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SIMULTANEOUS DECOLORIZATION OF TERNARY DYE MIXTURE FROM AQUEOUS SOLUTION BY ELECTROCOAGULATION

The current study focused on the treatment of a ternary mixture of dyes which includes Disperse Blue 56 (DB56), Basic Yellow 28 (BY28) and Acid Violet 90 (AV90) using the electrocoagulation (EC) process with iron electrodes. In the presence of all dye molecules, the optimum pH was found to be 6, optimum NaCl concentration was 3000 mg/dm³ and optimum current density was 8.66 mA/cm². Under the optimized conditions in the case of 100 mg/dm³ each dye concentration, the average colour removal efficiency was reached 93%. Dye concentration dependent highest COD removal efficiency was measured as 88.70% at 150 mg/dm³ dye concentration.

1. INTRODUCTION

Dyes are extensively used in many fields such as textile, leather, paper, food industries. These extensive applications of synthetic dyes create environmental pollution and their toxic properties cause health risk [1]. The most widely used methods to remove dyes are adsorption [2], ultrafiltration [3] and nanofiltration [4], oxidation [5], biological methods [6], etc. Electrocoagulation (EC) process has been mostly applied to treat dye-containing wastewaters because of the simplicity and high efficiency of the decolorization. This process was based on the formation of coagulants via electrolytic reactions at electrode surfaces. The production of destabilization agents brings about neutralization of electric charge for removing pollutant [7]. Electrocoagulation process also facilitates flocculation by turbulence generated by oxygen and hydrogen evolution at the cathode and anode electrodes. With the gas evolution, particles are

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destabilized and they start attracting each other and generate bigger particles. EC process depends on pH, particle size, concentrations, and the conductivity of the continuous phase. These experimental factors affect the results in different ways. Electrocoagulation has some advantages including simple equipment requirement, easy automation of the process, environmental compatibility, versatility, rapid reactions and smaller systems [8, 9]. The EC process has no chemical requirements and dosing of coagulants depends on the cell potential.

Many EC investigations have been focused on single dye removal. This study concerned simultaneous removal of dyes and also COD from aqueous solution via electrocoagulation. When more than one dye was analyzed in a mixture, their absorption spectra would most probably overlap in a certain wavelength region. Chemometric and graphical calibration techniques [10] in spectral analysis can be used to solve this problem without any separation procedure before the determination step. In this study, due to the spectral overlap, the chemometric calibration technique was applied to determine the remaining dye amount in the solution. The utilized method to calculate the amount of dye in solution is a partial least square (PLS) method. PLS regression is one of the most popular multivariate calibration procedures owing to its good prediction ability and ease of use. It follows from the fact that PLS searches for a compromise between better fitting and better prediction.

Electrocoagulation reactor designs are classified as batch or continuous systems [11] and used electrodes can be made generally of iron or aluminum. A batch system and iron electrodes are used in this study. The removal of dyes from aqueous solution under such conditions has high efficiency in the decolorization process [12]. In addition, sacrificial iron electrodes have been used successfully in removing some other pollutants such as: oil-grease, heavy metal ions, phosphorus compounds, pesticides and domestic wastewaters, etc.

The recent development of EC process has focused on improvement of removal efficiency or/and cost reduction. Eyvaz et al. [13] reported that alternating current system has higher removal percentage than direct current system on dye treatment by EC process and they obtained nearly the same operating costs. Alternating current prevents the formation of impermeable oxide layer on the cathode material and corrosion of the anode material due to oxidation. El-Ashtoukhy and Amin [14] found cathodically evolved H_2 gas stirring as effective as mechanical stirring because H_2 improves mixing conditions and eliminates concentration polarization. Elshazly [15] used gas sparring technique to improve the performance of the EC process. They announced that percentage dye removal increased by increasing the gas flow rate and lower gas flow rate can reduce the operating costs.

The objective of the present study is to investigate simultaneous removal of Disperse Blue 56 (DB56), Basic Yellow 28 (BY28), Acid Violet 90 (AV90) and also COD from aqueous solution via electrocoagulation using iron as an electrode material. The main operational parameters governing the EC process were studied in a wide

range of values. Although EC process was extensively studied in literature, this study concerned a ternary dye system, a mixture which is similar in composition to real situations and the PLS chemometric method was used to better assess the analytical results.

