

Decolorization of Crystal Violet Solution by Electrocoagulation

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Abstract

Electrocoagulation (EC) was tested as an alternative method for satisfactory removal of crystal violet dye (CI 42555) from aqueous medium. A batch electrocoagulation unit was considered using aluminum sheet as electrode. Important parameters (like; current density, initial dye concentration, initial pH, interelectrode distance and quantity of different salts) that affect the extent of crystal violet removal were studied in detail. Experiments were conducted to find the desired conditions for removal of particular concentration of the dye. The results showed that 99.75% of crystal violet was decolorized for initial dye concentration of 100 mg/L with the current density of 1112.5 A/m², solution conductivity of 1.61 S/m and initial pH of 8.5 at the end of 1hr of operation. Cost estimation for the electrocoagulation was adopted and presented well. Up to 100 mg/L of initial dye concentration, the optimum total cost was 0.2141 US\$/m³. By products obtained from EC bath was characterized by SEM and corresponding elemental analysis (EDAX). These finding might be helpful in order to treat wastewater containing crystal violet dye.

Keywords: Electrocoagulation; crystal violet; aluminum electrodes; decolorization; current efficiency.

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Introduction

Electrocoagulation (EC) is an electro-chemical technique also known as electro-assisted coagulation that offers enhanced coagulation by in-situ in which metal ions are generated in electrochemical reactor, which forms complex metal oxy/hydroxides well accompanied by electro floatation for removal of impurities. On application of potential difference, the metal ions generated by anodic oxidation form metal hydroxides due to simultaneous electrolysis of water; these metal hydroxides have higher sorption capacity and thus favor enhanced removal due to their in situ generation and application; while generation of cathodic gases assist in electro floatation of impurities.

The dyestuffs are widely used in different industries like textile, pulp and paper manufacturing, plastics, printing and microbiology for coloration. Crystal violet is a cationic dye and widely used as a purple dye for textiles such as cotton and silk. It provides a deep violet color for paints and printing ink. It is also used to dye paper. But the untreated effluents from above mentioned sources can create variety of environmental related issues. Different technological approaches like; adsorption,

coagulation, biological treatment, advanced oxidation process, UV treatment, ozone treatment, membrane separation technologies etc have been investigated in detail for the removal of such dyestuffs. All the above processes have been reported in the literature with certain limitation in their application. Adsorption and coagulation can be time consuming methods. Biological methods also suffer due to toxicity of dyestuffs and they are eventually very time consuming too [1]. Fenton's reagents, UV and other advanced oxidation processes have been found to be quite successful in treating crystal violet effluents. However, addition of chemicals in these processes increases the secondary pollution in discharge [2]. In membrane separation technique (Nanofiltration or reverse osmosis) flux decline is a common problem, which makes the process inefficient [3,4].

Electrocoagulation offers some distinct advantages over existing processes depicted elsewhere such as ambient operability conditions, no threat of secondary pollution due to the absence of any extra chemicals. The EC process is attractive due to its simplicity of operation, control and effective removal efficiency [5]. Electrocoagulation has been found potent in treating urban waste water [6],

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treatment of restaurant waste water [7], treatment of potable water [8], potato chips waste water [9], arsenic removal [10] fluorine removal from underground and waste waters [11], treatment of levafix orange textile dye solution [12], treatment of copper, lead and cadmium in natural water and simulated waste waters [13], treatment of laundry waste water [14], boron removal [15], olive mill waste waters [16], alcohol distillery waste water [17]. All the studies [6-17] have been focused mainly on few parameters such as current density, pH and the time of operation for the wastewater treatment using EC. However, in the decolorization treatment of crystal violet dye using EC several influential parameters like inter electrode distance, initial dye concentration, conductivity along with pH, current density and time of operation were inadequately reported so far. Therefore, a detailed investigation on the effects of the above mentioned parameter is essentially required to know more insight of the process. In addition to this, the techno-economical analysis for the crystal violet removal using EC is another important aspect to assess the feasibility of the process

In this work, electrocoagulation was tested as an alternative method for treating the synthetic solutions of crystal violet dye with initial concentration ranging from 50 to 120 mg/L. Effects of different parameters like, applied current density, initial concentration of dye, pH, inter electrode distance, conductivity etc over the extent of dye removal were studied in detail, in order to determine desired operating conditions. Operating cost for the removal of dye was calculated and presented well. In the calculation of the operating cost, only material and energy costs were considered, other cost items such as labour, maintenance, solid/liquid separation costs were not taken into account. The simplified cost equation was used to evaluate the operating cost. This fundamental study will be helpful for further application in designing an electrocoagulation unit for the treatment of dye containing effluent coming out from dyeing industries.

Technology understanding

In electrocoagulation process, an applied potential generates the coagulant species as the sacrificial aluminum (or ferric) anode dissolves, while hydrogen is simultaneously evolved at the cathode. Coagulant species do help in the aggregation of the suspended particles followed by the precipitation and adsorption of dissolved contaminants accordingly. Different electrodes have been reported in the literature like carbon [18], mild steel [19], graphite, titanium [20], iron [21] and aluminum [22]. But Iron and aluminum have been reported to be effective and successful in pollutant removal at favorable operating conditions. In this work, aluminum has been selected as electrode material. The electrode reactions are summarized as follows:

Anode:

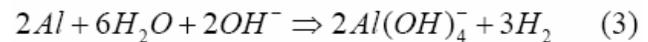


Cathode:

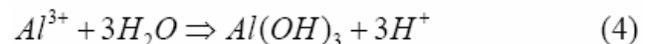


Flotation is the dominant pollutant removal path for high operating currents, while sedimentation is dominant at lower currents. The shift is due to the insufficient bubble concentration at low currents to remove the aggregated material, hence allowing sedimentation to dominate [5]. At sufficiently high anodic potential, secondary reactions may also occur, such as direct oxidation of organic compounds and of Cl⁻ ions present in wastewater:

$2Cl^- \Rightarrow Cl_2 + 2e$; the chlorine produced is a strong oxidizing agent which can oxidize some organic compounds. On the other hand, the cathode may be chemically attacked by OH⁻ ions generated during H₂ evolution, especially at high pH values:



