Electrochemical Degradation of Indigo Carmine Textile Dye Powered by Solar Photovoltaic Energy

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Abstract: The proposed photovoltaic electro oxidation process combines the autonomous and environmentally friendly photovoltaic solar energy with the capability of electro oxidation at boron doped diamond electrodes to effectively decolorize and degrade indigo carmine textile dye from wastewater. The photovoltaic array can be connected directly to the electrochemical reactor without batteries increasing, in this way, the system sustainability and eliminating the environmental threat of improper battery disposal. The system is made versatile according to the instantaneous solar irradiation by adjusting the wastewater flow rate to the current intensity supplied by the photovoltaic panel. All operating parameters affecting the efficiency of the proposed process, such as wastewater conductivity, pH, flow rate, current density, electro processing time and solar irradiance were studied and optimal conditions were investigated. The experimental results showed that by applying current densities of 1, 2.5 and 5 mA cm^2 the initial dye concentration of 100 mg L^{-1} in the treated wastewater was quantitatively eliminated in 45, 20 and 10 minutes of electro processing respectively. The process is appropriate for treatment of colored industrial textile dye house effluents and especially for applications in remote and isolated locations without connection to public electric grid.

1. INTRODUCTION

The textile industry consumes enormous amounts of water during dyeing and finishing operations. Typical medium-scale textile factories produce approximately 1000 m^3 of wastewater per day. It is estimated that around 30% of the applied dyes remain unfixed and are discharged in the effluent. Dye bearing wastewaters are toxic for the environment since dyes are stable compounds and may cause carcinogenesis. Conventional biological treatment processes are often less successful because most dyes are barely or non biodegradable [1] Dye house industries are under pressure to reduce the color in effluents and search for 'greener' methods, more effective and less polluting.

Indigo Carmine (5.5'–indigo disulfonic acid disodium salt) is a dark blue dye mainly used in the textile industry for the dyeing of polyester fibers and denim (blue jeans) [2]. Indigo Carmine is also used as dye in food and cosmetics industry. Several processes have been suggested for removal of Indigo Carmine and other dyes from wastewater including adsorption [3], photochemical [4] and electrochemical methods [5-9].

Increased environmental pollution and social concern about the environment in the last decades have led to the development of new renewable energy forms. The photovoltaic (PV) solar energy is one of the most popular and well studied renewable energy sources, which, as autonomous and environmentally friendly, is appropriate for small applications and especially in remote and isolated locations with lack of electric grid. Electrochemical processes directly powered by photovoltaic energy have been recently reported in literature [10-14]. As we are aware, none of them deals with indigo carmine removal from synthetic or industrial effluents.

The present paper demonstrates the possibility of decolorizing and degrading colored indigo carmine bearing wastewater using the electro oxidation process with boron doped diamond electrodes, which is directly powered by a PV panel without batteries. The photovoltaic electro oxidation (PV-EO) system is made versatile according to the instantaneous solar irradiation by adjusting the wastewater flow rate to the current density supplied by the PV generator. All operating parameters affecting the PV-EO process, such as wastewater pH, current density, conductivity, flow rate, contact time and solar irradiation are determined.

2. METHODS

The reactive dye indigo carmine (Disodium (2E) -3-oxo-2-(3-oxo-5-sulfonato-1,3-dihydro-2H-indol-2-

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ylidene)-5-indoline-sulfonate) was purchased from Aldrich (CAS Nr: 860-22-0). Its structure is shown in Figure **1**.
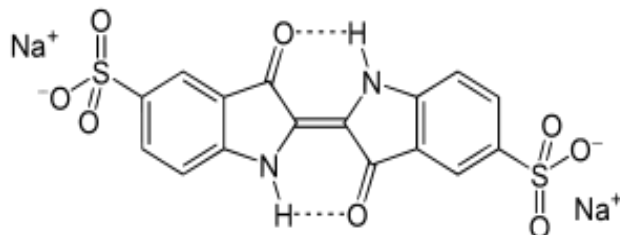

Figure 1: Chemical structure of reactive dye indigo carmine, Mr: 466.36, Linear Formula: $C_{16}H_8N_2O_8S_2Na_2$).

