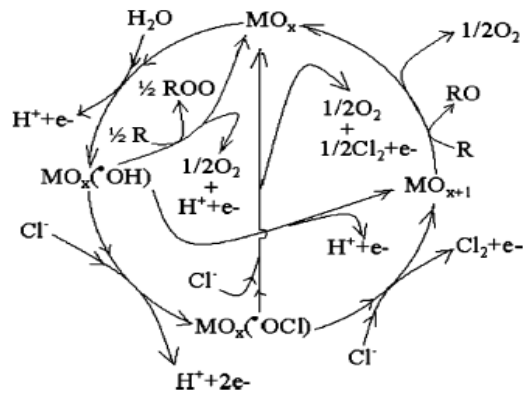


Fig. 2. Scheme of electrochemical oxidation of organic pollutants in presence of chloride ion

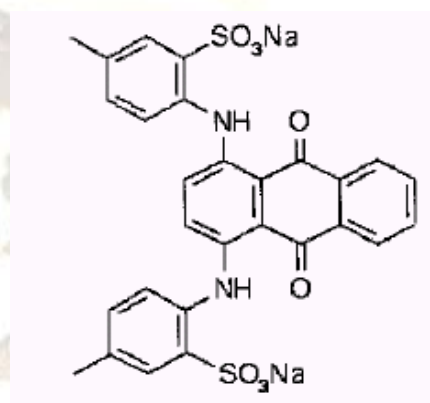


Fig. 3. Structure of Acid green V dye

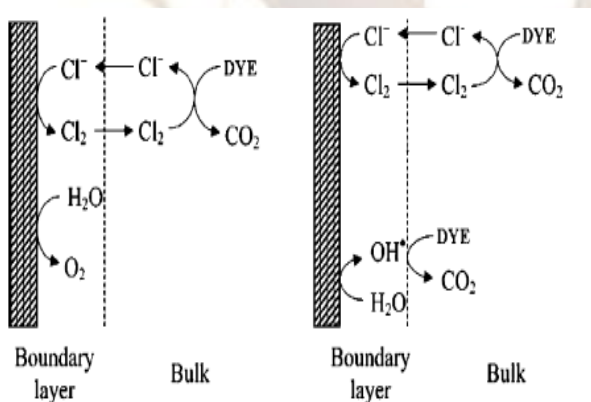


Fig. 1. Scheme of the reactions and processes involved in the dye oxidation