2. EXPERIMENTAL

Materials and instrumentation. The structures of dyes used in the experiments are shown in Fig. 1. Disperse Blue 56 (DB56), Basic Yellow 28 (BY28) and Acid Violet 90 (AV90) were provided from the UMUT KİMYA Boya ve Diş Ticaret Ltd. Şti (Turkey). In order to determine dye concentrations, the solutions were analyzed using UV-Vis spectrometer (Schimadzu UV-Vis 160) by recording the full absorption spectrum of mixtures in the range of 200–800 nm. Data treatments, regressions and statistical analysis were performed by using the EXCEL and MATLAB software. COD removal experiments were carried out by using standard procedures (APHA 1992). COD was spectrophotometrically determined by using an Hach DR/4000 spectrophotometer.

Design and method. The experiments were carried out in a batch reactor which consists of a direct current (DC) power supply and iron electrodes in a beaker having capacity of 1000 ml. The distance between the two electrodes was 2.2 cm and submerged area of the electrodes was 115.5 cm². The stirrer was used during the electrocoagulation. The electrodes were washed before every experiment with dilute HCl and distilled water. pH of solutions was adjusted by using HCl and NaOH. The conductivity was changed by using NaCl within the concentration range of 1500–3500 mg/dm³. The applied current density was in the range of 4.33–17.32 mA/cm². Solutions of dye mixture were prepared by dissolving appropriate amount of dyes in 1000 cm³ distilled water to the concentration of 50, 100, 150, 200 and 250 mg/dm³ for each dye. The optimization experiments were done at the concentration of 100 mg/dm³ for each dye. The COD removal experiments were carried out under the following conditions: concentration range of each dye 50–250 mg/dm³, initial pH – 6, current density – 8.66 mA/cm², concentration of salt 3000 mg/dm³ and distance between the electrodes 2.2 cm, during the 15 min electrocoagulation time period. The experiments were done at 293.15 K. The decolorization efficiency from the ternary solution was performed using the following formula

$$R(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are concentrations of dye before and after electrocoagulation, respectively.

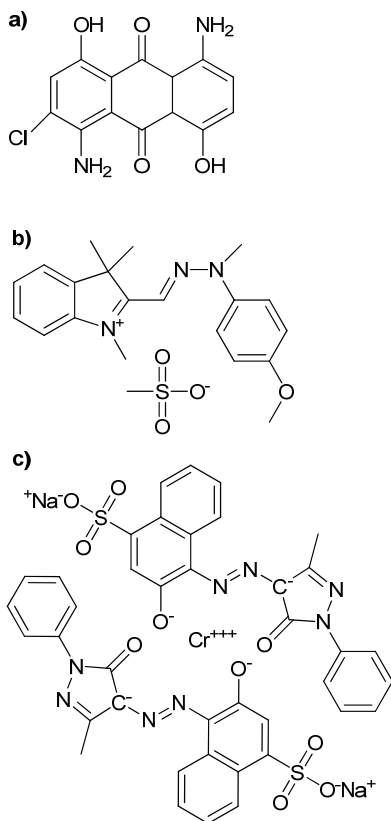


Fig. 1. Schematic structure of Disperse Blue 56, MW – 304.69 g/mol (a), Basic Yellow 28, MW – 433.52 g/mol (b), and Acid Violet 90, MW – 941.80 g/mol (c)

Electrical energy consumption was calculated using the following formula

$$E = UIt_{EC} \quad (2)$$

where E is the electrical energy (Wh), U is the cell voltage (V), I is the current (A) and t_{EC} is the time of EC process per hour.

COD removal efficiency after EC process was calculated using the formula

$$R(\%) = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \quad (3)$$

where COD_0 is the initial concentration and COD_t is the concentration after EC process (both in mg/dm^3).

The particulates of colloidal ferric oxyhydroxides gave yellow-brown colour into the solution after EC. All the suspended solids were removed by electrocoagulation and electrolytic flotation. Thus, during electrolysis, the clear solution was ob-

tained. All the samples were centrifuged (5000 rpm) and analyzed by taking their clear part. We did not use a filter paper to eliminate any interference that might come from filter papers to measure the remaining dye concentration and COD.

