

**Electrochemical Pre-Treatment of Wastewater from color Photograph processing unit**

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**Introduction**

Wastewater from color photo-processing units is unique in that it is produced in a very small quantity (5 to 20 L per day) compared to that of other industries. But, the quality of wastewater is of very serious environmental concern due to the highly recalcitrant nature of organic compounds present in it, which is reflected by its very low (BOD/COD) ratio (<0.1). For treatment of such a small amount of recalcitrant wastewater, conventional biological or physicochemical treatment methods are not feasible, both technically and economically. However, a small electrochemical reactor, which degrades the recalcitrant organic compounds by electrochemical-oxidation method seems to be an ideal option. Many researchers have reported its successful application in the treatment of wastewater from industries such as tannery¹, textile² and tobacco processing³. Compounds like chlortetracycline, EDTA, chlorophenols and reactive dyes were oxidized to CO_2 and H_2O in simulated aqueous solutions⁴⁻⁷.

In the present study, we have investigated the feasibility of electrochemical oxidation of wastewater from photo-processing units located in the city of Mysore, India, using cast iron electrode. The reason for selecting cast iron was due to its tested ability to treat wastewater from textile industry and highly saline wastewater^{2,7} and also the lower cost of the material compared to other anode materials used for electro-oxidation purpose. Electrochemical oxidation was performed to achieve the quality of effluent, which could meet both sewer disposal standards and surface water disposal standards. Energy consumption for both the options was calculated from the experimental data.

Materials and Methods

Wastewater Sampling and Characterization: The wastewater samples were collected from different color photo-processing units in the city of Mysore, which were analyzed for pH, SS, COD and BOD.

Electrolysis: The batch experiments were conducted in a reactor made of Plexiglas of 650-ml capacity, using cast iron plates of different sizes by applying specific current density. The current was supplied by a direct

current (DC) power unit (Life Electronics, India) equipped with current and voltage-reading meters. The samples were collected at different times from the sampling port of the reactor and were analyzed for COD, BOD and pH. The COD and BOD values were determined by following the Standard Methods for Water and Wastewater Analysis (APHA 1991). A digital pH meter (pH SCAN-I SINGAPORE) was used for measuring the pH.

Results and Discussion

The range of physicochemical characteristics of wastewater collected from ten different photo-processing units is given in Table 1.

Table 1—Physicochemical Characteristics of Wastewater from Photo-Processing Units in Mysore City.

Sr. No.	Parameter	Range of concentration
1.	Colour	Dark brown
2.	pH	2.10 - 4.35
3.	Suspended solids, mg/L	< 80
4.	Dissolved Solids, mg/L	43350 - 58460
5.	COD, mg/L	14220 - 16340
6.	BOD (5-day), mg/L	120 - 145
7.	BOD/COD	0.0084 - 0.0087
8.	Flow, L/day	5 - 20

It can be seen that, the wastewater in general is highly acidic with high COD and very low BOD, suggesting recalcitrant nature of organics in the wastewater. Moreover, almost all the organics are present in dissolved form, which can be inferred from the very low suspended solids concentration of < 80 mg/L. Similarly, the BOD/COD ratio was found to be very low (< 0.0087).

The preliminary experiments on electrolysis of wastewater samples indicated that, cast iron could be used as anode for significant removal of COD from the wastewater at higher current density of 154 A/m^2 . Table 2 summarizes the COD and BOD values before and after electrochemical oxidation of wastewater at different applied current densities and electrolysis times.

It was found that an increase in applied current density from 154 A/m^2 to 347 A/m^2 decreases the

Table 2—Electrochemical Oxidation of Photo-Processing Wastewater Using Cast Iron Anode

Current density, A/m ²	Electrolysis time, hrs.	COD _i mg/L	COD _f mg/L	% Removal	BOD _i mg/L	BOD _f mg/L	BOD _f /COD _f ratio	Power consumption, KW h ⁻¹ Kg ⁻¹ COD
154	6	14,800	2015	86.38	128	425	0.020	10.62
222	5.2	14,800	1840	87.56	128	320	0.173	10.47
347	4.5	14,800	1800	87.83	128	324	0.180	10.42

COD_i = COD initial; COD_f = COD final; BOD_i = BOD initial and BOD_f = BOD final

duration of electrolysis from 6 hours to 4.5 hours and reduces the overall power consumption rate marginally from 10.62 KW hr⁻¹ to 10.42 KW hr⁻¹ for each Kg of COD removed.

It was also found that BOD of wastewater increased at the initial span of electrolysis and then decreased at the end of reaction. The COD and BOD of final treated effluent were 1800 mg/L and 324 mg/L respectively, at an applied current density of 347 A/m² after 4.5 hours of electrolysis. In all experiments the pH of treated effluents was found to range from 6.5 to 8.4. It can be seen from Table 2 that the BOD and pH of treated effluent conform to the stipulated standards of public sewer disposal, but they do not conform to those of inland surface water discharge.

The (BOD/COD) ratio of treated effluent (< 0.18) shows the presence of recalcitrant organics. Therefore, further electrolysis experiments were conducted by adding concentrated hydrogen peroxide solution (50 - 150 mg/L) to the wastewater sample. The purpose of adding H₂O₂ was to generate strong oxidizing OH-free radicals through the electro-Fenton reaction. The experiments were conducted at constant applied current density of 347 A/m² for 4.5 hours. The results of these experiments are given in Table 3.

It can be seen from the table that addition of 50mg/L of H₂O₂ enhances the COD removal from 87.38% to 94% and reduces energy consumption from 10.42 kwh to 8.66 kwh for one Kg of COD removal. It was also found that increase in H₂O₂ concentration from

50mg/L to 150mg/L increases the COD removal from 94% to 97.7%. A significant increase in BOD/COD ratio was also observed due to the addition of hydrogen peroxide. The BOD/COD ratio of treated effluents was found to be in the range of 0.405 to 0.747. This suggests the increase in biodegradability of wastewater after the electro-Fenton reaction. The pH and BOD of the effluents were found to conform to the standards of public sewer disposal, but they exceed the standards for inland surface water discharge.

The electrolysis of wastewater in presence of 150mg/L of H₂O₂ at an applied current density of 347A/m² for a longer duration of 8 hours resulted in the treated effluent COD and BOD of 250 mg/L and 35 mg/L respectively and pH of 8.8, which conform to the standards for surface water discharge. But, the power consumption was found to be quite high being 14.44 KW h⁻¹ per Kg of COD removal.

Conclusions

From the studies outlined herein, it is concluded that, electrochemical oxidation of photo-processing wastewater using cast iron electrode results in the removal of COD of wastewater from photo-processing units. Further, an increase in biodegradability is observed due to the electro-Fenton process. Also, in presence of hydrogen peroxide the electrolysis process could be an ideal option for public sewer disposal; but its treatment to meet surface water discharge standards seemed to be non-viable.

Table 3—Electrochemical Oxidation of Photo-processing wastewater with hydrogen peroxide

H ₂ O ₂ mg/L	Electrolysis time, hrs.	COD _i mg/L	COD _f mg/L	% Removal	BOD _i mg/L	BOD _f mg/L	BOD _f /COD _f ratio	Power consumption, kw h Kg ⁻¹ of COD
50	4.5	14,800	888	94.00	128	360	0.405	8.66
100	4.5	14,800	540	96.35	128	340	0.629	8.45
150	4.5	14,800	340	97.70	128	254	0.747	8.33

COD_i = COD initial; COD_f = COD final; BOD_i = BOD initial and BOD_f = BOD final

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