Two major interaction mechanisms are being considered in recent years: precipitation and adsorption, each one has been proposed for a separate pH range. Flocculation in the low pH range is explained as precipitation while the higher pH range (>6.5) as adsorption. Al³⁺ and OH⁻ ions generated by electrode reactions (1) and (2) react to form various monomeric species such as Al(OH)²⁺, Al(OH)⁺, Al₂(OH)₂⁴⁺, Al(OH)₄⁻ and polymeric species such as Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁴⁺, Al₁₃O₄(OH)₇²⁺, Al₁₃(OH)₃₄⁵⁺, which transform finally into Al(OH)_{3(S)} according to complex precipitation kinetics:



Freshly formed amorphous Al(OH)_{3(S)} 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 H₂ flotation. These flocks polymerizes as:



Experimental

Materials

The dye used in this study was crystal violet (CI 42555, Class: basic dye 3, chemical formula: $C_{25}H_{30}N_3Cl$, molecular mass: 407.98 g/mol, λ_{max} : 584 nm, dye content: 98%, supplied by Aldrich Chemical Company, USA). Structure of crystal violet molecule is shown in Fig. 1a. Sodium chloride (used for the change in conductivity of the dye solution) was procured from S.D. Fine Chem. Ltd. (India). All chemicals were of analytical grade.

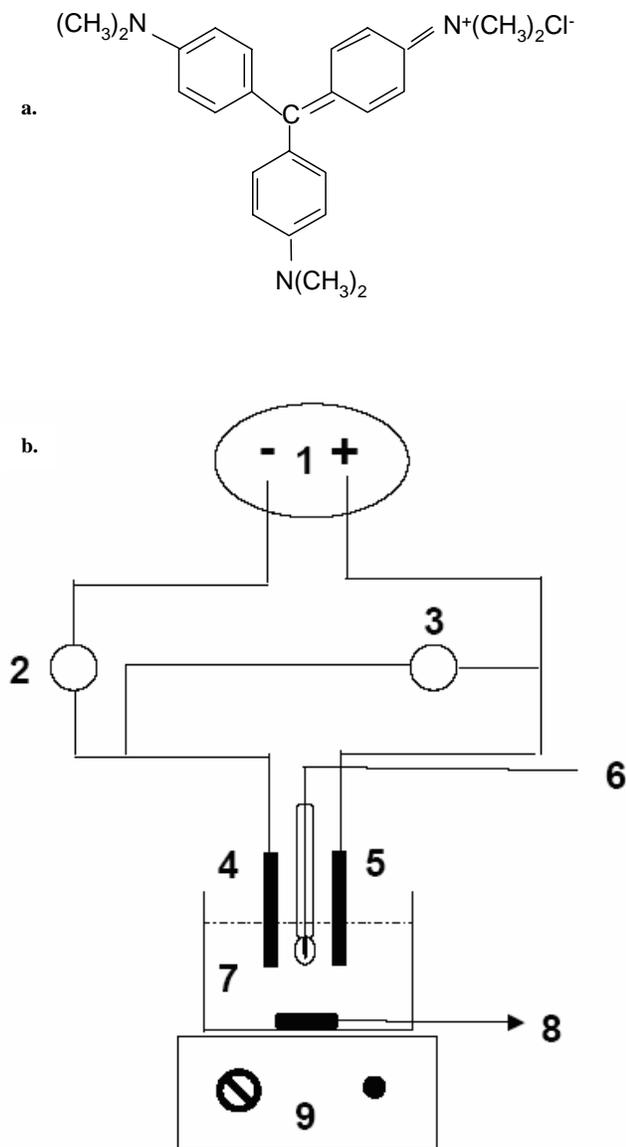


Fig. 1. The structure of crystal violet (a) and the schematic diagram of the experimental setup (b). 1. DC power supply, 2. Digital ammeter, 3. Digital voltmeter, 4. Anode, 5. Cathode, 6. pH meter, 7. Dye solution, 8. Magnetic bar, 9. Magnetic stirrer.

Electrochemical cell

A Perspex tank having dimension of $0.18\text{ m} \times 0.18\text{ m} \times 0.18\text{ m}$ with a working volume of about $3 \times 10^{-3}\text{ m}^3$ was used to conduct the experiments. Two aluminum sheets of $0.15\text{ m} \times 0.10\text{ m} \times 0.002\text{ m}$ were used as electrodes for electrocoagulation. The gap between the anode and cathode was varied from 0.005 m to 0.02 m. The entire electrode assembly was fitted on non-conducting wedges and hanged from the top of the electrocoagulation tank. The effective surface area of each electrode was $40 \times 10^{-4}\text{ m}^2$. The assembly was connected to D.C power source (Textronics 36 D, Agarwal Electronics, Mumbai, India) to constitute an electrochemical cell with galvanostatic mode for constant current supply. The schematic diagram of experimental setup is shown in Fig. 1b.

Methods

A measured quantity ($1 \times 10^{-3}\text{ m}^3$) of aqueous crystal violet (CI 42555) solutions at a desired pH and concentration was taken in to the electrochemical cell. The solutions were prepared in different concentrations of NaCl to achieve the desired conductivity. The pH of the aqueous sample was adjusted using dilute HCl and NaOH and measured using a pH meter. The electrode assembly was placed in the cell and the electrodes were connected to the respective anode and cathode leads to the D. C rectifier and energized for a required duration at a fixed current. All the runs were performed at constant temperature of $25\text{ }^\circ\text{C}$ and stirring speed 200 rpm. In each run, $1 \times 10^{-3}\text{ m}^3$ dye solution was placed into the electrolytic cell. The current density was adjusted to a desired value and the operation was started. After the experiment, the power was switched off and the electrodes were dismantled. The treated dye sample collected at different time interval was filtered using a filter paper of grade HM2 and 11 cm diameter (Make: Indiamchem, India) before analysis. Dye concentration was determined using UV spectrophotometer at 584 nm. Treated samples were analyzed for chemical oxygen demand (COD). Before each run, the electrodes were washed with acetone to remove surface grease, and the impurities on the aluminum electrode surfaces were removed by dipping for 5 min in acetone solution. After each experiment the used anode and cathode plate was interchanged for effective electrode utilization.