Due to the significant spectral overlapping, conventional calibration procedures would have a limited application for quantitative determination of this complex system. Therefore, simultaneous determination of these dyes requires application of chemometric calibration for resolution of this complex system. Partial least-square regression (PLS) method was used to determine the concentration of DB56, BY28 and AV90 in synthetic dye mixtures. All calculations were performed using MATLAB 7.0 (The MathWorks, Inc.) for Windows and the PLS Toolbox 4.1. The selection of optimal factor was done by cross-validation procedure by using 20 absorption spectra of dye mixtures. In the application of the PLS algorithm, it is well known case that the spectral range and the number of PLS factors are critical parameters. The spectral range gives location and quality of spectral information and the number of factors allows us to model as much of the complexity of the system without overfitting the concentration data. To accomplish this goal, we use the crossvalidation method leaving out one sample at a time. The 200–800 cm^{-1} range was used to cover whole spectral area for three dyes.

Table 1

Calculated linear equations for the each dye

DB56	BY28	AV90
$y = 0.9945C_{\text{DB56}} + 0.1035$	$y = 0.9863C_{\text{BY28}} + 0.2192$	$y = 0.9913C_{\text{AV90}} + 0.2075$
$R^2 = 0.9985$	$R^2 = 0.9964$	$R^2 = 0.9989$

The optimum number of factors was identified as the one that gave a minimum standard error of cross validation. PLS uses linear relationship between absorbance and component concentrations. PLS method has a calibration step where the relationship between the spectra and component concentrations is estimated from a set of reference samples. The calculated linear equations of added and found amounts of dyes are given in Table 1. In order to assure the performance of the model on other samples, validation was performed. In this study, models were validated using cross-validation with fifteen segments. This step was followed by the prediction in which the results of the calibration are used to predict the component concentrations from the unknown sample spectrum.

3. RESULTS AND DISCUSSION

In an electrochemical process, electrode material has significant effect on the treatment of wastewaters to remove the pollutants. In this study, EC process was car-

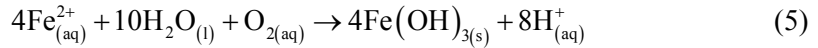
ried out using iron electrodes. Dissolution process of iron is one of the important parameters for removal of wastes in water. Hector et al. explained the whole electrochemical process of electrocoagulation and depending on their findings, Fe(III) hydroxide formation is the highest between pH 4 and 10 [16]. Electrocoagulation of ternary mixture of dye solution using iron electrodes takes place according to the following mechanisms [12, 17] for the production of $\text{Fe}(\text{OH})_n$, where $n = 2$ or 3.

• Mechanism 1

Anode:



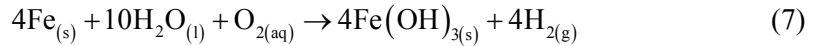
Bulk of solution:



Cathode:



Overall:

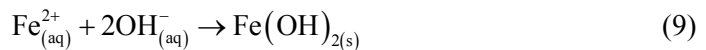


• Mechanism 2

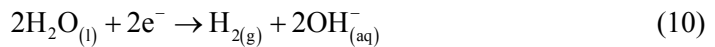
Anode:



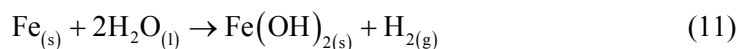
Bulk of solution:



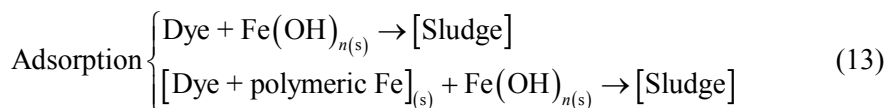
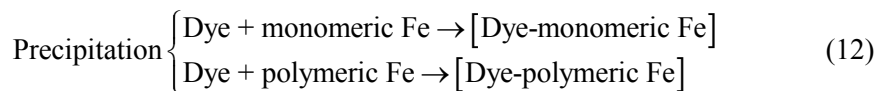
Cathode:



Overall:



The removal of dyes from aqueous solution by these species occurred via adsorption and/or precipitation mechanisms. The removal of dyes with precipitations and adsorption takes place according to the following reactions [12, 17]:



Effect of initial pH on the removal efficiency of EC process. Lorenz et al. reported that one of the important parameters for the dissolution and passivation rate of iron is pH [18]. The dependence of removal efficiency on initial pH was studied over pH range of 2–12. Depending on pH of the solution, generated ions produce metal hydroxides and complexes such as $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^{2+}$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$, $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{4+}$ [19]. At lower initial pH, the produced Fe^{2+} at the anode is converted to Fe^{3+} . In contrast, OH^- ions are produced at the cathode, causing increase of pH of solutions. $\text{Fe}(\text{OH})_{n(s)}$ and ferric hydroxyl complexes formed in aqueous solutions can remove dyes by precipitation. The adsorption rate of dyes by those species is lower than precipitation at lower pH because of the protonated functional groups of dye molecules. At higher initial pH, deprotonated functional groups of dyes enable adsorption of dyes on $\text{Fe}(\text{OH})_{n(s)}$ and ferric hydroxyl complexes. Hence dye removal by precipitation is easier at lower pH while both adsorption and precipitation occur at higher pH [20].

