

Electrocoagulation of methylene blue and eosin yellowish using mild steel electrodes

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Abstract

The paper presents the study of electrocoagulation (EC) of aqueous dye solutions of two different industrial dyes in a batch stirred cell. Experiments were carried out with 200 mg/l individual concentration of methylene blue (MB) and eosin yellowish (EY) in presence of NaCl as electrolyte. Effect of operating time and current density on the decolorization of dye solutions, reduction of chemical oxygen demand (COD) and variation in conductivity, pH during treatment has been studied. Small difference between color diminution and COD reduction has been found with the progress of treatment. First-order rate equation for dye removal has been developed from the experimental results. Sludge formation during EC and problems associated with this solid waste generation and disposal has been assessed. Energy consumption in KWh/m³ with reduction of COD (kg) during treatment has been reported. Electric power consumption of 1.5 KWh reduces 0.21 and 0.11 kg COD from 0.24 and 0.14 kg of initial COD for MB and EY, respectively, starting from 200 mg/l dye concentration.

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Keywords: Electrocoagulation; Dyeing effluents; Decolorization; COD; Sludge formation

1. Introduction

Organic colored wastewaters are common in various industries like textile, paper, plastic, leather, food, and mineral processing industries. The organic compounds in these effluents undergo chemical as well as biological changes, consume dissolved oxygen (DO), and demolish aquatic life. Some dyes and their degradation products are also carcinogens and toxic [1–3]. Therefore, it is necessary to treat dye effluents prior to their discharge to the receiving water stream and meet the stringent environmental regulations. Conventionally biological, chemical, and physical methods have been employed for dye removal, but the first two techniques have not been very successful due to the non-biodegradable nature of most dyes [4,5]. When chemical oxidation or coagulation is used to treat dye-containing wastewater, added chemical substances might cause the secondary water pollution [6].

Adsorption is often used to remove dyes from aqueous solutions [7,8]. Activated carbon is a commonly used adsorbent, though it is difficult to regenerate and its performance is limited by equilibrium [9].

Others treatments with more sophisticated technologies like reverse osmosis/ultra-filtration have the disadvantages of high cost and low throughput [10–13].

Successful electrochemical oxidation/electrocoagulation (EC) treatment of various organic effluents have been reported by many authors [14–20]. Among these, statistical investigation of operating variables [20], decolorization of reactive dyes with Al electrodes [21], electrocoagulation of aqueous dye solution of orange II by using iron as sacrificial electrodes [22], and estimation of operating cost [23] have proved successful for electrocoagulation of dyes from waste water. Recently, Yousuf et al. [24] have been published a very comprehensive review paper on treatment wastewater by electrocoagulation with iron and aluminum electrodes.

Therefore, the focus of the present study is on decolorization of aqueous solutions of methylene blue (MB) and eosin yellowish (EY), reduction of chemical oxygen demand

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(COD), variation of conductivity during electroprocessing, power consumption, and the quantity and quality of sludge production.

2. Experimentation

Methylene blue and eosin yellowish of AR grade obtained from M/s Loba Chemie, (India) were used for the experiments. Their physical and chemical properties are shown in Table 1. Dye solutions in purified water were prepared having 200 mg/l individual concentration. To increase solution conductivity, NaCl was added to the solutions. Concentration of NaCl in the solution was 400 mg/l. The experiments were carried out in a batch electrolytic cell (Fig. 2.1).

Mild steel electrode pairs with 15 cm × 2 cm × 1.5 cm dimension, having submerged surface area of 6.2 cm² and 1.2 cm electrode spacing was used. The electrodes were placed in 70 ml aqueous dye solutions in a 100 ml glass electrolytic reactor. DC potential was applied from Aplab regulated DC power supply (model-7145). Cell current density was varied by changing the impressed cell voltage. A Sunwa Electronics multimeter, model-YX-360TR_{EB}, was used for measurement the current and the potential between the two electrodes. The solution was agitated with a magnetic stirrer hot plate (Model-MC02, Tarsons India Ltd.) during electroprocessing at 450 rpm. Electrodes were sanded and washed with dilute H₂SO₄ between the experiments. Experiments were conducted at 27 °C in water bath.