Operating conditions

The chosen parameters in the present experiments were current density, initial dye concentration, pH, inter electrode distance, conductivity, dose of supporting electrolyte and operating time. All the conditions are given in Table 1.

Table 1. Operating conditions for the EC of crystal violet dye.	
Parameters	Values
pH	4.5, 5.5, 6.5, 7.5, 8.5, 10
Current density (A/m ²)	362.5, 612.5, 862.5, 1112.5
Crystal violet concentration (mg/L)	50, 60, 80, 100, 120
Dose of electrolyte (mg/L)	2, 4, 6, 8, 10
Inter electrode distance ($\times 10^{-2}$, m)	0.5, 1, 1.5, 2
Time of operation (min)	60

Analytical techniques

The UV vis spectrum of crystal violet (CI 42555) and its change during electrocoagulation was recorded using UV–Vis spectrophotometer (Perkin-Elmer Precisel, Lamda-35). The characteristic peak of pure crystal violet was observed at 584 nm. The standard method [23] was followed in order to determine the concentration of the dye in the effluents. The conductivity and pH of all samples (feed and treated dye solutions at each operating conditions) were measured using a deluxe water and soil analysis kit, model no 191E, manufactured by Toshniwal Instruments Ltd. India. Microscopic observation of byproducts from the electrocoagulation unit was carried out by a scanning electron microscope (SEM, Make: LEO 1430VP, UK), which directly provides the visual information of morphology of electrocoagulation byproducts. Energy dispersive X-ray analysis (EDAX) was an integrated feature of a scanning electron microscope (SEM). This analysis was performed to identify the elemental composition of the byproducts obtained from the electrochemical unit.

Results and Discussion

Effect of current density

In any electrocoagulation process current density (A/m²) and time of electrolysis are important operational parameters setting the ultimate removal and defining the electrical energy and power consumption so eventually the ultimate operating cost for the process. Some investigators have reported that in electrocoagulation, current density can influence the treatment efficiency [6], while others have reported that current density has no significant role on pollutant removal [7]. Therefore, it remains unclear that whether the current density affects the treatment efficiency or not. Choice of electrode material is also vital affecting the cell voltage (different oxidation potential for different electrode materials) and the removal efficiency. In this work, aluminum was selected as the sacrificial electrode material because of its availability, harmless and it requires

comparatively less oxidation potential. Fig. 2 shows the aqueous phase crystal violet concentration as a function of time for four different current densities. It was observed from the figure that the concentration was declined rapidly at the beginning for all the current densities. The declination in concentration became gradually thereafter. It may also be found that lower current density has lesser effect on the final total dye removal, but removal is rapid with high current density.

In electrocoagulation, initially the aluminum cations contribute to charge neutralization of the pollutant particles as the isoelectric point is attained. Here a sorption coagulation mechanism occurs resulting in the formation of loose aggregates. As time progresses, further aluminum cation addition results in amorphous aluminum hydroxide precipitation that promotes pollutant aggregation via a sweep coagulation mechanism. During the final stages, coagulated aggregates interact with bubbles and float to the surface or settle to the bottom of the reactor. As shown in the figure there is sharp decrease in concentration due to fresh electrodes surfaces initially but the concentration reduction is achieved further as the time progresses with more generation of aluminum hydroxides for coagulation of the particles.

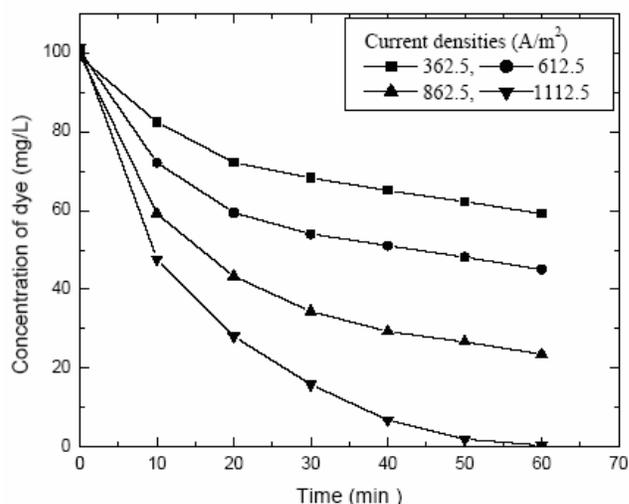


Fig. 2 Variation of concentration of crystal violet dye with time at different current densities. Inter electrode distance: 0.5×10^{-2} m, initial dye concentration: 100 mg/L, pH: 8.5, conductivity: 16.13×10^{-1} S/m.

Effect of initial dye concentration

Initial dye concentration plays an important role in the decolorization process using EC. Therefore, the decolorization treatments of crystal violet with different initial concentrations ranging from 50 mg/L to 120 mg/L at a current density of 1112.5 A/m² were investigated. Fig. 3 reveals the decolorization performance in terms of percentage removal as a function of time. It was seen that the complete dye removal was achieved at the end of one-

hour operation up to initial dye concentration of 100 mg/L. In addition to this, it was noticed that the required time for complete (i.e. 100%) dye removal was increased with initial dye concentration up to 100 mg/L. The removal was drastically reduced when initial concentration was increased to 120 mg/L. This is more likely due to the insufficient number of aluminum hydroxide complexes formed during EC to coagulate the dye molecules. Hence, it is quite clear that under the present operating conditions, the lower is the dye concentration better would be the removal efficiency.