The optimum pH must be chosen in order to achieve the best coagulation conditions. During the EC process, hydrogen gas is evolved at the cathode and the rate of reaction depends on the removal of H^+ via H_2 evolution and CO_2 release from aqueous solution owing to H_2 bubble disturbance, causes pH increase [21, 22]. The effect of initial pH on the removal efficiency of both dyes is presented in Fig. 2a. The optimization experiments showed that the maximum removal efficiency reached 87.24% for DB56, 96.07% for BY28 and 98.29% for AV90 from their mixture in solution at pH 6 and total removal for all dyes was 93.66 % for 15 min EC process. The removal percentages are satisfactory. Both of adsorption and precipitation mechanisms proceed during the electrocoagulation at pH 6. Adsorption occurred via deprotonated sulfonate and hydroxyl groups of dyes. Especially, sulfonate groups play important role in adsorption. Total removal efficiency for all dyes decreased due to the absence of more anionic groups of DB56. The total removal efficiency of dyes and energy consumptions is shown in Fig. 2b. At higher pH, removal efficiency decreased because of the

increased electrostatic repulsion between ferric hydroxyl complexes. This interaction limited to adsorption of dyes.

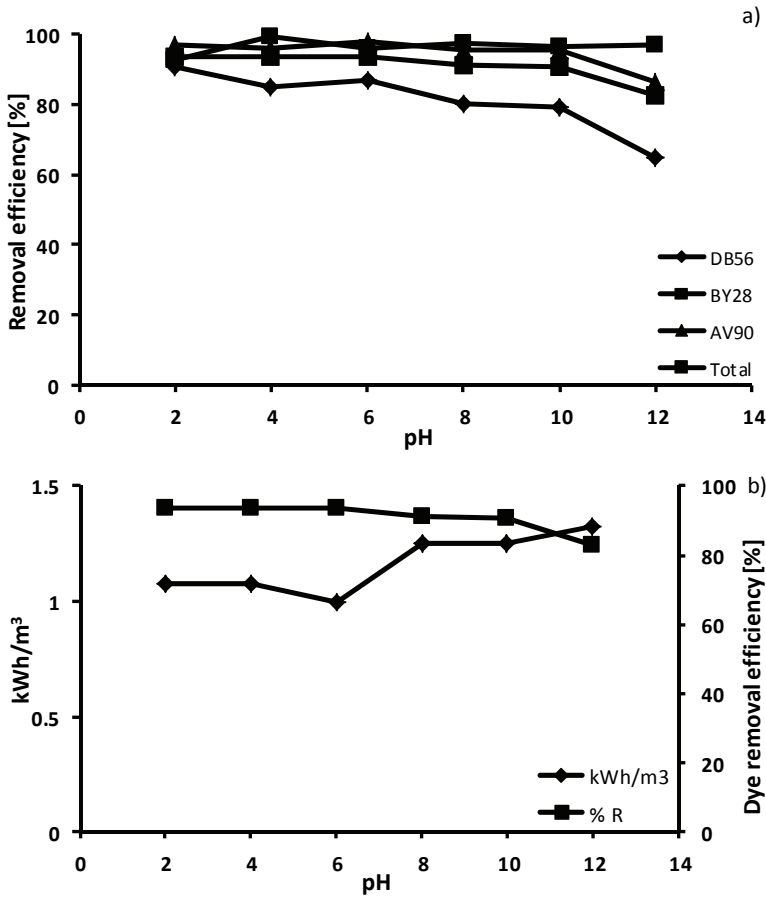


Fig. 2. Effect of initial pH on the removal efficiencies (a) and energy consumption (b), $t = 15$ min, $C_0 = 100$ mg/dm³, $i = 8.66$ mA/cm², $T = 293.15$ K, NaCl = 3000 mg/dm³

Effect of electrolyte concentration on the removal efficiency of EC process. The salt present in solutions affects the current efficiency, cell voltage and consumption of electrical energy because of direct effect to the conductivity. To examine the effects of electrolyte concentration on dye removal and energy consumptions, the conductivity of aqueous solutions was adjusted using NaCl in the range of 1500–3500 mg/dm³ at initial pH 6 and current density of 8.66 mA/cm². The presence of chloride ions in the solution increases iron dissolution in water [23].

