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TREATMENT OF COLORED DOMESTIC WASTEWATER BY ELECTROCOAGULATION

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ABSTRACT

In this work, applicability of electrocoagulation for the treatment of colored domestic wastewater has been studied using aluminum electrodes. Synthetic wastewater was prepared using 'UJALA', a violet coloured liquid solution (containing acid violet dye), used for increasing brightness of white clothes. The effect of operational parameters such as, current density, time of electrolysis, initial UJALA concentration and solution conductivity were studied to reach higher removal efficiency. The finding in this study shows that an increase in the current density from 34.7 to 138.8 A/m^2 enhanced the colour removal efficiency with initial UJALA concentration of 1mL/L. It was also observed that, an increase in salt (NaCl) concentration in the solution reduces the specific electrical energy consumption.

Key words: Electrocoagulation, Aluminum electrode, Wastewater treatment, Color removal.

INTRODUCTION

Water is the source of life and energy. However in 21st century, getting pure water is one of the most important challenges faced by people. The overexploitation of water resources is a serious cause of water shortage and degradation of its quality. Apart from industries, very high amounts of domestic wastewater are being generated from homes, commercial establishments and public institutions. Domestic wastewater is mainly composed of organic matters, nutrients, suspended solids and colored materials. For domestic purposes, we use various types of colored materials to improve the brightness of our clothes, hairs, walls etc. After use these colored materials (mainly dye) reach to effluent stream either by direct disposal or along with rain water. If these wastewaters are directly discharger to river, ponds then it can be toxic to aquatic life and cause natural waters to be

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unfit as potable water sources. Hence, decontamination and reuse domestic wastewater is an important challenge for environmental engineers. Most of the domestic wastewater treatment plants in rural areas use microbial degradation of waste material like; waste stabilization pond, upflow anaerobic sludge blanket reactor, bio-filter, aerated lagoon, oxidation ditch and constructed wetland. However, wastewater containing colored pollutant is very difficult to treat by microbial method since the dyes are recalcitrant organic molecules and are resistant to aerobic digestion.

Apart from microbial method, Fentons reagent[1], adsorption[2], photo degradation[3], photocatalytic degradation[4], electrocoagulation (EC)[5] can also be used for removal of colored pollutants from wastewater. All the methods have their own merits and demerits. When considered for the applicability in rural areas, EC process is preferable due to its simplicity, ambient operability, reliable and cost-effective, large volume handling ability, eco friendly, non-toxicity because of non-consumption of chemicals, no eventual secondary pollutants to discard at acceptable physical and chemical condition. It also requires comparatively less time for treatment.

The most widely used electrode materials in EC process are aluminum and iron. If aluminum electrode is connected by DC power source in an electrolytic system, it produces coagulant $Al(OH)_3$ by the following mechanism[6]:

$$Al \rightarrow Al^{3+} + 3e^- \quad \ldots(1)$$

$$3H_2O + 3e^- \rightarrow \frac{3}{2}H_2 + 3OH^- \quad \ldots(2)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad \ldots(3)$$

$$Al + 3H_2O + OH^- \rightarrow Al(OH)_4^- + \frac{3}{2}H_2 \quad \ldots(4)$$

The Al^{3+} and OH^- ions produced at the electrodes can react to form various mono-nuclear ($Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$) and poly-nuclear [($Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$)] species, which are finally transformed into aluminum hydroxide; $Al(OH)_3$. Freshly formed amorphous $Al(OH)_3$ occurs "sweep flocs" having large surface areas. These flocs are active in rapid adsorption of soluble organic compounds and trapping of colloidal particles and are easily separated from aqueous medium by sedimentation or H_2 flotation.