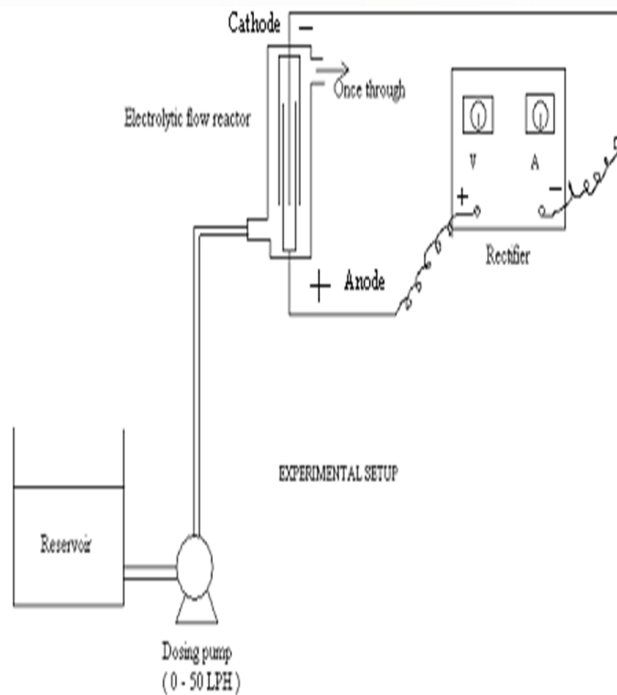


Fig. 4. Schematic diagram of Experimental set Up

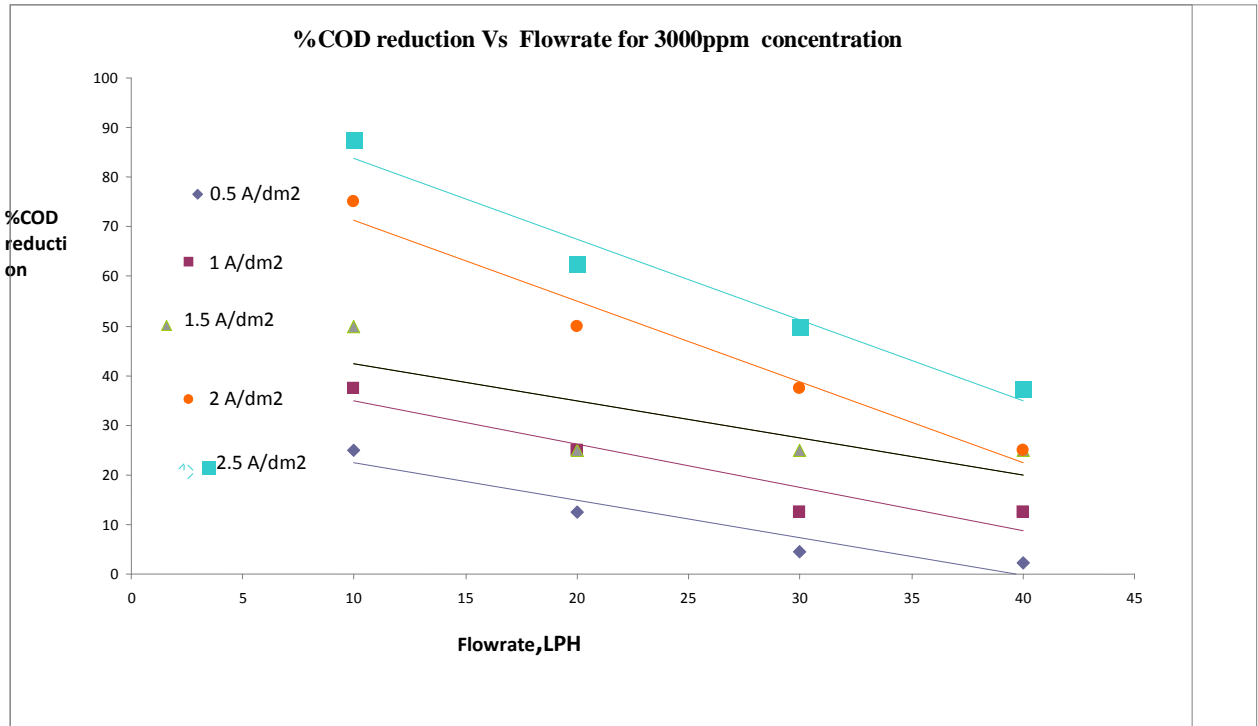


Fig. 5. Effect of COD reduction on flow rate at different current densities for 3000ppm concentration of synthetic dye effluent