Figure 3 shows the effect of electrolyte concentrations on total dye removal and energy consumptions. Removal percentages are between 85.76–87.94% for DB56, 94.02–96.42% for BY28 and 97.13–98.57% for AV90. The calculated energy con-

sumptions are 1.75 kWh/m^3 at 1500 mg/dm^3 , 1.00 kWh/m^3 at 3000 mg/dm^3 and 1.00 kWh/m^3 at 3500 mg/dm^3 . The same results were obtained at 3000 and 3500 mg/dm^3 electrolyte concentration. The increased salt amount decreased to the cell voltage and electricity consumption. The increased salt concentration resulted in decreased electrical energy consumption via increasing solution conductivity and the operating cost includes mainly electrical energy. For the maximum colour removal efficiency and the lowest cost of electrocoagulation process, the determined optimum amount of NaCl was 3000 mg/dm^3 .

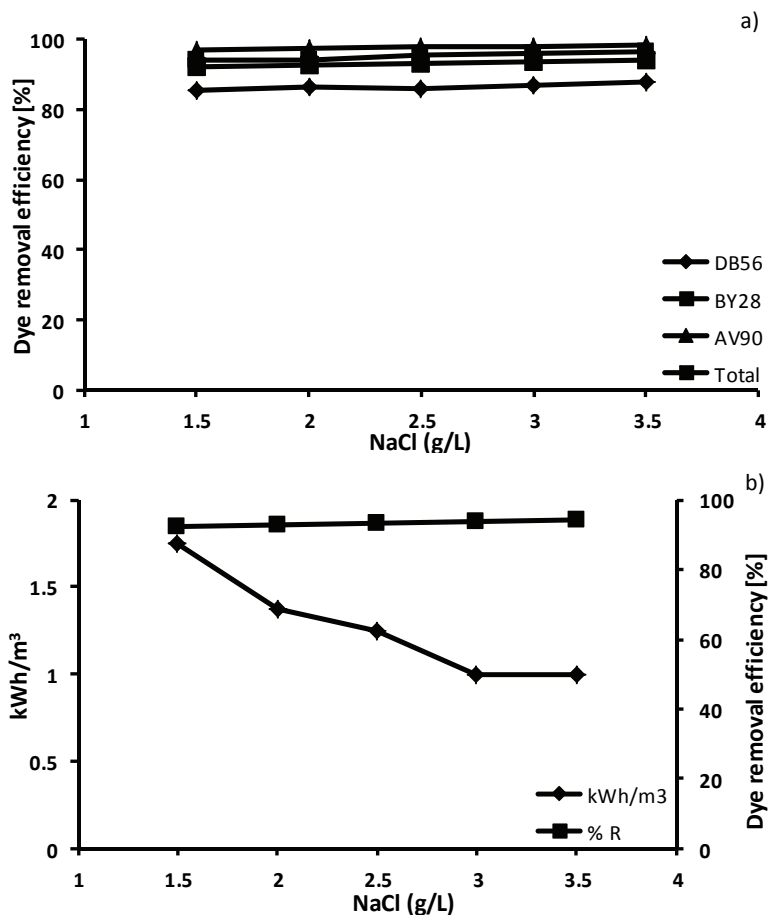


Fig. 3. Effect of salt concentration on the removal efficiencies (a) and energy consumption (b); $t = 15 \text{ min}$, $C_0 = 100 \text{ mg/dm}^3$, $i = 8.66 \text{ mA/cm}^2$, $T = 293.15 \text{ K}$, $\text{pH} = 6$

Effect of current density on the removal efficiency of EC process. The current density determines the coagulant production rate and the size of the bubble production and hence effects their growth [9, 24]. The effect of current density on the efficiency of

colour removal was investigated by carrying out the experiments at various current densities in the range of 4.33–17.32 mA/cm² at pH 6. Figure 4 shows the effect of current density for the total removal of dyes from aqueous solutions of ternary dye mixture and energy consumption. Upon increasing current density, the amount of oxidized iron increased and amounts of metal hydroxide compounds for precipitation and adsorption of the matrix were also increased [25]. The removal efficiency of DB56 increased from 82.29% to 96.25% by increasing the current density from 4.33 mA/cm² to 17.32 mA/cm², 85.23% to 99.81% for BY28 and 98.44% to 98.91% for AV90 and 88.65% to 98.32% for all dyes from their mixture in solution at 15 min electrocoagulation time period. As seen in Fig. 4, increasing current density caused increase in energy consumption. The selected optimum current density was 8.66 mA/cm² due to high energy consumption at higher current densities.