The photovoltaic module used was SUNPOWER (Maxeon Cell Technology) SPR-327NE-WHT-D made from monocrystalline silicon with a surface area of 1.63 m^2 and a peak power of 327 W. The experiments were conducted in Kavala Institute of Technology (latitude 40° 55´, longitude 24° 22´ and altitude 138 m above the sea level).

DC voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductometer (WTW). The pH and the temperature were measured using a Hanna pH-meter. The wastewater was circulated by a peristaltic pump.

Electrolyses were conducted at room temperature in a cylindrical glass cell of 400 ml in which 200 ml of wastewater were placed and slowly stirred with a magnetic bar at 500 rpm. The electrodes used for electrooxidation were one central Boron Doped Diamond (BDD) electrode, (DiaCCom, Germany) of size 10cm x 5cm x 0.2cm immersed to a 6 cm with an effective area of 60 cm^2 serving as anode and two outer graphite plate electrodes of same dimensions serving as cathodes. The interelectrode distance was 0.5 cm. Na_2SO_4 as supporting electrolyte was added to the treated solution for decrease of the excessive ohmic resistance in the solution. Samples were extracted every 2.5 minutes, filtered using Whatman filter paper (Grade 40). UV-VIS Spectrophotometry (HITACHI U-2000, Japan) was used for spectrographic analysis of dye concentrations. Known concentrations of the indigo carmine dye solution were scanned at optimum absorption wavelength of 612 nm for generating the calibration plot. Samples were diluted using distilled water if the absorbance exceeded the range of calibration curve. Figure **1** shows a flow diagram of the proposed PV-EO process.
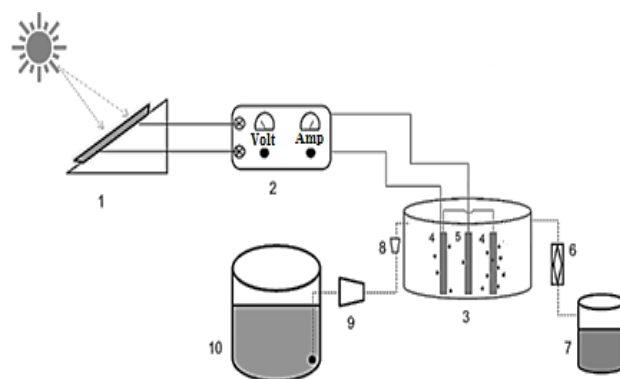
Figure 2: Diagram of the experimental setup. 1. PV Solar module 2. Regulator 3. Electrooxidation reactor 4. Electrode (a) 5. Electrode (b) 6. Filter 7. Treated solution 8. Flow meter 9. Peristaltic pump 10. Wastewater deposit.
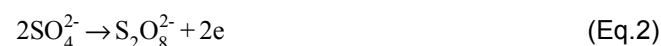
3. RESULTS AND DISCUSSION

3.1. Effect of Operating Parameters

The PV-EO process is affected by several operating parameters, such as initial pH, current density, conductivity, flow rate and contact time. In the present study all these parameters have been explored in order to evaluate a treatment technology for indigo carmine removal from wastewater.

3.1.1. Effect of Initial pH

In our previous work [15] the treatment of indigo carmine aqueous solutions was optimized by means of conventional electrooxidation with platinized titanium (Ti/Pt) and graphite electrodes and has been shown that the electrochemical degradation of indigo carmine is pH dependant with pH=3 being the optimum. Also other researchers [7,9,16,17] reported that acidic electrolyte solutions favor the electrooxidation process, due to the increased oxidation power of the intermediate oxidants which are produced during the electrooxidation process according to reactions (1-4):

$$H_2O \rightarrow OH^* + H^+ + e \qquad (Eq.1)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e \qquad (Eq.2)$$

$$2Cl^- \rightarrow Cl_2 + 2e \qquad (Eq.3)$$

$$2OH^* \rightarrow H_2O_2 \qquad (Eq.4)$$

The most powerful oxidant in water is the hydroxyl radical OH* with a redox potential of 2.8_{NHE}. Chemical Advanced Oxidation Processes (AOPs) and Electrochemical Advanced Oxidation Processes (EAOPs), therefore, are characterized by the production and use of these hydroxyl radicals for

oxidative destruction of organic substances. BDD electrodes show the largest overvoltage for oxygen production and the widest potential window in water ever found for an electrode material [18,19]. These electrodes are also chemically and mechanically stable. Therefore, BDD electrodes, compared to other electrodes are the most suited for producing free OH* radicals and performing EAOPs with very high current efficiencies [16,19-21].