EC has been found a promising technique in removal of various types of contaminants present in water like; arsenic[7], fluoride[8], iron[6], chromium[9], removing of hardness of drinking water[10]. Hence, in the present work, it was chosen as the most suitable method for domestic colored water treatment. In the present work, the results of the experimental studies on the removal of colored pollutant from water by EC process. Synthetic colored wastewater was prepared using "UJALA", a diluted acid violet dye solution, used for increasing the brightness of white clothes in India. Experiments were conducted to observe the effects of different operational parameters such as effect of current density (CD), initial color concentration (C_0), inter electrode distance (IED) and effect of salt concentration on the color removal efficiency. All these parameters are very important in designing large scale plant for industrial application of EC. This fundamental study will be helpful for further application in designing an EC unit for the removal of colored pollutants from domestic water.

EXPERIMENTAL

UJALA, diluted acid violet dye (λ_{max} = 548 nm) solution was purchased from local shop and was used as domestic colored pollutant (abbreviated as DCP) to prepare colored waste water solution. The conductivity of DCP solutions were adjusted in by the addition of analytical grade NaCl (Merck, India). Schematic of EC cell used in this study is shown in Fig. 1. Batch experiments were carried out using a 2 L capacity glass beaker with 1 L of DCP solution at ambient temperature (298 ± 2 K). Aluminum plates of dimension 15 × 6 × 1 cm purchased from the local market were used as electrodes. The gap between the anode and cathode was maintained by placing different wooden blocks of varying size from 1-3 cm. The entire electrode assembly was fitted on a non-conducting wooden rod and hanged from the top of the glass beaker. During the experiments, the height of electrode dipped in the solution was 6 cm giving an effective surface area of 72 cm^2 (0.0072 m^2). The electrodes were connected to a DC power supply (Make: Aplab, India, Model: L6410) with galvanostatic operational options for controlling the constant current density by setting the constant current mode of operation. A magnetic stirrer (Make: Remi instruments, India, Model: Q19A) was used for agitation. The conductivity of the solution was measured using a Conductivity meter (Make: Lutron, Taiwan, Model: CD-4302). All the experiments were performed at pH 7 (Natural pH of DCP solution). Color concentrations of solutions were measured by a UV-Vis spectrophotometer (Make: Elico Instruments Ltd., India, Model: SL 159). After the experiment, the DC power source was switched off and the electrodes were dismantled. Before each run, the electrodes were abraded with sand-paper to remove scale and then cleaned with successive rinses of water and finally washed with acetone to remove any impurities on the electrode surface. Details of various experimental parameters studied are summarized in Table 1. Samples were taken at 5 minutes interval and were filtered before analysis. All the experiments were repeated twice and the average experimental variation less than 3%. The color removal efficiency was calculated using the Equation as -

$$R(\%) = \frac{I_0 - I}{I_0} \times 100 \qquad \ldots(5)$$

Where, I_0 is the initial absorbance and I is the absorbance of DCP solution at any time t measured by UV-Vis spectrophotometer (λ_{max} = 548 nm).