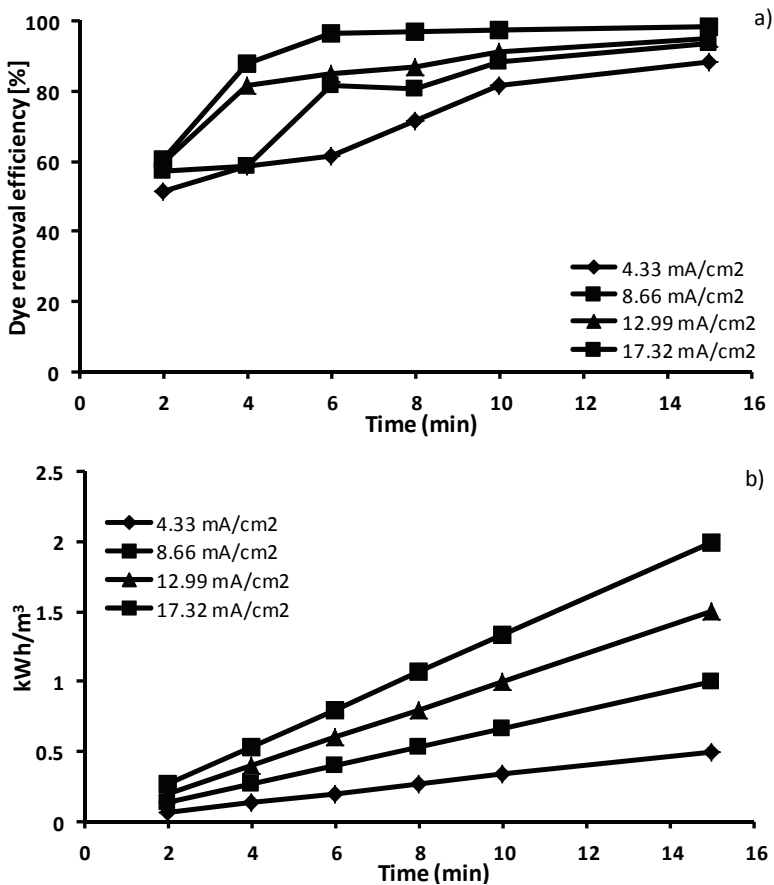


Fig. 4. Effect of current density on the removal efficiencies of total dye (a) and energy consumption (b). $C_0 = 100 \text{ mg/dm}^3$, $T = 293.15 \text{ K}$, $\text{pH} = 6$, $C_{\text{NaCl}} = 3000 \text{ mg/dm}^3$

Effect of electrolysis time on the removal efficiency of the EC process. Electrolysis time influenced the treatment efficiency of the electrochemical process. It determined the production rate of iron ions from electrodes. The efficiency increased upon time due to hydroxyl and iron ion production on the electrodes. The effect of electrolysis time on the efficiency of colour removal was investigated by carrying out the experiments at various times in the range of 2–20 min at pH 6, current density of 8.66 mA/cm^2 , salt concentration of 3000 mg/dm^3 and each dye concentration of 100 mg/dm^3 in the solution.