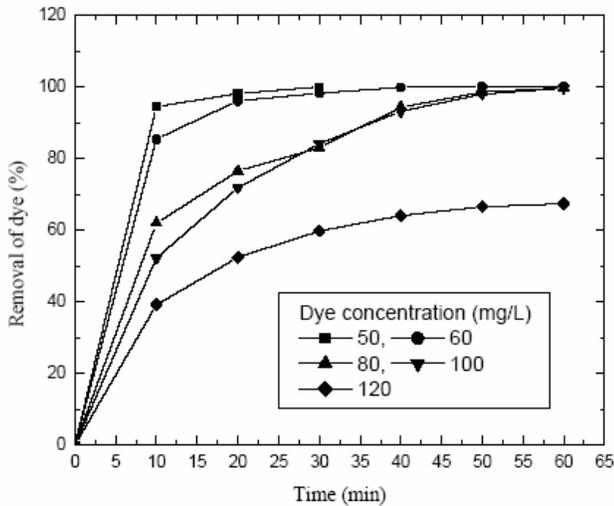


Fig. 3. Variation of extent of dye removal with time for different initial dye concentrations. Inter electrode distance: 0.5×10^{-2} m, current density: 1112.5 A/m^2 , pH: 8.5, conductivity: $16.13 \times 10^{-1} \text{ S/m}$.

Effect of initial pH

The EC process is highly dependent on the pH of the solution. To examine its effect, the dye solutions are adjusted to the desired pH for each experiment by adding sodium hydroxide or hydrochloric acid solution. The dye removal efficiency, as a function of pH, is shown in Fig. 4 for the initial dye concentration of 100 mg/L, current density of 1112.5 A/m^2 and at the end of one hr of operation. It can be seen that the initial pH has a significant effect on the dye removal efficiency. There is minimum removal efficiency at acidic pH. Close examination of the dye removal efficiency versus pH clearly indicates that the removal efficiency increases with pH. From figure it is seen that for 100 mg/L of dye solution the removal is almost 100% at a pH of 8.5 and remains unaltered thereafter. Therefore, the desired pH of crystal violet degradation by EC process should be 8.5. The effect of pH on the process performance is explained as follows: the dominant aluminum species are different according to the solution pH; Al^{3+} and $\text{Al}(\text{OH})^{2+}$ are dominant in pH 2–3, and with pH between 4 and 9, various

polymeric species such as $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ are formed and precipitated as $\text{Al}(\text{OH})_3(\text{s})$. Since hydroxide ions, which are generated at the cathode, are neutralized by H^+ ions, sufficient amount of aluminum hydroxide complexes are not formed at this pH. At basic pH, dye removal efficiency is increased as number concentration of OH^- ion increases which help in formation of different aluminum hydroxide complexes.

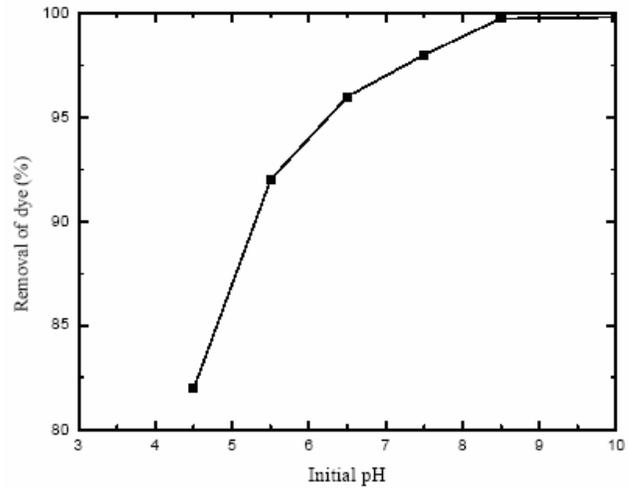


Fig. 4. Effects of solution pH on the dye removal. Inter electrode distance: 0.5×10^{-2} m, current density: 1112.5 A/m^2 , conductivity: $16.13 \times 10^{-1} \text{ S/m}$, initial dye concentration: 100 mg/L, time: 60 min.

Effect of inter electrode distance

The set up of electrode assembly is very important for required effective surface area of electrode and inter electrode distance. With the increase of inter electrode distance IR resistance increases which increases the cell voltage and adversely affect the dye removal. Variation of percentage removal of dye and IR drop with inter electrode distance is shown in Fig. 5. It may be observed from the figure that with the increase of inter electrode distance, percentage removal of dye decreases whereas IR drop increases. At minimum inter electrode distance the resistance encountered for current flow in the solution medium is lower that facilitates the electrolytic process for enhanced dye removal. The variation in IR drop is governed by following equation:

$$\eta_{\text{IR}} = I \cdot \frac{d}{A \cdot \kappa} \quad (6)$$

Where,

I = current (A)

d = distance between the electrodes (m)

A = active anode surface (m^2)

κ = specific conductivity (10^3 mS/m) [8].

Above equation infers that at constant anodic surface area and conductivity of solution, voltage drop (IR) increases with the increase of inter electrode distance. It is well known that, during the electro-coagulation as the potential is applied to the electrodes initially, the anodic oxidation is started. Now as the time proceeds a very fine film of metal hydroxides would get formed on the anode generating an extra resistance that even increases with increasing inter-electrode distance. Consequently, after some time of the operation current falls down. To maintain a constant current, applied potential has to be increased. Now it is very much clear that current is remained constant but the resistance is increased. Hence the ohmic loss (IR resistance) increases which in turn inhibits the rate of anodic oxidation. As the rate of anodic oxidation becomes lower, numbers of cations at anode also decreases. Therefore, the increase in IR drop is not recommended for EC process in order to have acceptable energy consumptions as well as desired effective separation. In order to achieve 100% removal for the initial dye concentration of 100 mg/L, the desired inter electrode distance is 0.005 m (Fig. 5).