SPEKOL-1200 spectrophotometer (Germany) having operating range of 200–1100 nm was used for spectrographic analysis of dye solutions. Known concentration of MB and EY solutions were scanned at 658 and 518 nm wavelengths respectively, for generating the calibration plots. “Open reflux method” of COD measurement [25] was used for determin-

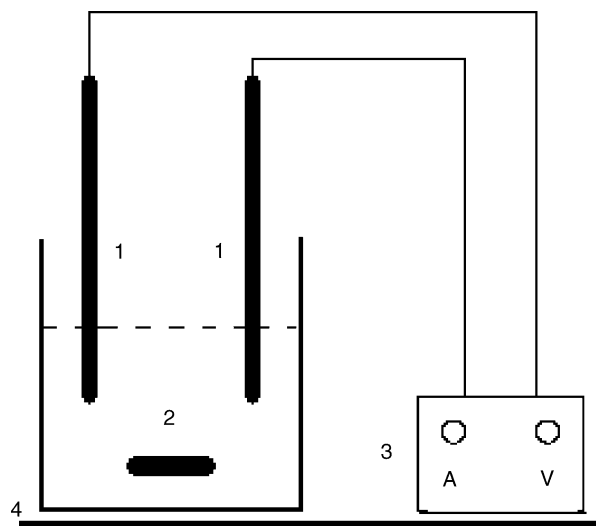


Fig. 2.1. Schematic process arrangement: (1) mild steel electrode pair, (2) stirrer bar, (3) glass cell, and (4) base plate.

ing COD of the solutions. AR/GR grade chemicals procured from M/s E. Merck (India) were used for determination of COD. Conductivity measurements were carried out with auto-ranging conductivity meter (Chemito-130, Toshnival Instrument India limited). Sludge generating during treatment was separated from the solutions by filtration using Indica filter paper (Kolkata, India), grade HM 2. The filtered sludge was air-dried and the weight of dry sludge was measured by subtracting the blank filter paper weight. Solution pH was measured by deluxe water and soil analysis Kit-191E (India). Initial pH of the solutions was ≈6.8 and no significant change was observed during electroprocessing. This due to that some buffering species like Fe(OH)₃/Fe(OH)₄⁻ [21] is formed during electrocoagulation.

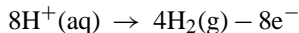
Table 1
Properties of dyes used for this study

Dye	Structure	λ_{\max} (nm)	M.W.	C.I.
Methylene blue [3,7-bis(dimethylamino) phenazathionium chloride trihydrate]	 $(\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot 3\text{H}_2\text{O})$	658	373.9	52015
Eosin Y [2,4,5,7-tetra-bromofluorescein di-sodium salt]	 $(\text{C}_{20}\text{H}_6\text{Br}_4\text{Na}_2\text{O}_5)$	518	691.86	45380

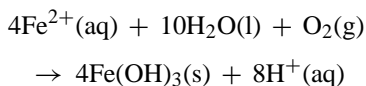
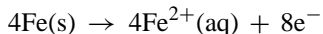
3. Outline of electrocoagulation

Theory of electrocoagulation has been discussed by a number of authors [24,26–28]. Electrocoagulation strongly depends on pH, particle size, concentrations, and conductivity of the continuous phase. Electrocoagulation of wastewater using iron electrodes takes place according to the following reactions: the following mechanism is involved [24] for the production of $\text{Fe}(\text{OH})_n$, where $n=2$ or 3.

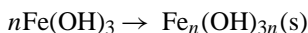
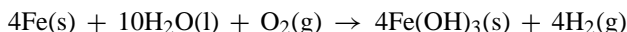
Cathodic reaction:



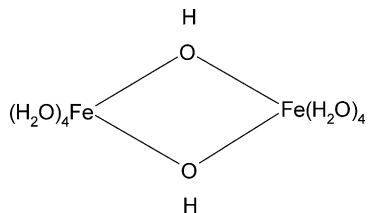
Anodic reactions:



Overall reaction:



The $\text{Fe}(\text{OH})_n(\text{s})$ remains in the aqueous phase as a suspension, which can remove the pollutants from wastewater either by complex formation or by electrostatic attraction, followed by coagulation. Iron-hydroxo complexes have pronounced tendencies to form polynuclear complexes. During EC with iron various species are formed such as: $\text{Fe}(\text{OH})_4^-$, $\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3^0$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})^{2+}$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$, and $\text{Fe}(\text{H}_2\text{O})_6(\text{OH})_4^{4+}$ [26,29]. The bi-nuclear ions formed have sufficient stability to exist in appreciable concentrations in solutions. The two metal ions are thought to be bound by two hydro bridges:



4. Results and discussion

4.1. Decolorization

Progress of dye decolorization efficiency during electroprocessing is shown in Figs. 4.1 and 4.2. Initial decolorization was quite fast for both of MB and EY. At higher dye concentration, dye molecules at the vicinity of the sacrificial electrode electrocoagulate easily but with progress of treatment higher diffusional resistance to come over to the surface

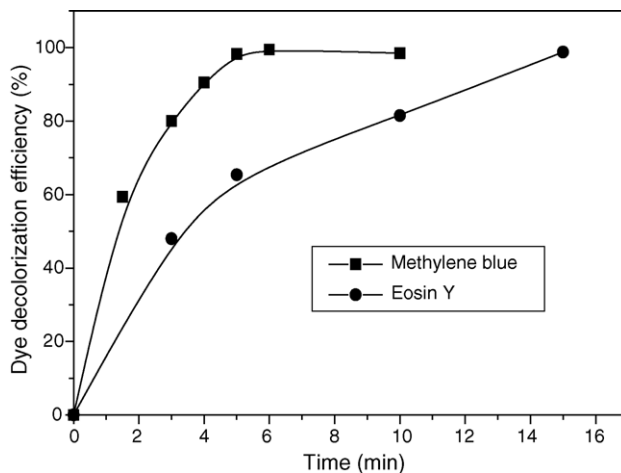


Fig. 4.1. Decolorization efficiency vs. treatment time with 400 mg/l NaCl electrolyte, 16.1 mA/cm² current density (100 mA cell current), stirrer at 450 rpm.

of anode reduces the rate. During first 5 min of electrolysis at 16.1 mA/cm², about 97% of MB was removed. To achieve the same level of conversion with EY, it takes about 15 min (Fig. 4.1). Can et al. [21] reported about 80% decolorization of Remazol Red after 10 min EC with initial concentration of 250 ppm, current density of 10 mA/cm², pH 7.0. This is of the same order as obtained in the experiments conducted in this work.

Up to current density 24 mA/cm² in 5 min of operating time almost complete color diminution was observed for MB. But the same was only 75% for EY (Fig. 4.2). This is attributed to the difference in effective surface charge densities leading to mobility difference.

The plot of rate of EC versus time of treatment of EC is shown in Fig. 4.3. The rate of degradation MB is seen to be higher than EY. Differential analysis of the data was used to

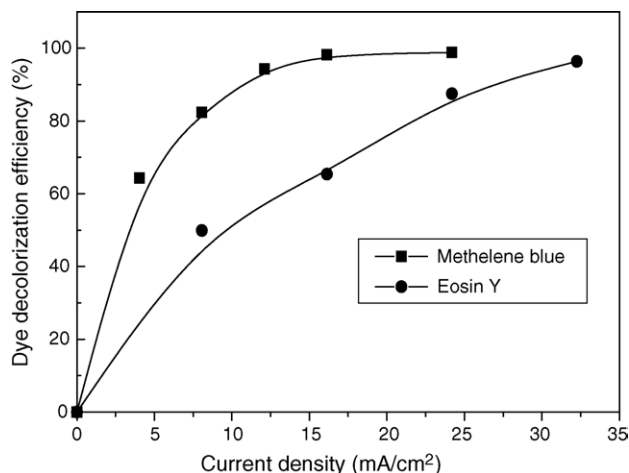


Fig. 4.2. Dye decolorization efficiency after 5 min, for different current densities with 400 mg/l NaCl electrolyte, initial dye concentration 200 mg/l, stirrer at 450 rpm.

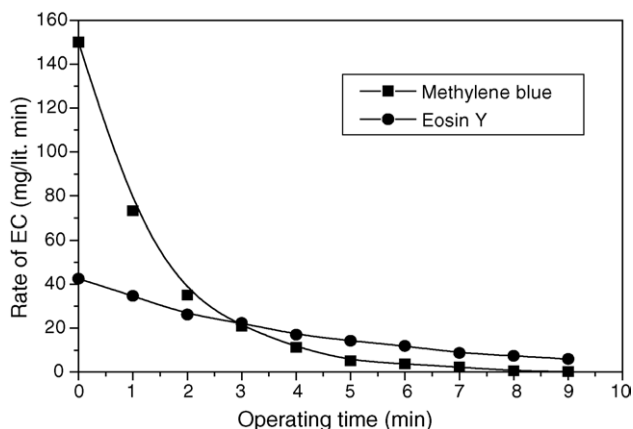


Fig. 4.3. Rate of EC vs. time of treatment with 200 mg/l MB or EY, 400 mg/l NaCl, 16.1 mA/cm² current density (100 mA cell current), 450 rpm, and mild steel electrode.