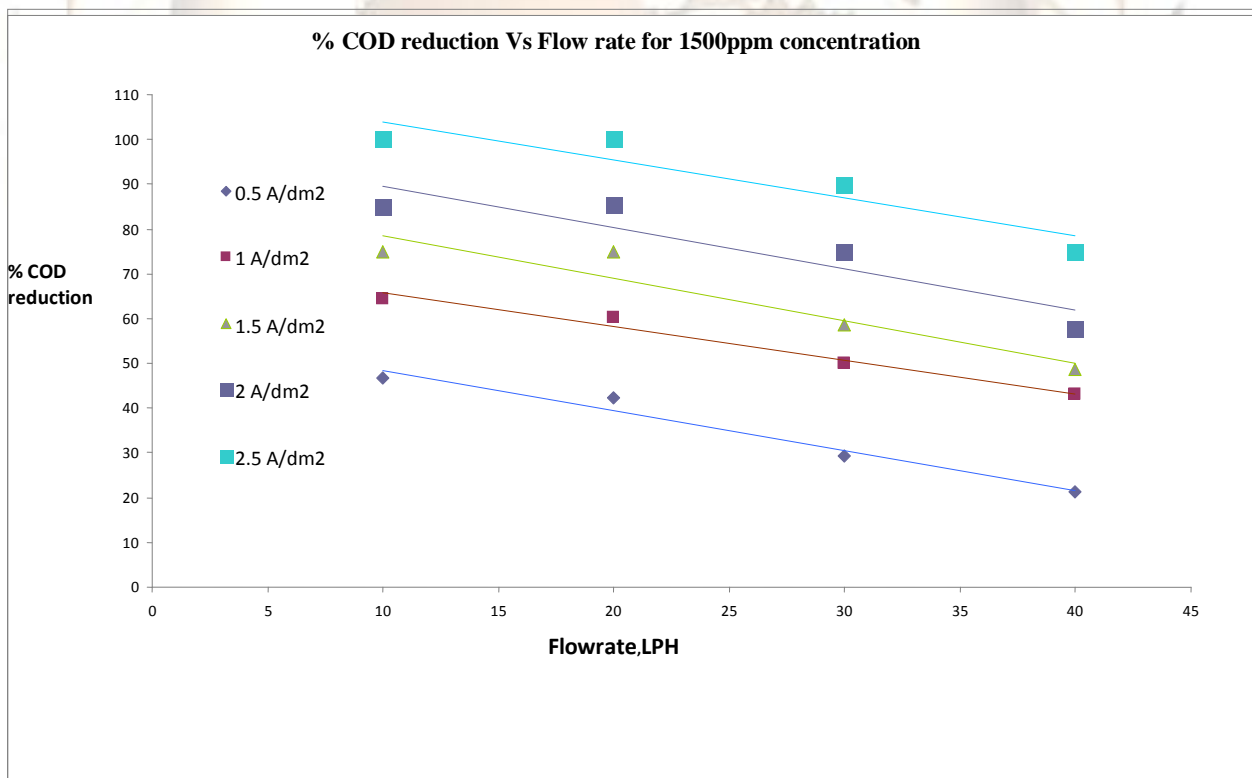


Fig. 6. Effect of COD reduction on flow rate at different current densities for 1500ppm concentration of synthetic dye effluent

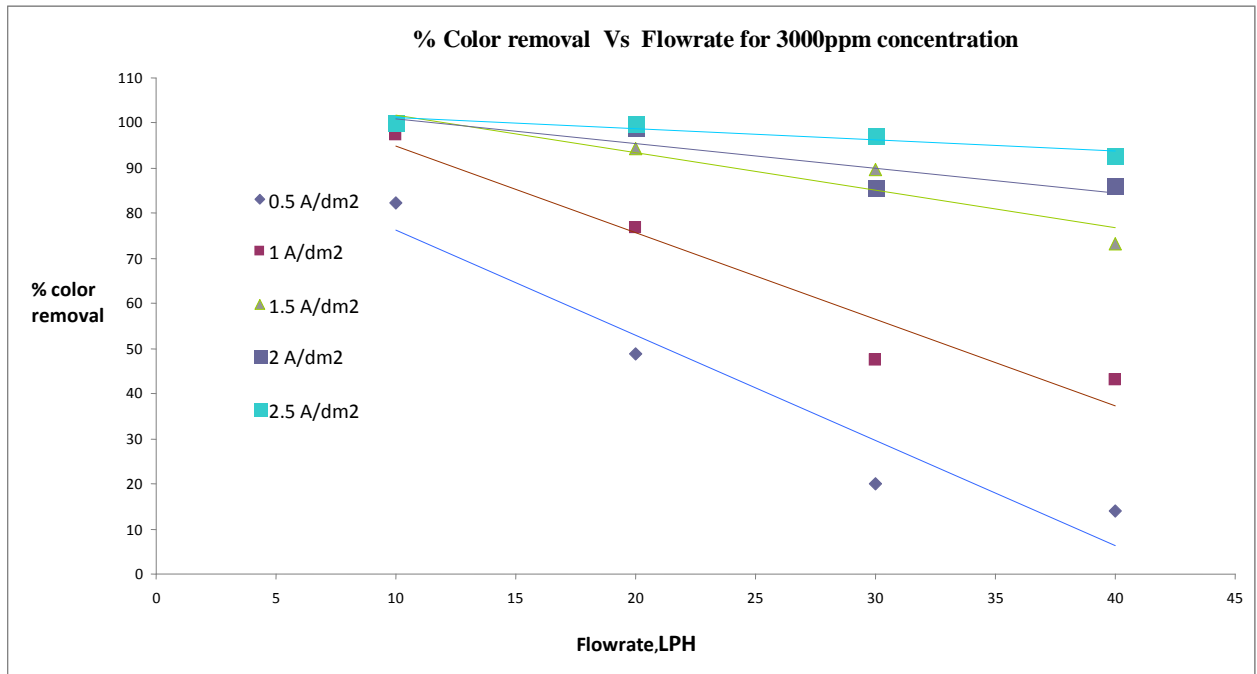


Fig. 7. Efficiency of color removal on flow rate at different current densities for 3000ppm concentration of synthetic dye effluent