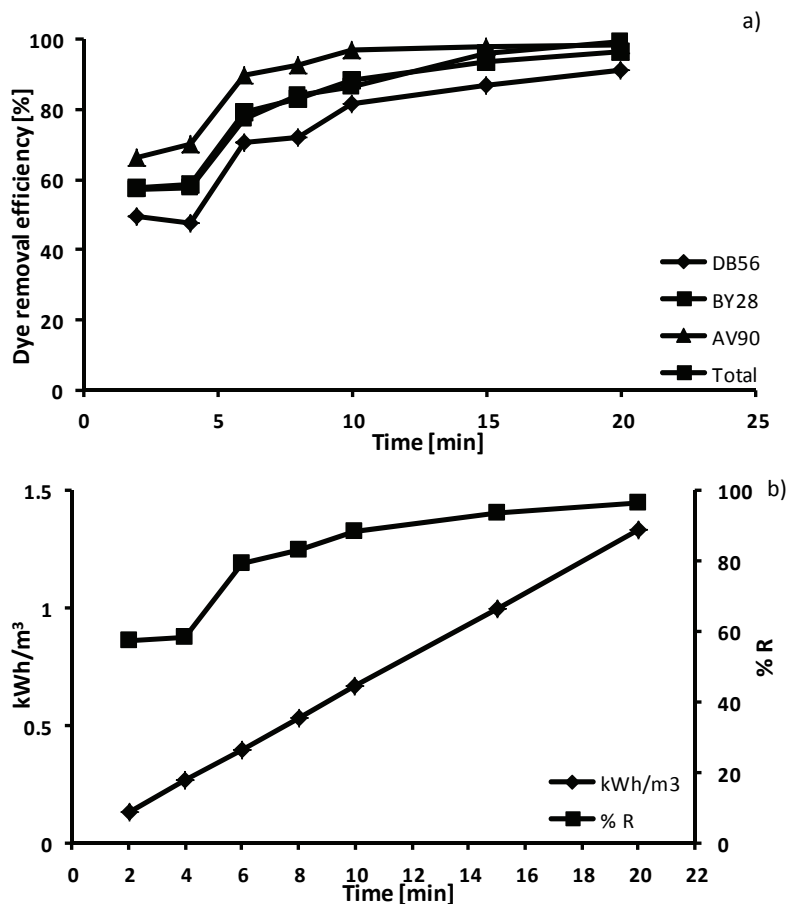


Fig. 5. Effect of electrolysis time on the removal efficiencies (a) and energy consumption (b); $C_0 = 100 \text{ mg/dm}^3$, $i = 8.66 \text{ mA/cm}^2$, $T = 293.15 \text{ K}$, $\text{pH} = 6$, $C_{\text{NaCl}} = 3000 \text{ mg/dm}^3$

Figure 5 shows the effect of time on the total colour removal efficiency of EC process. It increased from 49.48% to 91.37% for DB56, 57.27% to 99.64% for BY28 and 66.14% to 98.32% for AV90 and 57.63% to 96.45% for all dyes from the mixture

by increasing the EC time from 2 to 20 min. $\text{Fe}(\text{OH})_{(n)(s)}$ and ferric hydroxyl complexes production rate increased by enhancing the electrolysis time and caused increase of amounts of adsorbed and precipitated dyes from their mixture in solutions. The optimum time was 15 min for electrocoagulation due to increasing electrical energy consumption with time. Although the differences between the removal percentages of all dyes from the mixture do not differ significantly, the energy consumption increases from 1.00 to 1.33 kWh/m^3 when electrolysis time increases from 15 min to 20 min.

Effect of initial concentration on the removal efficiency of the EC process. The dye solutions were investigated in the range of initial concentrations from 50 to 250 mg/dm^3 . By keeping constant all other parameters, initial dye concentrations were changed and removal efficiencies were calculated.

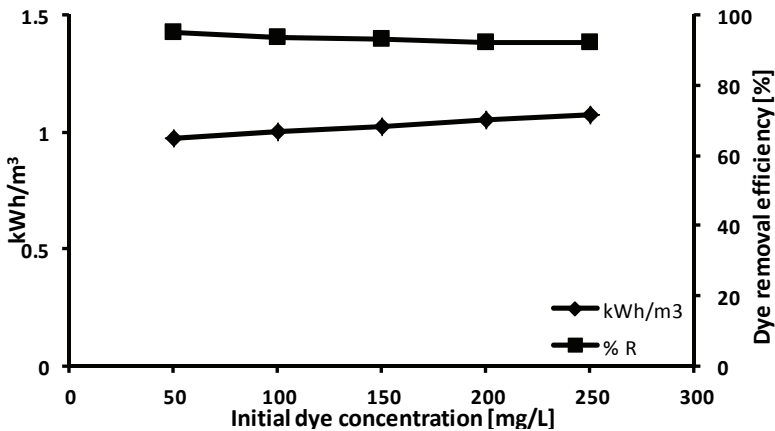


Fig. 6. Effect of initial concentration on the total removal efficiency and energy consumption, $t = 15$ min, $i = 8.66$ mA/cm^2 , $T = 293.15$ K, $\text{pH} = 6$, $C_{\text{NaCl}} = 3000$ mg/dm^3