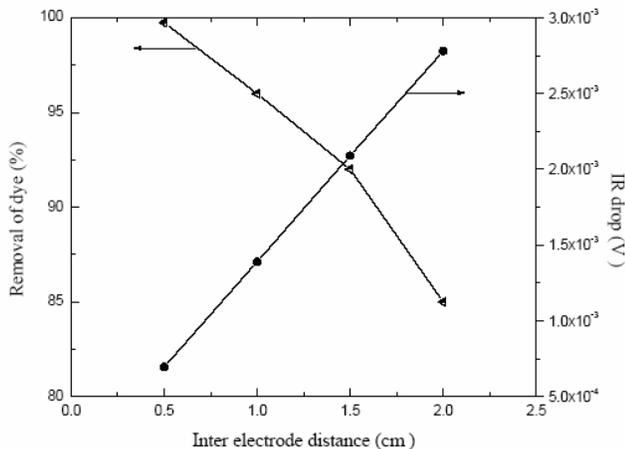


Fig. 5. Effects of inter electrode distance on the dye removal. Current density: 1112.5 A/m^2 , conductivity: $16.13 \times 10^{-1} \text{ S/m}$, Initial dye concentration: 100 mg/L, time: 60 min, pH: 8.5.

Effect of conductivity

Textile effluent have a broad variation in ionic strength due to the chemical substances added at a high concentration from dyeing and finishing processes in the textile industry. The greater ionic strength will generally cause an increase in current density at the same cell voltage, or the cell voltage decreases with increasing effluent conductivity at constant current density. Therefore, it is necessary to investigate the effect of effluent conductivity on electrocoagulation in terms of dye removal. The conductivity of solution depends both on the type and concentration of electrolyte. Variations of conductivity, applied voltage and percentage dye removal have been shown in Table 2 using same amount ($8 \times 10^{-3} \text{ Kg/L}$) but different types of electrolyte (NaCl, BaCl₂, KCl and KI). It may be seen from the table that NaCl has highest dye removal capacity (99.75%), high conductivity with low applied voltage as compared to other electrolytes. Hence, NaCl can be recommended as superior electrolyte and economically viable in industrial scale. The variations of percentage removal of dye and cell voltage with conductivity of solution are shown in Fig. 6. Conductivity is varied with the addition of NaCl. It is seen that with the increase of conductivity dye removal increases where as cell voltage decreases. For 100 mg/L of dye solution optimum conductivity is 1.613 S/m. The amount of NaCl increases the conductivity about 11 times. Consequently, with respect to:

$$V = E_C - E_A - \xi_A - \xi_C - IR_{\text{Cell}} - IR_{\text{circuit}} \quad (7)$$

the necessary voltage to access a certain current density will be diminished, so the consumed electrical energy is decreased. When chlorides are present in the solutions the products from anodic discharge of chlorides are Cl₂ and OCl⁻. The OCl⁻ itself is a strong oxidant, which is capable of oxidizing dye molecules present in solution. Therefore, it is clear that added NaCl not only increases the conductivity but also acts as an oxidizing agent to oxidize crystal violet dye during EC treatment.

Electrolyte	Conductivity ($\times 10^{-1}$, S/m)	Applied voltage (V)	Dye removal (%)
NaCl	16.13	6.75	99.75
BaCl ₂	9.67	10.75	75
KCl	18.75	15.75	94
KI	9.18	26.75	98

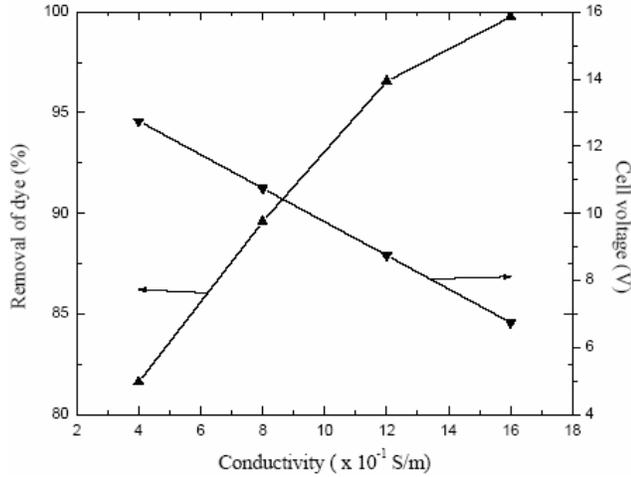


Fig. 6. Effects of solution conductivity over dye removal and cell voltage. Current density: 1112.5 A/m^2 , conductivity: $16.13 \times 10^{-1} \text{ S/m}$, initial dye concentration: 100 mg/L , time: 60 min , pH: 8.5 , inter electrode distance $0.5 \times 10^{-2} \text{ m}$.

Energy consumption

Electrical energy consumption and current efficiency are very important economical parameters in EC process and calculated using the commonly used equation [24]:

$$E = UI t_{EC} \quad (8)$$

where E is the electrical energy in kWh/(kg dye removed), U the cell voltage in volt (V), I the current in ampere (A) and t_{EC} is the time of EC process in second. The result shows that an increase in the current density causes an increase in color removal efficiency (Fig. 7a). It also increases energy consumption. So, to achieve an optimized current density, both percentage removal of dye and energy consumption should be evaluated. The current efficiency (φ) of EC process is calculated as:

$$\varphi = \frac{\Delta M_{Exp}}{\Delta M_{Theo}} \times 100 \quad (9)$$

This calculation is based on the comparison of experimental weight loss of aluminum electrodes (ΔM_{exp}) during EC process with theoretical amount of aluminum dissolution (M_{theo}) according to the Faraday's law:

$$\Delta M_{theo} = \frac{MI t_{EC}}{nF} \quad (10)$$

where M is the molecular weight of the aluminum (g/mol), n the moles of electron and F is the Faraday constant ($F = 96487 \text{ C/mol}$). As $\text{Al}(\text{OH})_3(\text{s})$ is supposed to be the formed

species, the number of electron moles in dissolution reaction is equal to 3. The specific electrical energy consumption (S_{eec}) is calculated as a function of aluminum electrodes weight consumption during EC in kWh/ (kg Al) [25,26] using the Eq.

$$S_{eec} = \frac{n \times F \times U}{3.6 \times 10^3 \times M \times \varphi} \quad (11)$$