In order to show the dependence of electrooxidation from initial solution pH, the electrooxidation process was conducted at three different initial pH values of 3, 7 and 11 using 200 mL solution volume with initial 100 ppm dye concentration, constant current density 2.5 mA/cm^2 and constant electroprocessing time 20 min. (Table **1**).

Table 1:   Removal Percentage of Indigo Carmine by Electrooxidation at Various pH Values

	pH=3	pH=7	pH=11
Dye removal(%)	>99	75.3	46.4

3.1.2. Effect of current density

Measurements were carried out at different current densities 1.0-5.0 mA/cm^2, using 200 mL solution volume with initial 100 ppm indigo carmine concentration and optimum pH 3. According to Table **2** the removal rate of the dye increased, as expected, with increasing current density. In 45, 20 and 10 minutes of electrolysis time at the corresponding

current densities of 1.0, 2.5 and 5.0 mA/cm^2, indigo carmine has been quantitatively decolorized and degraded (>99%) and its concentration fell under the apparatus detection limit (0.08 mg/L).

3.1.3. Effect of Conductivity

The wastewater conductivity affects immediately the applied voltage and therefore the electrical energy consumption. The removal percentage of indigo carmine is hardly affected and remains constant over 99 % for the three tested wastewater conductivities of 2000, 4000 and 8000 μS/cm (Table **3**).

3.1.4. Effect of flow rate

The current density supplied by the PV array depends on the solar irradiation and the temperature of the PV modules. These parameters cannot be controlled and will change continuously through the hours in a day or suddenly through clouds crossing or changes in wind speed. Ortiz *et al.* and Valero *et al.* [11,12] proposed a clever mode of operation in order to make the PV-EO system versatile to instantaneous solar irradiation by keeping constant the ratio current density/flow rate. Thus, when the current density supplied by the PV array changes, also the working flow rate must proportionally change to maintain this ratio constant. This operation way implies that the volume of treated wastewater is directly related to the solar energy incident on the panels. Advantages for not using batteries are the lower installation costs, the higher electrical energy utilization, the avoidance of environmental problems related to improper battery

Table 2:   Concentration Variation of Indigo Carmine with Time at Different Current Densities

Time (min)	Dye concentration (mg/L)		
	1.0 mA/cm^2	2.5 mA/cm^2	5.0 mA/cm^2
0	100	100	100
5	66	42	23
10	44	18	0
15	31	4	
20	19	0	
25	12		
30	8		
35	5		
40	2		
45	0		

Table 3:   Electrooxidation Results for Different Wastewater Conductivities

Conductivity (µS/cm)	Voltage(V)	Energy consumption (kWh/m^3)	Removal percentage (%)
2000	20.4	5.2	>99
4000	11.7	3.1	>99
8000	6.2	1.6	>99

disposal and the increase of the system sustainability. The experiments with constant current density and flow rate were conducted at a sunny midday and in short periods to keep approximately constant values of solar irradiation. As can be obtained from Table **4**, by increasing the current density the cell voltage and flow rate increase proportionally, while the residence time decreases. The removal percentage of indigo carmine is hardly affected and remains high >99 % in all experiments.

3.2. Solar irradiation and *I-V* curve of photovoltaic module

The solar irradiation intensity depends on the occasional meteorological/geographical conditions and influences the photovoltaic output current and therefore, the performance of the electrooxidation process. As stated in section 3.1.4, the flow rate of the treated wastewater can be used as the control parameter.