evaluate all the terms in the rate equation including the derivative, $-\frac{dC_i}{dt}$. The best fit values for the order ‘*n*’ and constant ‘*k*’ for the rate equation $-\frac{dC_i}{dt} = kC_i^n$ were found out from Fig. 4.4. The values of *n* are 1.09 and 1.06, and the values of *k* are 0.42 and 0.15 for MB and EY, respectively. During EC, the solution is continuously was agitated continuously at 450 rpm and turbulent coagulation exhibits [30] and the overall process order being close to 1. If the process is assumed to be of first-order, the experimental data fits the (first-order) equation in a least square sense with values of *k* (s⁻¹) being 0.56 and 0.20 for MB and EY.

4.2. COD reduction

Dye concentration results reported so far were based on the spectrophotometric analysis of the dye solutions. Diminution of color does not necessarily imply reduction of COD. Color removal may be due to (1) degradation of the dye, (2) formation of organic/organometallic complexes, and/or

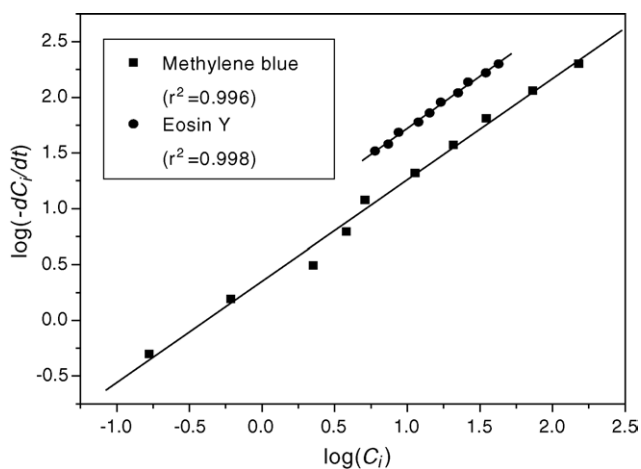


Fig. 4.4. log(d*C_i*/dt) vs. log(*C_i*) with 200 mg/l, 400 mg/l NaCl electrolyte, 16.1 mA/cm² current density (100 mA cell current), and stirrer at 450 rpm.

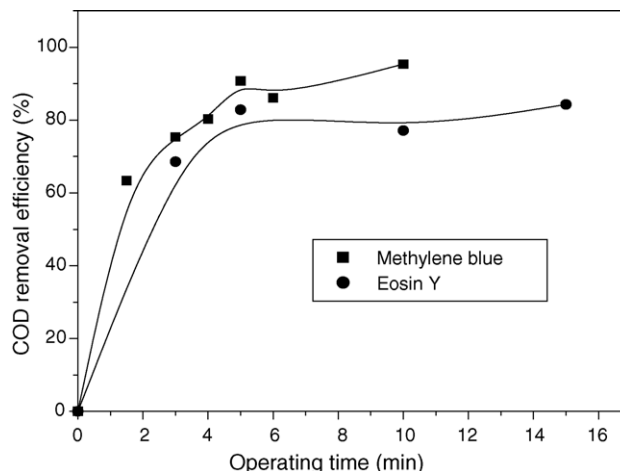


Fig. 4.5. COD reduction efficiency at different time of electrolysis during electrolysis with mild steel electrodes, 200 mg/l dye concentration, 0.0161 A/cm² current density (100 mA cell current), 400 mg/l NaCl, and 450 rpm.

(3) a combination of two. Complete degradation of a dye is expected to reduce the COD most effectively.

Experiments were conducted with 200 mg/l initial concentration of individual dye. The initial COD were 240 and 140 mg/l, respectively, for MB and EY. COD reduction efficiency during EC is shown in Fig. 4.5. It was noted from the figure that after 5 min of electroprocessing at current density of 16.1 mA/cm², about 87 and 78% reduction of COD occurred with MB and EY solutions, respectively. Fig. 4.6 shows the reduction of COD in 5 min when the cell was operated at different current density values. At a current density of 25 mA/cm², COD removals were 87 and 99% for EY and MB, respectively (Fig. 4.6).

