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A New Combination Treatment System of Ozonation and Electrocoagulation for C.I Acid Red 114 Dye Removal from Dyeing Wastewater

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ABSTRACT

In this study, a combined system integrating an ozonation reactor and electrocoagulation (EC) reactor was investigated to remove C.I Acid Red 114 (AR 114) dye in the synthetic dyeing wastewater. The separated EC and ozonation systems were performed as control experiments as well. Hydraulic retention time (HRT) of each system was determined. These systems were operated with 100 mg/L AR 114 dye wastewater at determined optimal conditions. The results showed that colour, dye and CODcr were highly removed by the combined system with only the HRT of 2 min in the ozonation reactor and 0.85 min in the EC reactor. Their average efficiencies were archived up to 93%, 94.25% and 80.6%, respectively. In addition, the energy consumption, volume and mass of waste sludge were evaluated to be low (0.4 kWh/m^3, 30 L/m^3 and 77 g/m^3). When compared between the combined system and the control systems based on the same decolorization performance, the results indicated that the combined system has shorter HRT, less energy consumption than others and less waste sludge generation than the separated EC system.

INTRODUCTION

C.I Acid Red 114 is a red powder belonging to the azo dye group that is widely used in the world to dye wool, silk, jute and leather (US National Toxicology Program 1991). It had clear evidence of carcinogenic activity in animals (rats) and is possibly carcinogenic to humans (US National Toxicology Program 1991, WHO 1993). The removal of AR 114 dye by adsorption, photo-chemical, biological, ozonation and EC methods were studied (Brown et al. 1983, 1987, Laszlo 1994, Revathi et al. 2010, Huynh et al. 2016, Lee et al. 2003, Nikazar et al. 2008, Rajamohan et al. 2013, Thinakaran et al. 2008). The effect of ozonation and electrocoagulation (EC) using aluminum electrodes were studied in the batch operation and archived good results (Huynh et al. 2016).

In some previous studies, the removal efficiencies of ozonation were able to be enhanced by combining with other substances such as H_2O_2, UV, TiO_2 (Rosal et al. 2009, Esplugas et al. 2001, Song et al. 2006). Ozone enhancing the EC with iron electrodes was researched and received better results (Bernal-Martínez et al. 2010, Song et al. 2006, 2007). So, the combination of ozonation and EC using aluminum electrodes may also be a new way in the treatment of dyeing wastewater, but it has not been researched yet.

Hence, in this study, the combined system of ozonation and EC was investigated to remove C.I AR 114 dye in the dyeing wastewater. The hydraulic retention time (HRT) of each reactor was determined. This study not only focused on its efficiency in terms of decolorization and dye degradation, but also investigated the energy consumption and secondary waste sludge. In addition, removal of AR 114 dye by the separated ozonation and EC systems was carried out as well to compare with this combined system.

MATERIALS AND METHODS

Material: The synthetic wastewater was prepared in tap water. The initial dye concentration was 100 mg/L AR 114 dyestuff powder procured from Tokyo Chemical Industry Co. Ltd.

Experimental setup and analytical methods: The combined system and the control systems were set up as Fig. 1.

In the EC system (Fig. 1a), the wastewater was continuously supplied into reaction tank containing a pair of cylindrical aluminum electrodes (ID × H: 95 mm × 550 mm, OD × H: 50 mm × 500 mm) contacted to distribution part. The