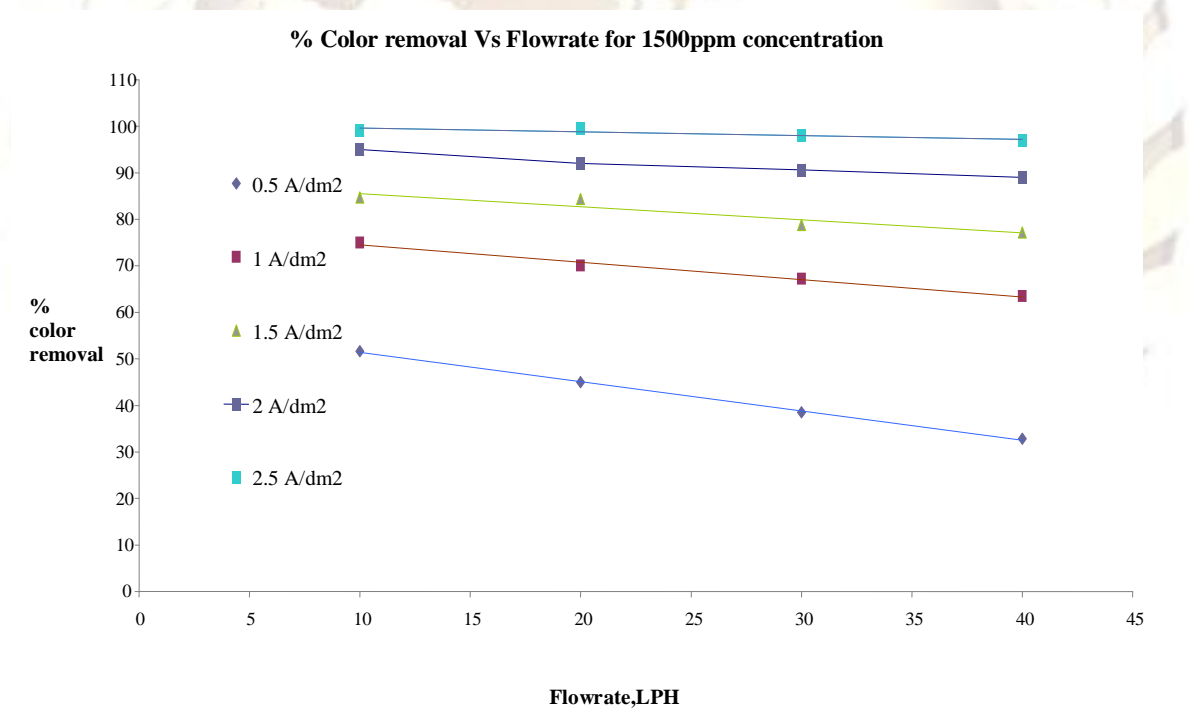


Fig. 8. Efficiency of color removal on flow rate at different current densities for 1500ppm concentration of synthetic dye effluent

Table 1

Characteristics of the effluent

Trade Name: Covacap Vert W 7103

Initial Concentration: 3000 ppm; maximum wave length, λ_{max} : 637 nm

Particulars	Acid green V dye effluent before treatment	Acid green V dye effluent after treatment (current density 2.5 A/dm ² at 10l/h flow rate)
pH	4.55	6.97
COD (mg/l)	960	600
Molecular weight	622.58	-
Molecular formula	C ₂₈ H ₂₂ N ₂ O ₈ S ₂ .2Na	-
Density (kg/m ³)	1003.29	-
Color index	61570	-
Viscosity at 30°C (kg/m s)	9.9661 x 10 ⁻⁴	-

Table 2

Initial Concentration: 1500 ppm; maximum wave length, λ_{max} : 637 nm

Particulars	Acid green V dye effluent before treatment	Acid green V dye effluent after treatment (current density 2.5 A/dm ² at 10 l/h flow rate)
pH	6.49	7.19
COD (mg/l)	480	0
Molecular weight	622.58	-
Molecular formula	C ₂₈ H ₂₂ N ₂ O ₈ S ₂ .2Na	-
Density (kg/m ³)	980.74	-
Color index	61570	-
Viscosity at 30°C (kg/m s)	8.664 x 10 ⁻⁴	-