Difference in percentage reduction of COD and color diminution of the dye (measured spectrophotometrically)

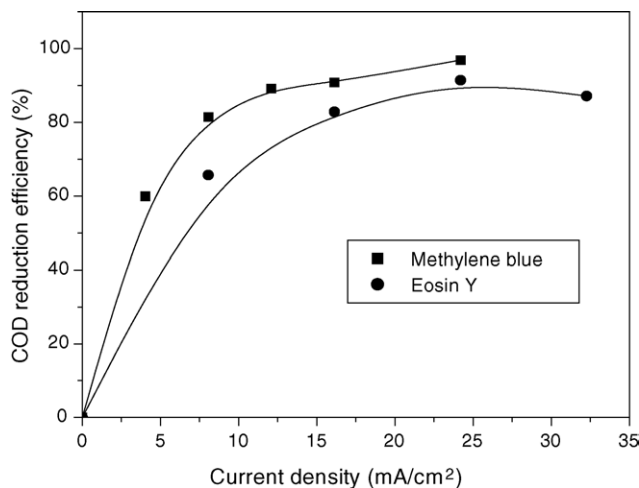


Fig. 4.6. COD removal efficiency vs. concentration diminution at const. current density of electrolysis with mild steel electrodes, 200 mg/l dye, 400 mg/l NaCl, 5 min electroprocessing, and 450 rpm.

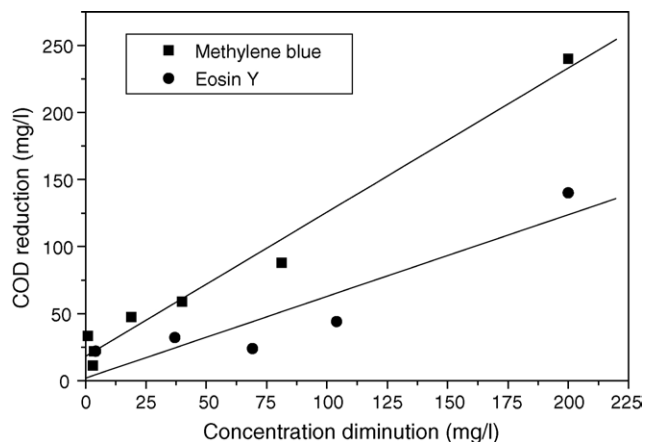


Fig. 4.7. COD removal vs. concentration diminution at constant current density of electrolysis with mild steel electrodes, 200 mg/l dye, 400 mg/l NaCl, 5 min electroprocessing, and 450 rpm.

with mild steel electrodes are observed (Fig. 4.7). Such differences also reported earlier by various workers [15,22].

4.3. Conductivity variation

Textile wastewaters have a broad variation in conductivity. Higher conductivity increases current density for the same potential difference applied. To enhance the conductivities of the dye solutions, NaCl was added (400 mg/l) to the solutions as electrolyte. This amount of NaCl increases the conductivity about 11 times, i.e., it increases from 59 to 780 $\mu\text{S}/\text{cm}$. According to Vlyssides et al., when chlorides are present in the solutions the products from anodic discharge of chlorides are Cl_2 and OCl^- . The OCl^- itself is a strong oxidant, which capable of oxidizing organics molecules present in wastewater. So, added NaCl not only increases the conductivity but also contributes strong oxidizing agents.

Figs. 4.8 and 4.9 depict that with increase in operating time as well as current densities conductivity decreases up to around 4 min and around 12.5 mA/cm², respectively. Then,

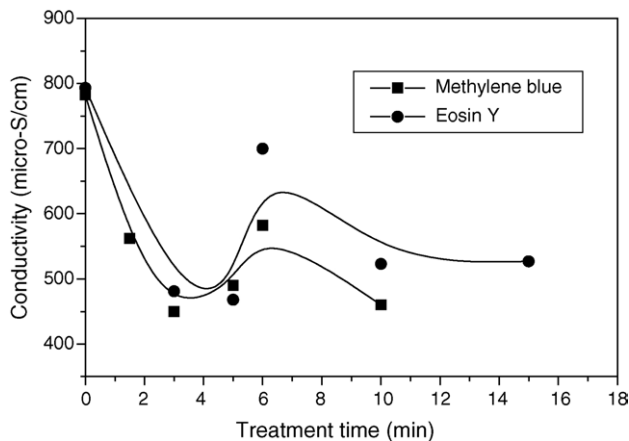


Fig. 4.8. Change of solution conductivity as a function of operating time with MS electrodes, 200 mg/l dye concentrations, 0.0161 A/cm² current density, 400 mg/l NaCl, and 450 rpm.