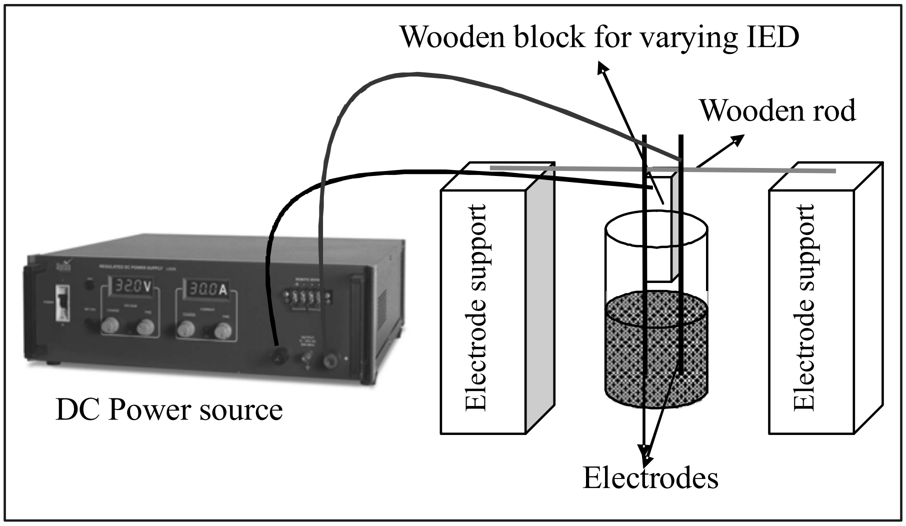

Fig. 1: Schematic of the experimental set up used for EC experiments

Table 1: Various experimental parameters studied in this work

Parameter studied	Parameter varied during experiment	Parameter kept constant during experiment
Effect of salt (NaCl) concentration	C_S: 0.1, 0.2, 0.3, 0.4, 0.5 g/L	C_0:1 mL/L, CD: 69.4 A/m^2, IED: 1 cm,
Effect of current density (CD)	CD: 34.7, 69.4, 104.2, 138.9 A/m^2	C_0: 1 mL/L, C_S: 0.1 g/L, IED: 1 cm,
Effect of initial color concentration (C_0)	C_0: 0.5, 1, 1.5, 2 mL/L	CD: 69.4 A/m^2, C_S: 0.1 g/L, IED: 1 cm,
Effect of inter electrode distance (IED)	IED:1, 1.5, 2.0, 2.5, 3.0 cm	C_0: 1 mL/L, C_S: 0.1 g/L, CD: 69.4 A/m^2

RESULTS AND DISCUSSION

Effect of current density and time of electrolysis on color removal

The variation in percentage color removal with contact time at different current densities of 34.7 to 138.9 A/m^2 are presented in Fig. 2. It may be seen from the figure that color removal rate increased with increase in current density. For current densities above 69.4 A/m^2, more than 90% color removal was observed after 20 minutes of operation. In the same time, only 73% color removal was observed for current density of 34.7 A/m^2. However, after 30 minutes of operation, more than 97% color removal was observed for all values of current density except 69.4 A/m^2. Maximum color removal of 99.5% was observed for current density of 138.9 A/m^2 after 30 minutes of operation. So, variations in current density above 69.4 A/m^2 has less effect on the final total color removal. But it needs to be noted that the rate of color removal is higher with high current densities. This is due to fact that an increase in current density increased the rate of production of coagulant (Al^{3+} ions) on the anode. These increased the flocs generation rate and hence color removal efficiency. In other words, higher current density will generate significant amount of flocs, which in turn will trap the dye molecules and enhance the color removal efficiency. After 20 to 25 minutes of operation, remaining concentration of DCP in water is very low and hence, the rate of adsorption of DCP in flocs decreased although the rate of flocs generation remain constant for constant current density. However, for very low current densities (34.7 A/m^2), it was observed that 81.9 % color removal was achieved after 30 minutes of operation. This is due to the fact that the total amount of produced flocs was not enough to remove all the DCP molecules in the solution and hence, it requires more time to achieve higher color removal efficiency.

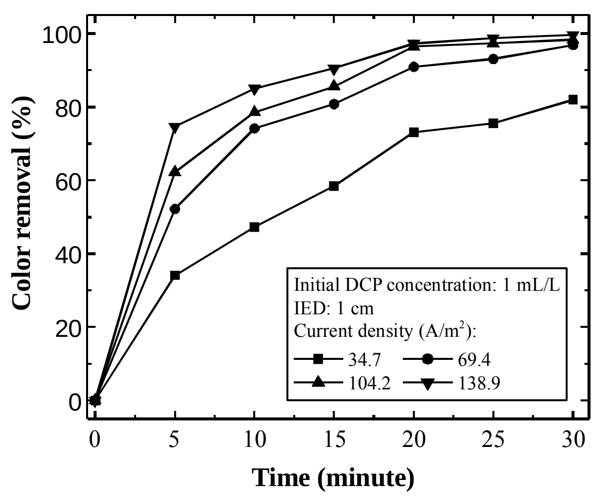

Fig. 2: Variation of color removal efficiency with time for different current densities.