Table 3

Effect of current density and flow rate on % COD reduction, % color removal and power consumption for the 3000ppm concentration of synthetic dye effluent

Current density, A/dm ²	Flow rate, LPH	Voltage, V	Current, A	Residence time, t sec	COD			pH	% color removal	Power consumption, kWh/kg COD
					COD		%COD reduction			
					Initial	Final				
0.5	10	2.75	1.2	126	960	720	25	8.21	82.1835	1.375
	20	2.75	1.2	63	960	840	12.5	5.93	21.1654	1.375
	30	2.75	1.2	42	960	959	12.5	5.51	6.296	110.00
	40	2.75	1.2	31.5	960	959	12.5	1.284	13.9987	82.5
1	10	3.25	2.3	126	960	600	37.5	8.17	97.3878	2.0764
	20	3.25	2.3	63	960	720	25	8.09	76.6912	1.5573
	30	3.25	2.3	42	960	840	12.5	6.65	47.5553	2.0764
	40	3.25	2.3	31.5	960	840	12.5	6.849	43.1346	1.5573
	10	3.75	3.5	126	960	480	50	8.06	99.6651	2.7344
	20	3.75	3.5	63	960	720	25	7.6	94.3737	2.7344

1.5	30	3.75	3.5	42	960	720	25	6.78	89.6852	1.8229
	40	3.75	3.5	31.5	960	720	25	6.399	73.2753	1.3672
	10	4.25	4.6	126	960	240	75	7.19	100	2.7153
	20	4.25	4.6	63	960	480	50	7.79	98.9283	2.0365
2	30	4.25	4.6	42	960	600	37.5	7.13	85.5995	1.8102
	40	4.25	4.6	31.5	960	720	25	6.205	86.2693	2.0365
	10	5	5.8	126	960	120	87.5	6.97	100	3.4524
	20	5	5.8	63	960	360	62.5	7.36	99.933	2.4167
2.5	30	5	5.8	42	960	480	50	6.83	97.0529	2.0139
	40	5	5.8	31.5	960	600	37.5	6.109	92.6993	2.0139

Table 4

Effect of current density and flow rate on % COD reduction, % color removal and power consumption for the 1500ppm concentration of synthetic dye effluent

Current density, A/dm ²	Flow rate, LPH	Voltage, V	Current, A	Residence time, t sec	COD			pH	% color removal	Power consumption, kWh/kg COD
					Initial	Final	%COD reduction			
0.5	10	2.75	1.2	126	480	360	25	6.24	29.4562	2.75
	20	2.75	1.2	63	480	360	25	6.86	15.71	1.375
	30	2.75	1.2	42	480	479	25	5.92	11.6314	110.000
	40	2.75	1.2	31.5	480	479	25	4.65	7.2508	82.50
1	10	3.25	2.3	126	480	240	50	7.52	96.9789	3.1146
	20	3.25	2.3	63	480	240	50	6.89	85.3474	1.5573
	30	3.25	2.3	42	480	240	50	7.52	71.7523	1.0382
	40	3.25	2.3	31.5	480	240	50	7.72	69.7885	0.7786
1.5	10	3.75	3.5	126	480	120	75	6.47	100	3.6458
	20	3.75	3.5	63	480	120	75	7.12	95.9215	1.8229
	30	3.75	3.5	42	480	240	50	7.94	93.3535	1.8229
	40	3.75	3.5	31.5	480	360	25	7.73	92.2961	2.7344
2	10	4.25	4.6	126	480	0	100	6.23	100	4.0729
	20	4.25	4.6	63	480	120	75	6.8	98.9426	2.7153
	30	4.25	4.6	42	480	120	75	7.75	100	1.8102
	40	4.25	4.6	31.5	480	240	50	7.6	99.6979	2.0365
2.5	10	5	5.8	126	480	0	100	7.19	100	6.0417
	20	5	5.8	63	480	0	100	6.56	99.8489	3.0208
	30	5	5.8	42	480	360	25	6.96	100	8.0556
	40	5	5.8	31.5	480	120	75	6.82	100	2.0139