Figure 6 shows the effect of initial dye concentrations on the total removal efficiencies of dyes and energy consumptions. At low concentration ranges, the removal efficiency was higher than the high initial dye concentrations. The colour removal efficiency decreased from 92.73% to 85.62% for DB56, 94.55% to 94.23% for BY28 and 98.82% to 96.79% for AV90 and 95.37% to 92.22% for all dyes from the mixture due to concentration increase from 50 to 250 mg/dm^3 for each dye. Insufficient production of $\text{Fe}(\text{OH})_{(n)(s)}$ and ferric hydroxyl complexes in the high dye concentrations decreased to the removal efficiency.

COD removal. High levels of COD are generated during dyeing processes employed in textile industries. The COD removal experiments were carried out for the concentration range of each dye of 50–250 mg/dm^3 , initial pH of 6, current density

8.66 mA/cm², concentration of salt 3000 mg/dm³, the distance between the electrodes 2.2 cm, during 15 min electrocoagulation time period.

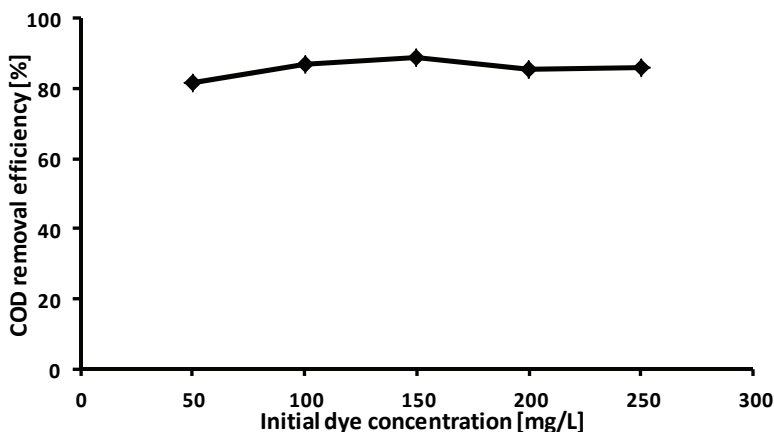


Fig. 7. COD removal efficiency for various dye concentrations

Figure 7 shows the percentages of COD removal with various concentrations. It can be seen that the percentage of COD removal increased from 81.55% to 88.70% in the 50–150 mg/dm³ concentration range and decreased to 85.81% and 86% at concentrations of 200 and 250 mg/dm³ due to insufficient production of Fe(OH)_{n(s)} and ferric hydroxyl complexes.

4. CONCLUSIONS

In the present study, EC has been evaluated for Disperse Blue 56 (DB56), Basic Yellow 28 (BY28) and Acid Violet 90 (AV90) dyes ternary mixture and COD removal from aqueous solutions by the EC process with iron electrodes. Electrocoagulation was employed in the laboratory to the synthetic dye mixtures and remaining dye amounts and COD levels were analyzed. PLS method was used for the calculation of remaining dye amount in the solutions. It enables one to calculate concentration of each dye in the mixture. The effect of various operational parameters on colour removal efficiency was investigated and optimized. Simultaneous removal of all dyes was found to be dependent on the initial pH of the solution, electrolysis time, initial dye concentration, current density and electrolyte concentration. The maximum percentage of colour removal was obtained at pH 6 by precipitation and adsorption. The current density is another important operational parameter for EC process. Although removal efficiency increased after increasing the current density, energy consumption increased as well. The selected current density was 8.66 mA/cm², optimum salt concentration was 3000 mg/dm³. The increased salt concentration decreased cell voltage

and electricity consumption. The colour removal efficiencies for DB56, BY28 and AV90 from the mixture were 87.24%, 96.07% and 98.29%, respectively and total removal for all dyes was 93.66% for initial pH of 6, initial dye concentration of 100 mg/dm³, current density of 8.66 mA/cm², salt concentration of 3000 mg/dm³, electrolysis time of 15 min and distance of 2.2 cm between the electrodes. It can be noticed that high COD removal efficiency of 88.70% was recorded for the dye mixture. The method presented in the paper can be used for the removal of dye mixtures from the wastewaters.

ACKNOWLEDGEMENTS

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