Effect of initial DCP concentration on color removal

Figure 3 shows the percentage removal of color for different initial DCP concentrations. As the results indicate, the color removal efficiency decreases with an increase in initial DCP concentration. For example, after 30 minutes of operation, color removal decreases from 99.5 to 85.4% when DCP concentration is increased from 0.5 to 2 mg/L. This is due to the fact that at constant current density and time, the same amount of aluminum hydroxide complexes is generated in all the solutions. Consequently, the same amount of flocs would be produced in the solutions. As a result, the flocs produced at high DCP concentration are insufficient to adsorb all of the colored molecules of the solution. For low concentration of DCP, the number of aluminum hydroxide complexes is higher compared to number of colored molecules. Hence, 99.5% color removal is obtained in quick time compared to higher concentration. Hence, it is quite clear that under the present operating conditions, lower the color concentration, the better would be the removal efficiency.

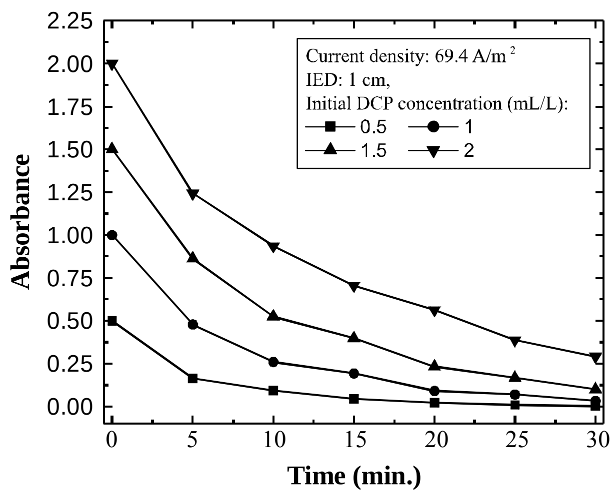

Fig. 3: Variation of color removal efficiency with time for different initial color concentrations

Effect of inter electrode distance on color removal

Variation of color removal with the inter electrode distance are shown in Fig. 4. From the figure, it is observed that the best efficiencies are obtained with shorter distances. For example with an inter electrode distance of 1 cm, color removal efficiency are 96.8% compared to 91.8% for inter electrode distance of 3 cm. Decrease in removal efficiency with increase in distance is due to weaker interaction between generated flocs and colored molecules at longer distance.

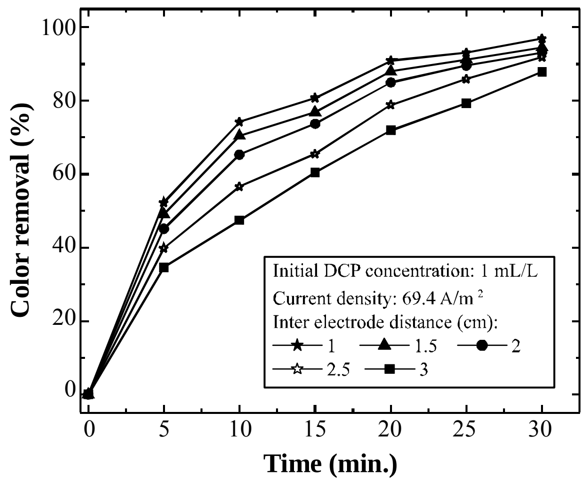

Fig. 4: Variation of color removal efficiency with inter electrode distance

Effect of salt concentration on color removal and SEEC

Table salt (NaCl) is usually employed to increase the conductivity of the wastewater to be treated by EC. Increase in salt concentration increases the ion concentration in the solution and hence reduces the resistance between the electrodes. As a result, cell voltage decreases at constant current density and reduces the power consumption in electrolytic cells. Current efficiency for different operating conditions is calculated based on the comparison of experimental weight loss of aluminum electrodes during EC process with theoretical amount of aluminum dissolution according to Faraday's law as[6]:

$$\varphi = \frac{\Delta M_{experimental}}{\Delta M_{theoritical}} \times 100 \quad \ldots(6)$$