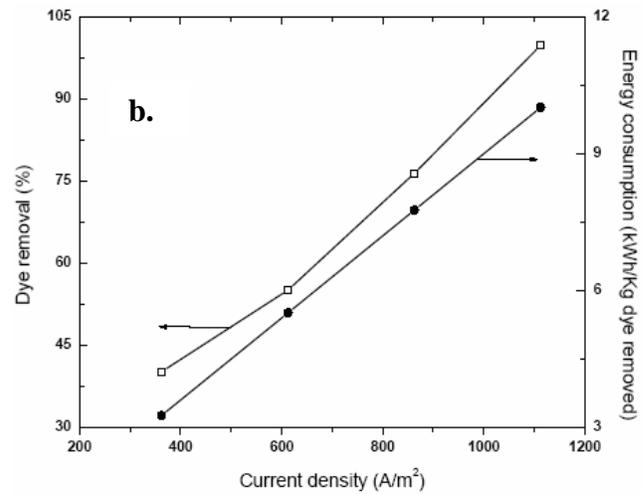
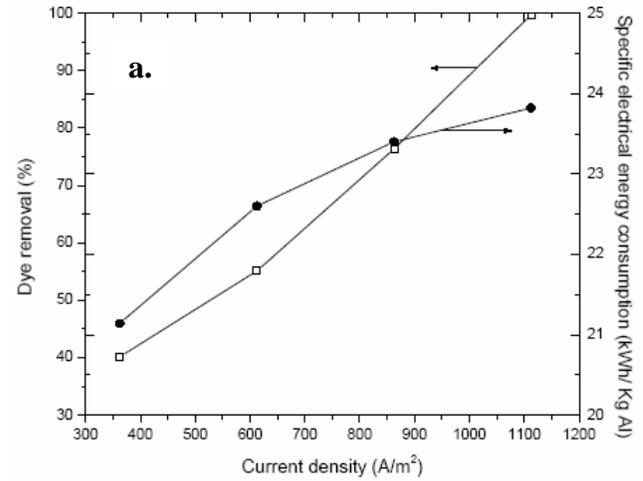


Fig. 7. (a) Effect of current density on percentage removal of dye and energy consumption, Initial dye concentration: 100 mg/L , conductivity: $16.13 \times 10^{-1} \text{ S/m}$, pH: 8.5 , inter electrode distance $0.5 \times 10^{-2} \text{ m}$. (b) Effect of current density on percentage removal of dye and specific electrical energy consumption. Initial dye concentration: 100 mg/L , conductivity: $16.13 \times 10^{-1} \text{ S/m}$, pH: 8.5 , inter electrode distance $0.5 \times 10^{-2} \text{ m}$.

It may be seen from Fig 7b that both percentage removal of dye and the specific electrical energy consumption increases with the increase of current density. For an example, at current density 1112.5 A/m^2 , the decolorization of crystal violet dye was 100% for the initial dye concentration of 100 mg/L . Therefore, the optimum current density for that dye concentration must be 1112.5 A/m^2 to achieve the maximum separation under the present operating conditions. More current density favors formation of more number of aluminum complexes, which also enhances the removal of dye as expected. This causes the higher weight loss of aluminum electrode and therefore increases the specific electrical energy consumption.

Operation cost

It is well-known that the performance of an electrically driven process like EC is dependent on electrical energy consumption which directly affects the operating cost of the process. For EC process the operating cost includes material, mainly electrodes and electrical energy costs, as well as labor, maintenance, sludge dewatering and disposal. In this preliminary economic investigation, energy and electrode material costs have been taken into account as major cost items in the calculation of the operating cost (US\$/m³ of dye solution).

$$\text{Operating cost} = a C_{\text{energy}} + b C_{\text{electrode}} \quad (12)$$

where, C_{energy} (KWh/m³ of dye solution) and $C_{\text{electrode}}$ (kg Al/m³ of dye solution) are consumption quantities for the dye removal, which are obtained experimentally. “a” and “b” given for Indian market in June 2007, are as follows: “a” electrical energy price 0.0065 US\$/ kWh; “b” electrode material price 0.3 US\$/kg. Cost due to electrical energy (KWh/m³ dye solution) is calculated as:

$$C_{\text{energy}} = \frac{U \times I \times t_{\text{EC}}}{v} \quad (13)$$

where, U is cell voltage (V), I is current (A), t_{EC} is the time of electrolysis (s) and v is the volume (m³) of dye solution. Cost for electrode (Kg Al/m³ dye solution) is calculated by the following equation by Faraday’s Law:

$$C_{\text{electrode}} = \frac{I \times t \times M_w}{z \times F \times v} \quad (14)$$

where, I is current (A), t is time of electrolysis (s), M_w is molecular mass of aluminum (26.98 g/mol), z is no of electron transferred ($z = 3$), F is Faraday’s constant (96487C/mol) and v is volume(m³) of dye solution [12]. Cost due to electrical energy consumption as well as electrode assembly is calculated for different initial dye

concentration (up to 100 mg/L) and shown in Fig. 8 for 100% dye removal at desired operating conditions. A model calculation is shown in Appendix A. It is seen from the figure that both the cost (electrical and electrode) increases with the initial dye concentration. Operating cost also increases with the initial dye concentration.

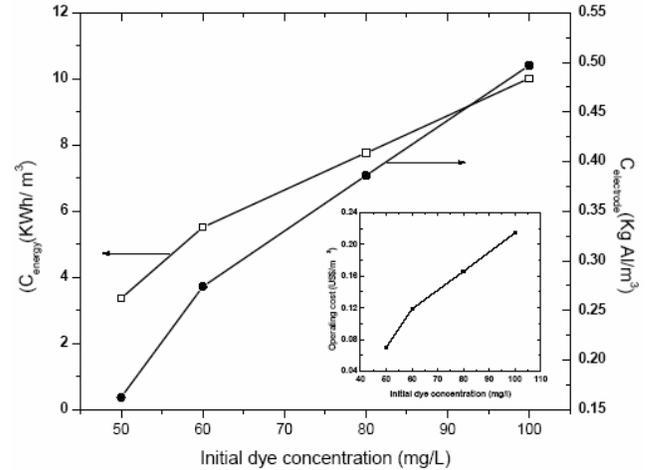


Fig. 8. Cost for the treatment of dye solution containing different concentration of crystal violet. Current density: 1112.5 A/m^2 , conductivity: $16.13 \times 10^{-1} \text{ S/m}$, pH: 8.5, inter electrode distance $0.5 \times 10^{-2} \text{ m}$.