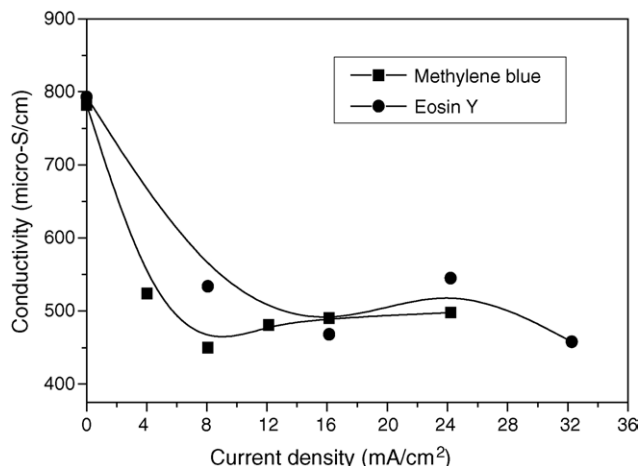


Fig. 4.9. Variation of conductivity with current density with 200 mg/l dye concentration, 400 mg/l electrolyte, 5 min of electroprocessing, 450 rpm, and mild steel electrodes.

it increases again then falls slightly. Initial rapid decrease in conductivity agrees the theory of EC evidenced by significant amount of dye and NaCl gets removed. Color diminution and COD reduction has been earlier reported to be showing similar initial rapid rates [23]. The later increase in conductivity may be attributed to soluble metal hydroxides being produced with time and higher current density. Formation of polymeric metal hydroxides facilitating coagulation with increase in operating time and current density has been reported by Bratby [26].

4.4. Sludge formation

Amount of sludge produced during electroprocessing is of industrial relevance. It points to the problem of solid waste generation and disposal associated with the process. Sludge contains large amount organics that may be carcinogenic. It also contains metals, which may have originated from use of metal electrodes. Investigation of the quality and the quantity of sludge generation during EC of MB and EY using mild steel electrodes was, therefore, carried out. 'Sacrificial electrodes' get dissolved during EC and require regular replacement. Oxide film formed on the electrodes leads to loss of efficiency of the cell. Sludge formation per kilogram of COD reduction of solution during EC is presented in Figs. 4.10 and 4.11 for solutions of MB and EY. With 200 mg/l initial concentration of MB (100%) and EY (100%), it is seen from Fig. 4.10 that after 5 min of operation, 1.23 and 2.68 kg of sludge gets generated per kilogram of COD reduction. Corresponding COD removals are 87 and 78%, respectively, from the initial COD of MB and EY being 240 and 140 mg/l, respectively.

4.5. Energy consumption

COD reduction has been plotted against power consumed. Energy consumption in KWh/m³ of sample has been obtained

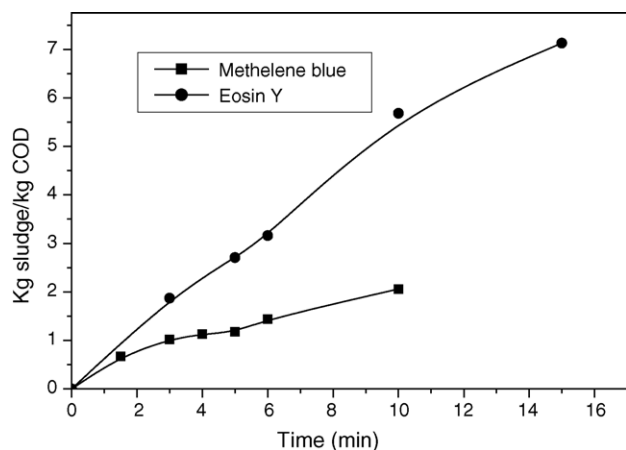


Fig. 4.10. Sludge wt./kg COD vs. cell operating time of colored solutions using mild steel electrodes, 16.1 mA/cm² current density, 450rpm, and 400 mg/l NaCl.