$$\Delta M_{theoritical} = \frac{M.I.t_{EC}}{n.F} \quad \ldots(7)$$

Where M is the molecular weight of the aluminum (g/mol), n the number of electron moles, F is the Faraday constant (F = 96487 C/mol) and t_{EC} is the time (s) of EC operation. Assuming $Al(OH)_3$ to be the formed species, n = 3. SEEC is calculated as a function of aluminum electrodes weight consumption during EC in KWH/ (Kg Al)

$$SEEC = \frac{n \times F \times U}{3600 \times M \times \varphi} \quad \ldots(8)$$

It is well known that the over potential caused by solution resistance has a significant effect on cell voltages (U) that depends on the distance between the electrodes, surface area of the cathode and specific conductivity of the solution and the current.

The effect of wastewater conductivity on color removal and specific electrical energy consumption was studied and various experiments were performed using NaCl as the electrolyte in the range of 0.1-0.5 g/L at current density of 69.4 A/m^2. Table 2 summarizes the variations of applied voltage and percentage color removal at constant current density for different salt concentrations. From the table, it may be observed that with an increase in salt concentration form 0.1 to 0.5 g/L, drastic improvement in solution conductivity (from 0.38 to 0.97 ms/cm) was observed. This improvement resulted in the reduction of cell voltage from 29.1 to 6.8 V and hence decreases in SEEC from 72.75 to 19.32 KWH/Kg Al. At the same time, percentage of color removal increased slightly. In other words, raising the conductivity of DCP solutions does has not have a considerable effect on color removal efficiency but has great effect in decreasing power consumption. However, it is also to be considered that addition of any salt to improve solution conductivity and decrease SEEC, also leads to addition of impurity in wastewater. Hence in the present work, we have used lower concentration of salt (0.1 g/L) for all the remaining experiments.

Table 2: Variation of solution the conductivity, color removal, voltage drop and SEEC with salt (NaCl) concentration

Salt (NaCl) concentration (mg/L)	Conductivity (ms/cm)	Color removal % (30 min.)	Voltage drop (V)	SEEC (KWH/Kg Al)
0.1	0.38	96.8	29.1	72.75
0.2	0.56	97.3	18.1	50.28
0.3	0.71	97.8	14.5	38.84
0.4	0.85	98.0	10.1	25.25
0.5	0.97	97.9	6.8	19.32

Kinetic analysis

From the previous sections it was observed that, the rate of color removal is proportional to the color concentration in the solution. So, the rate of color removal can be represented by the first-order kinetics as -

$$\ln\left(\frac{I_0}{I}\right) = kt \qquad \ldots(9)$$

Effect of current density on rate constant

Figure 5a shows the plot of ln (I_0/I) versus t is a straight line with slope of k. The calculated values of regression coefficient (R^2) are 0.981, 0.985, 0.983 and 0.987 for current densities of 34.7, 69.4, 104.2 and 138.9 A/m^2, respectively. From the observed fitness and R^2 values, it is confirmed that the decrease in color concentration during EC follows first order reaction kinetics. Calculated values of *k* for different current density (CD, A/m^2)) are shown in Figure 5b and are found to fit the generalized expression:

$$k = 1.42 \times 10^{-3} \times CD \qquad R^2 = 0.944 \qquad \ldots(10)$$

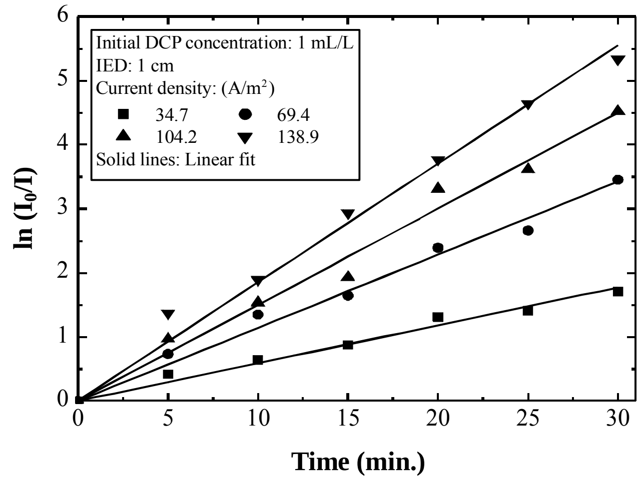

Fig. 5(a): Plot of first order equation for different current densities

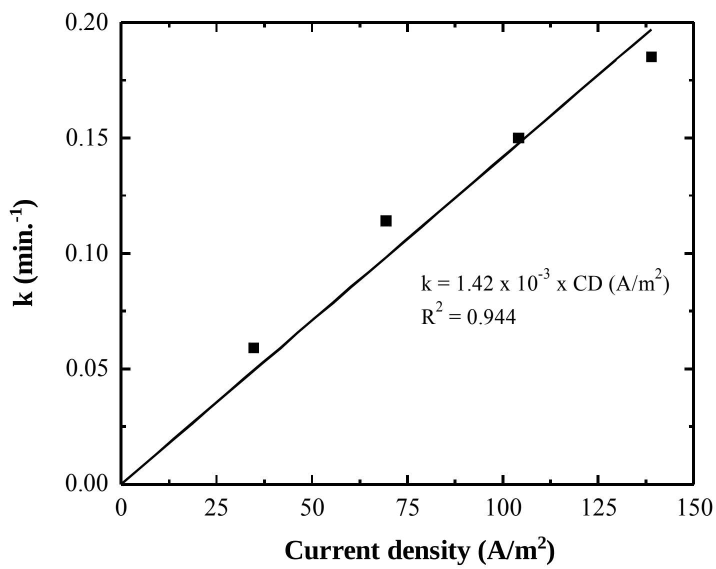

Fig. 5b: Variation of color removal rate constant with current density.

Effect of initial color concentration on rate constant

Figure 6a shows the plot of $ln(I_0/I)$ versus t is a straight line with slope of k for different initial DCP concentrations. The calculated values of regression coefficient (R^2) are 0.980, 0.985, 0.992 and 0.985 for initial DCP concentration of 0.5, 1, 1.5 and 2 ml/L, respectively. Calculated values of k for different current density are shown in Figure 6b and are found to fits the generalized expression:

$$k = -0.0714 \times \ln(I_0) + 0.1165 \qquad R^2 = 0.997 \qquad \ldots(11)$$

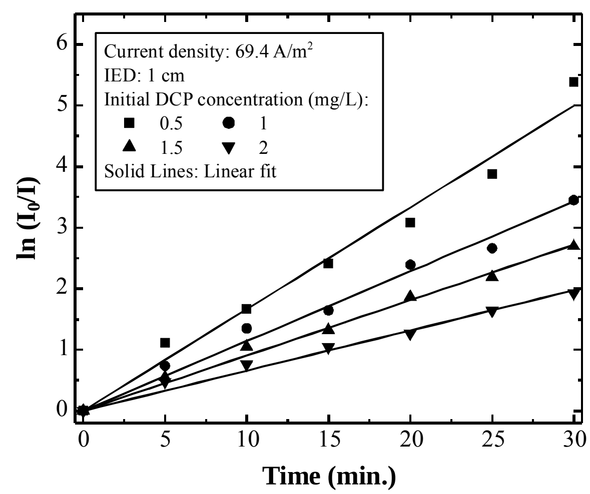

Fig. 6(a): Plot of first order equation for different color concentrations

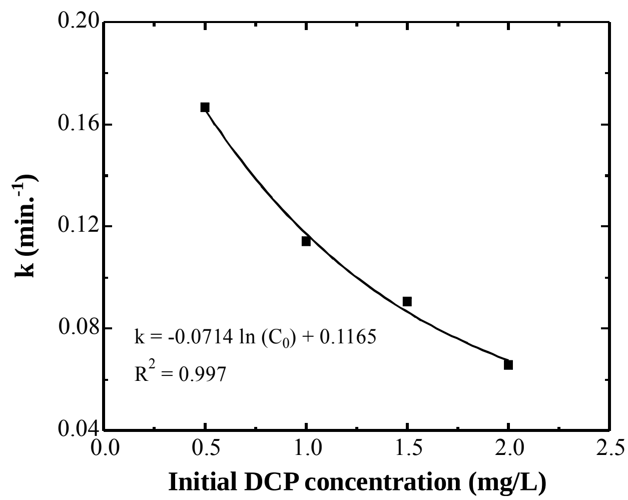

Fig. 6(b): Variation of color removal rate constant with initial color concentration

Effect of inter electrode distance on rate constant

Analysis of color removal rate was carried out for all the IED and CD s by first order equation. Fig. 7a shows the plot of $ln(I_0/I)$ versus t is a straight line with slope of k for CD of 69.4 A/m^2. From the figure it is confirmed the color removal for all the cases followed first order reaction. Further the calculated values of k for are found to fits the generalized expression (are shown in Fig. 7b).

$$k = -23.22 \times 10^{-3} \times IED + 136.7 \times 10^{-3} \quad R^2 = 0.994 \qquad \ldots(12)$$

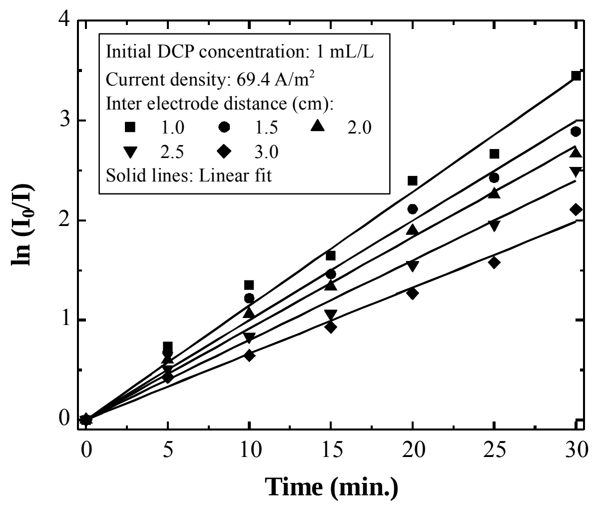

Fig. 7(a): Plot of first order equation for different inter electrode distance

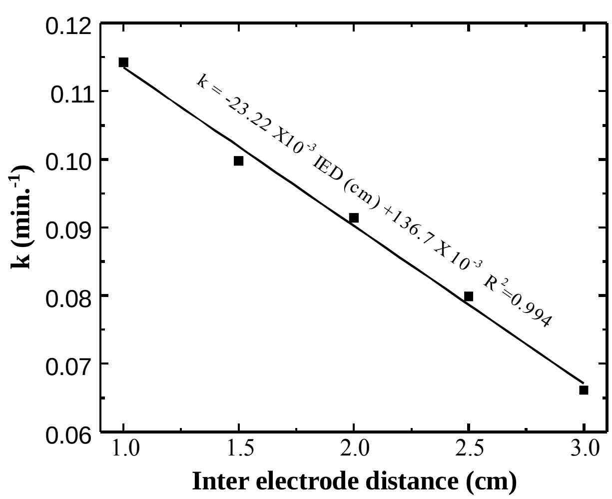

Fig. 7(b): Variation of color removal rate constant with inter electrode distance

CONCLUSION

In this work, EC technique was carried out to remove colored pollutants from domestic wastewater. Variation in different operating parameters such as, current density, initial color concentration of wastewater and operating time were studied in detail. EC time of 30 minutes was found to be enough for the 99.5% removal of color from the wastewater solution. The results showed that the removal efficiency increases with the increase in current density from 34.7 to 138.9 A/m^2. Simple kinetic model developed in this study will be helpful in better understanding of color removal by EC.

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