The most important characteristics of the current-voltage curve of the photovoltaic module for a solar irradiation of 1000 w/m^2 and temperature of 25° C are given in Figure **2**. The short circuit current I_{sc} is the maximum current supplied by the PV panel at zero voltage between terminals. It depends mainly on solar irradiation and amounts to 6.46 Ampere. The open circuit voltage is the maximum voltage reached in absence of load. It depends mainly on temperature and amounts to 64.9 Volt. The characteristic *I-V* curve of the PV module refers to the specific unit used for the experiments. The inserted blue line in the diagram shows the behavior of the photovoltaic panel after the unavoidable increase of the cell temperature to 50 ^{0}C.
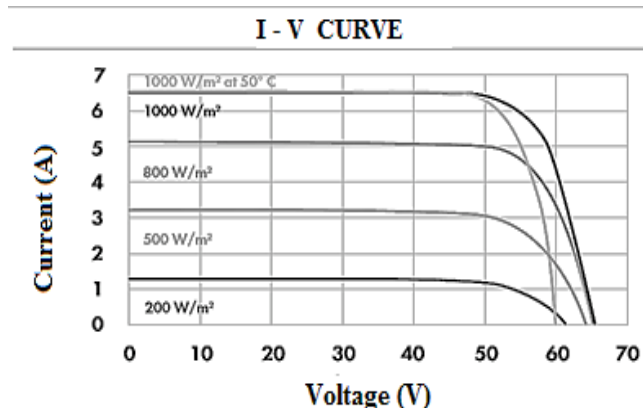
Figure 2: I-V Curve of photovoltaic module.

The photovoltaic panel produces electrical energy also at periods of low intensity. Table **5** shows the measured solar irradiation and solar electricity generation at both, sunny and cloudy days throughout the months of the year. It is implied that the volume of the treated wastewater depends on solar intensity and the generated electrical energy.

Based on Tables **3** and **5**, for a sunny and a cloudy day e.g. in May and a wastewater conductivity of 8000 µS/cm, the estimated volume of treated wastewater amounts to 1.73 and 1.36 m^3 per day respectively. For higher quantities of wastewater a photovoltaic array of more panels is needed.

4. CONCLUSIONS

This paper shows the feasibility of performing remediation of indigo carmine wastewater by directly connecting the electrooxidation reactor to the photovoltaic generator. The current density supplied by the PV panel depends on the solar irradiation and the

Table 4:   Electrooxidation Results for Different Wastewater Flow Rates

Flow rate (L/h)	Current density (mA/cm^2)	Voltage (V)	Residence time (min)	Dye removal percentage (%)
0.5	1.0	4.8	24	>99
1.0	2.5	9.2	12	>99
1.5	5.0	17.4	8	>99

Table 5: Experimental Conditions and Measured Parameters for Different Meteorological Conditions

Month	Unshaded % of the area	Ideal Tilt Azimuth=180	Actual Unshaded Solar Radiation Sunny day kWh/m²	Actual Unshaded Solar Radiation Cloudy day kWh/m²	Actual Unshaded Solar Radiation Sunny day kW/m²	Actual Unshaded Solar Radiation Cloudy day kW/m²	Solar electricity generation Sunny day kWh	Solar electricity generation Cloudy day kWh
January	100,00%	52	3,02	2,15	0,378	0,268	1,13	0,81
February	100,00%	43	3,63	2,6	0,404	0,289	1,33	0,96
March	100,00%	31	4,61	3,34	0,512	0,371	1,86	1,37
April	100,00%	18	5,53	4,15	0,582	0,437	2,25	1,72
May	100,00%	6	6,27	4,83	0,66	0,508	2,78	2,19
June	100,00%	0	6,68	5,35	0,703	0,563	3,17	2,59
July	100,00%	2	6,43	5,24	0,677	0,551	2,97	2,46
August	100,00%	14	5,84	4,79	0,615	0,504	2,44	2,03
September	100,00%	30	5,09	4,15	0,566	0,461	2,11	1,74
October	100,00%	45	4,34	3,51	0,482	0,39	1,64	1,34
November	100,00%	56	3,64	2,8	0,455	0,35	1,38	1,08
December	100,00%	57	3,07	2,24	0,409	0,299	1,18	0,87
Yearly Avg					0,537	0,416	2,02	1,60

temperature of the photovoltaic modules. However, the PV-EO system is made versatile to instantaneous solar irradiation by adjusting the flow rate of the treated wastewater and keeping constant the ratio current density/flow rate. The removal percentage of indigo carmine remains high (>99 %) for the three tested wastewater flow rates of 0.5, 1.0 and 1.5 L/h and the three wastewater conductivities of 2000, 4000 and 8000 µS/cm. Based on the experimental results, the proposed PV-EO process could present some advantages for wastewater purification applications in isolated places with lack of electric grid. Furthermore, the process avoids problems concerning the maintenance of batteries and increases the system sustainability.

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