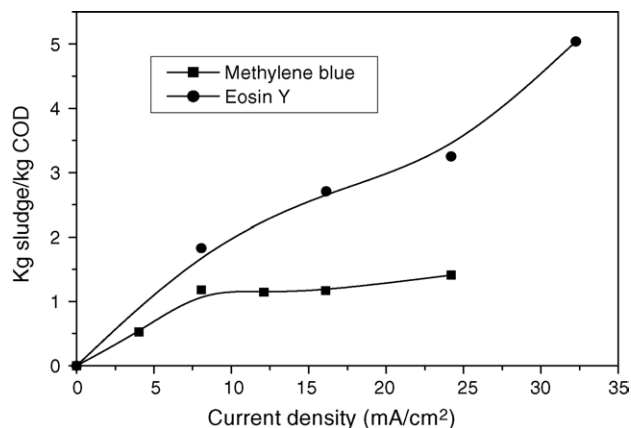


Fig. 4.11. Production of sludge per unit kilogram COD with current density during treatment of effluent with mild steel electrodes.

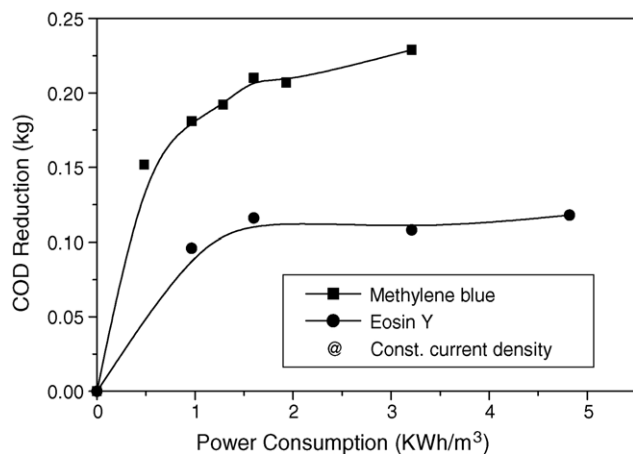


Fig. 4.12. COD reduction vs. power requirement during electro-treatment, 16.1 mA/cm² current density, 200 mg/l dye concentration, 400 mg l⁻¹ NaCl, 450 rpm, and mild steel electrodes.

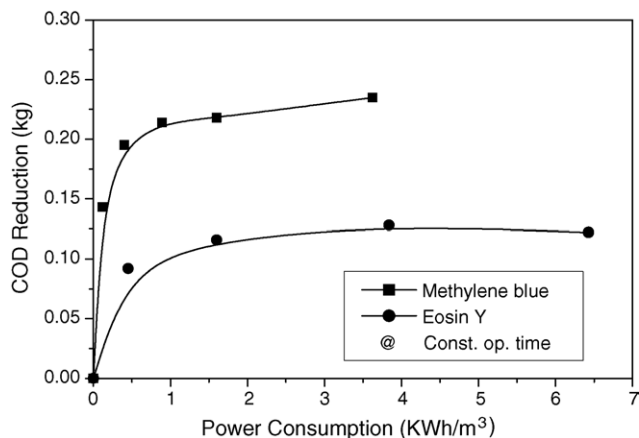


Fig. 4.13. COD reduction (in 5 min) vs. power consumption (5 min, initial dye concentration 200 mg/l, NaCl 400 mg/l, and stirrer at 450 rpm).

by linear scaling of the experimental results. Fig. 4.12 is generated from the data generated at constant current density, and Fig. 4.13 is from results after 5 min of EC carried out at different current density values. Both the plots indicate rapid initial reduction of COD and most of the dye electrocoagulated within the energy consumption of 1.5 KWh/m³. COD reduction of 0.21 and 0.11 kg was noted at that energy consumption of 1.5 KWh/m³ and the corresponding COD reduction were 89 and 74% in case of MB and EY, respectively. This implies that for 1 kg COD reduction of 200 ppm MB and EY solution, the energy consumption is 7.14 and 13.63 KWh.

5. Conclusions

In the scales of operation investigated, electrocoagulation time up to 5 and 15 min proves sufficient for decolorization of aqueous dye solutions of MB and EY with mild steel electrodes. Both the dyes almost followed first-order rate equations for concentration diminution. During electroprocessing of 200 mg/l solutions of MB or EY with mild steel electrodes, about 0.22 and 0.3 kg/m³ sludge generation was observed with corresponding 87 and 78% COD removal. It was also noted that 1.5 KWh/m³ power consumption reduced COD by 89 and 74% reduction for MB and EY, respectively.

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