Characterization of treated dye solution and byproducts obtained from EC bath

Fig. 9 shows the absorption spectra of the treated dye solution at the interval of every 10 minutes. It was seen that with the passage of time the absorption of the spectra was decreased. Therefore, it was confirmed that the decolorization was favored by electrocoagulation. Almost complete removal of dye is observed at the end of 1hr of operation without change in its λ_{max} value at 584 nm. Scanning electron microscopy (SEM) is an important tool to reveal the morphological information of any sample. These information include either the surface or the cross sectional overview depending upon the sample to be characterized. In the present study, byproducts formed during EC are aggregated as gelatinous aluminium hydroxide and dye molecule. Therefore, a surface characterization of EC byproduct was determined using SEM. From the Fig. 10 it can be visualized that the aggregated dye molecules (appeared black in the image) were remained on the whitish surface of aluminium hydroxides which are formed due to anodic oxidation of the sacrificial aluminium anodes. From the figure it was also observed that most of the aluminium hydroxide was covered by the dye molecules. EDAX spectra of solid precipitate (byproduct of EC) are presented in Fig. 11. The observation of peaks and trends in the EDAX graph convey that the by product of EC consisted of carbon (C)

and oxygen (O) from destroyed dye molecule, sodium (Na) and chlorine (Cl) peaks appeared due to added sodium chloride salt and aluminum (Al) peak was observed due to the dissolution of the electrode.

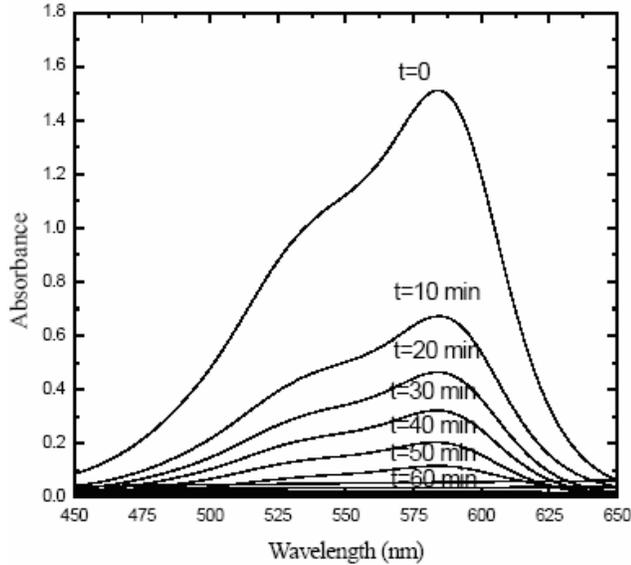


Fig. 9. Absorption spectra of EC treated samples with time (taken after every 10 minutes).

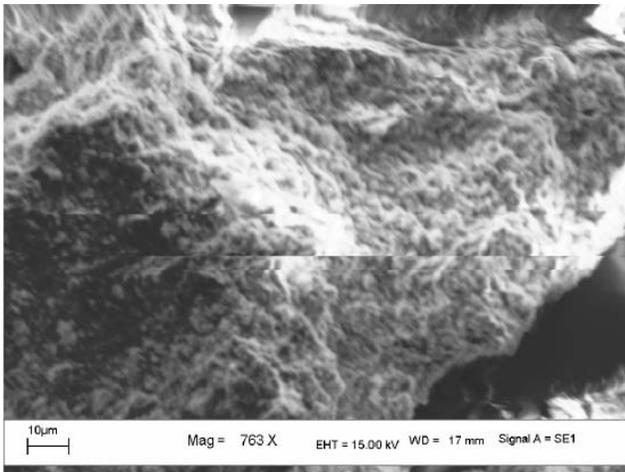


Fig. 10. SEM image of by products obtained from EC bath.

Conclusion

Electrocoagulation was used to remove crystal violet (CI42555) from its aqueous solution. The effects of various operational parameters on dye removal efficiency were investigated. The results showed that the removal efficiency was enhanced with the increase in current density from 362.5 to 1112.5 A/m². It was found that the proper electrolysis time was 1 hr for the removal of 99.75% dye and 99% COD reduction from dye solution. The dye solution was decolorized more efficiently when

the initial pH values of the solution was greater than 8.5. Dye removal efficiency was decreased when the initial dye concentrations were more than 100 mg/L. Conductivity of dye solutions should be more than 16.13×10^{-1} S/m to have acceptable energy consumption. That was obtained by adding proper amount of NaCl to the dye solutions. High conductivity is in favor of high process performances and low operating cost. Operating costs for the treatment of crystal violet dye using EC were evaluated for 100% removal of different initial dye concentrations with desired operating condition. Operating time and current density exhibit similar effects on the process performances and the operating cost. A detailed technical and economic analysis of the whole process is necessary. The simplified approach used in this study provides only preliminary data for a detailed analysis.

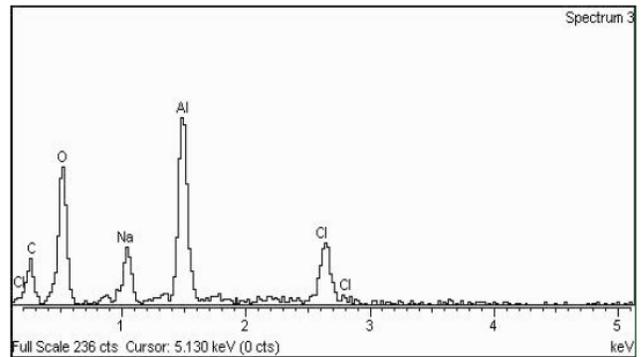


Fig. 11. Elemental analysis of by products obtained from EC bath.

Appendix A: Calculation of operating cost for the initial concentration of 50 mg/L

Operating cost was determined using the following relation as mentioned above.

$$\text{Operating cost} = a C_{\text{energy}} + b C_{\text{electrode}}$$

Where,

$$a = 0.0065 \text{ US\$/ kWh};$$

$$b = 0.3 \text{ US\$/ kg}$$

$$C_{\text{energy}} = \frac{U \times I \times t_{EC}}{v}$$

$$U = 6.75 \text{ V}$$

$$I = 4.45 \text{ A}$$

$$t_{EC} = 1200 \text{ s}$$

$$V = 1 \times 10^{-3} \text{ m}^3$$

Cost due to electrical energy was calculated using above values.

$$C_{\text{energy}} = 10.0125 \text{ kWh/m}^3$$

$$C_{\text{electrode}} = \frac{I \times t \times M_w}{z \times F \times v}$$

$$M_w = 26.98 \text{ g/mol}$$

$$z = 3$$

$$F = 96487 \text{ C/mole}$$

Cost for aluminum electrode was calculated using above values.

$$C_{\text{electrode}} = 0.497 \text{ Kg/m}^3$$

$$\text{Operating cost: } 0.2141 \text{ US\$/m}^3$$

References

- Daneshwar N, Oladegarazope A, Djafarzadeh N, (2006) Decolorization of basic dye solutions by Electrocoagulation: An investigation of the effect of operational parameters. *J Haz Mat B129*: 116-122.
- Alshamsi AF, Albadwawi AS, Alnuaimi MM, Rauf MA, Ashraf SS, (2007) Comparative efficiencies of the degradation of crystal violet using UV/hydrogen peroxide and Fenton's reagent. *Dyes and pigments*. 74: 283-287.
- Purkait MK, Vijay SS, DasGupta S, De S, (2004a). Separation of Congo red by surfactant mediated cloud point extraction. *Dyes and Pigments* 63 (2): 151-159.
- Purkait MK, DasGupta S, De S., (2004b) Resistance in series model for micellar enhanced ultrafiltration of eosin dye. *J. Colloid and Interf Sci* 270: 496-506.
- Maximova N, Dahl O, (2006) Environmental implications of aggregation phenomena: Current understanding. *Current Opinion in Colloidal and Interf Sci* 11 (4): 246-266.
- Pouët MF, Grasmick A, (1995) Urban wastewater treatment by electrocoagulation and flotation. *Water Sci and Technol* 31 (3-4): 275-283.
- Chen X, Chen G, Po LY, (2000) Separation of pollutants from restaurant wastewater by electrocoagulation. *Sep. Purif. Technol.* 19: 65-76.
- Vik EA, Carlson DA, Eikum AS, Gjessing T, (1984) Electrocoagulation of potable water. *Water Res* 18: 1355-1360.
- Kobyas M, Hiz H, Senturka E, Aydinler C, Demirbas E, (2006b) Treatment of potato chips waste water by Electrocoagulation. *Desalination* 190: 201-211.
- Kumar PR, Chaudhari S, Khilar KC, Mahajan SP, (2004) Removal of arsenic from water by Electrocoagulation. *Chemosphere* 55: 1245-1252.
- Drondina KV, Drake IV, (1994) Electrochemical technology for fluorine removal from underground and waste waters. *J Haz Mat* 37: 91-100.
- Kobyas M, Demirbas E, Can OT, Bayramoglu M, (2006a). Treatment of levafix orange textile dye solution by electrocoagulation. *J Haz Mat* 132 (2-3): 183-186.
- Escobar C, Soto-Salazar C, Toral MI, (2006) Optimization of the Electrocoagulation process for the removal of copper, lead and cadmium in natural water and simulated waste waters. *J of Environ Manage* 81: 381-391.
- Ge J, Qu J, Lei P, Liu H., (2004) New bipolar Electrocoagulation-Electrofloatation process for laundry waste water. *Sep and Purif Technol* 36: 33-39.
- Yilmaz AE, Boncukcuoglu R, Kocakerim MM, (2007) An empirical model for parameters affecting energy consumption in boron removal from boron-containing waste waters by Electrocoagulation. *J Haz Mat* 144 (1-2): 101-107.
- Tezcan U, Ugar S, Koparal AS, Ogutveren UB, (2006) Electrocoagulation of olive mill waste waters. *Sep and Purif Technol* 52: 136-141.
- Yavruz Y, (2007) EC and EF processes for the treatment of alcohol distillery wastewater. *Sep and Purif Technol* 53(1): 135-140.
- Gallegos AA, Pletcher D., (1999) The removal of low level organics via hydrogenperoxide formed in a reticulated vitreous carbon cathode cell, Part2:the removal of phenols and related compounds from aqueous effluents; *Electrochim. Acta* 44: 2483-2492.
- Golder AK, Hridaya N., Samanta A.N., Ray S., (2005) Electrocoagulation of methylene blue and eosin yellowish using mild steel electrodes; *J. Hazard.Mater.* 127 (1-3): 134-140.

20. Murugananthan M., Raju G.B., Prabhakar S., (2004) Separation of pollutants from tannery effluents by electrofloatation; *Sep. Purif. Technol.* 40: 69–75.
21. Yildiz YS., Koparal AS., Irdemdez S., Keskinler B., (2007) Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes; *J. Hazard. Mater.* B139: 373–380
22. Hernandez IL., Diaz CB., Movales GR, Bilyeu B., Nunez U., (2007) A combined electrocoagulation-sorption process applied to mixed industrial wastewater; *J. Hazard. Mater.* 144 :240–248.
23. Vogel AI, (1970) *Textbook of Practical Organic Chemistry* 385, 818.
24. Vorobiev E, Larue O, Vu C, Durand B, (2003) Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions. *Sep Purif Technol* 31: 177–192.
25. Alinsafi A, Khemis M, Pons MN, Leclerc JP, Yaacoubi A, Benhammou A, Nejmeddine A, (2005) Electro-coagulation of reactive textile dyes and textile wastewater, *Chem Eng Process* 44: 461–470.
26. Mollah MYA, Morkovsky P, Gomes JAG, Kesmez M, Parga J, Cocke DL, (2004) Fundamentals, present and future perspectives of electrocoagulation. *J Haz Mat B* 114: 199–210.