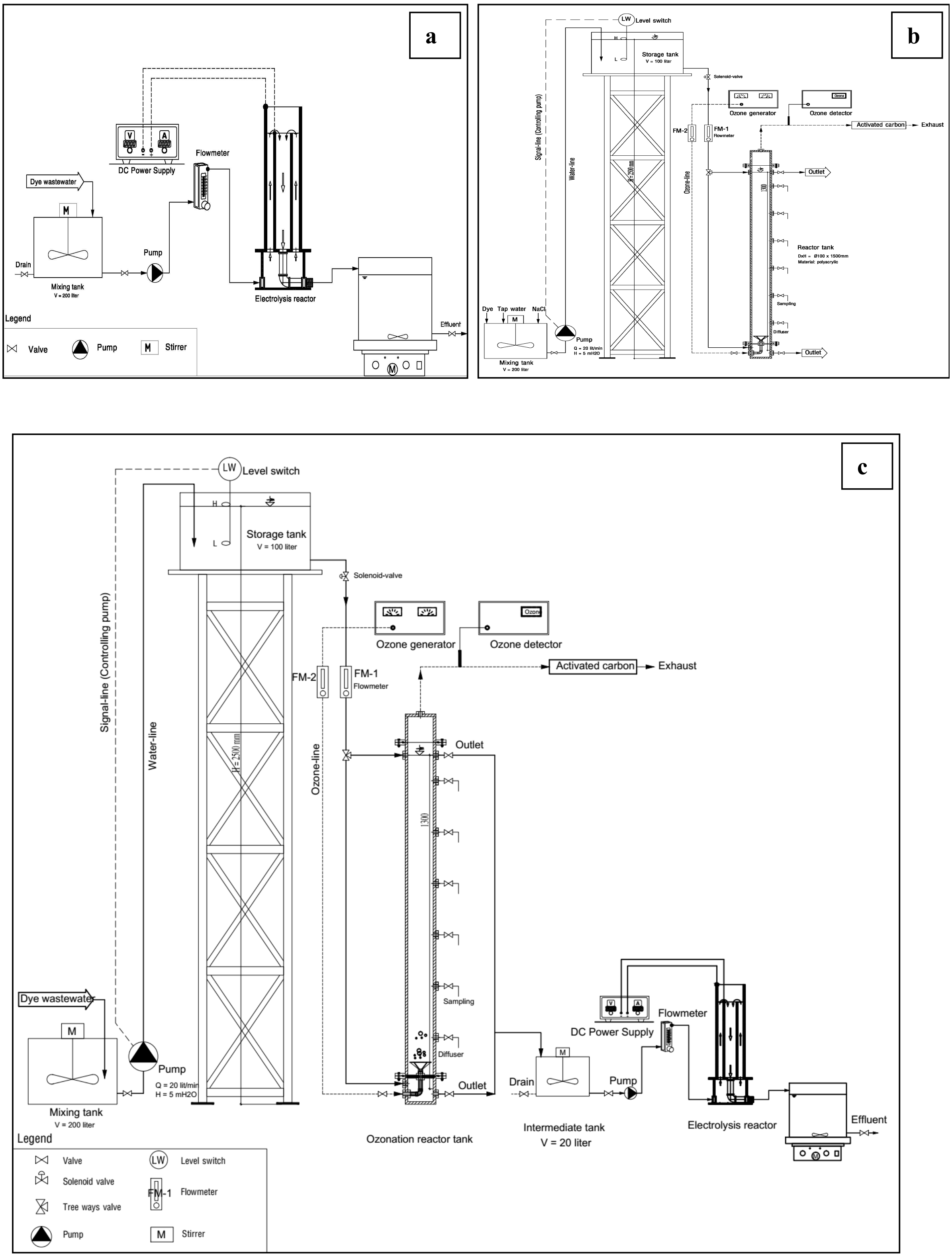

Fig. 1: Schematic diagrams of the EC (a), Ozonation (b) and combined system (c).

experimental EC was performed at the current density of 2.2 mA/cm^2, pH 7, conductivity of 1500 µS/cm (Huynh et al. 2016) and the following HRT variation as 1.278 min; 2.56 min; 5.12 min with respect to flow rate as 2 L/min; 1 L/min and 0.5 L/min, respectively. Treated water was led to a rectangular tank (3.6 L volume) installed with magnetic stirrer operated at 50 rpm to make good condition for flocculation and flotation in 15 min. The generated sludge was separated by settling 90 min and centrifuging 5 min at 400 rpm.

In the ozonation system (Fig. 1b), the wastewater was supplied into the bubble column with counter current and co-current flows. HRT of this reactor was changed from 5 min to 40 min through controlling the liquid flow rate from 0.25 L/min to 2 L/min. Ozone gas was bubbled into reaction column through ceramic diffuser at the bottom with flow rate of 0.7 L/min (Huynh et al. 2016).

In the combined system (Fig. 1c), the wastewater was firstly treated by ozonation with 0.7 L/min ozone gas flow rate. Then, it was passed through the EC reactor with the same operating condition in the EC system. After that, the treated water was mixed in the 3.6 L rectangular tank to enhance the flocculation and flotation.

Samples were taken and analysed for colour, dye concentration, COD, volume and mass of sludge. The dye concentration was measured using the spectrophotometer (DR 2800, USA) from a calibration curve made at the λ_{max} = 500 nm (using DR 2800, HACH, USA) (Huynh et al. 2016). The COD, colour and mass of generated sludge were determined following the Standard Methods for the Examination of Water and Wastewater (APHA, AWWA, WPCF 1995). The volume of sludge was determined by measuring sludge volume after 90 min settling of one litre treated water in the cylinder. The pH value and conductivity were observed by a pH meter (Denver/UB-10, Germany) and conductivity meter (ORION Model 130, Germany), respectively.

Each experiment was repeatedly carried out 3 times, and experimental results were analysed by ANOVA with α = 0.05.

Calculation methodology (Huynh et al. 2016): The removal efficiency was calculated as:

$$E_{ff} = \frac{C_0 - C_t}{C_0} \times 100 \quad ...(1)$$

Where, E_{ff} is the removal efficiency, %. C_0 and C_t are pollutants concentration at initial and t (min) reaction time, respectively.

Energy consumption was determined as energy required for the ozone generator to treat 1 m^3 wastewater:

$$E_{O_3} = \frac{P \times t}{3.6 \times V} \quad ...(2)$$

Where, E_{O_3} is energy consumption for ozonation, Wh/m^3. P is the power (W), t is the reaction time (s) and V is the working volume of reactor (L).

The current density was calculated by the equation:

$$CD = \frac{I}{S} \quad ...(3)$$

Where, CD is the current density, A/m^2. I is the current (A) and S is total surface area of the electrodes (m^2).

Electrical energy consumption by EC process:

$$E_{EC} = \frac{E_{cell} \times I \times t}{3.6 \times V} \quad ...(4)$$

Where, E_{EC} is the energy consumption for EC, Wh/m^3. E_{cell} is the cell potential (V). I is the total current (A). t is the electrolysis time (s). And V is the working volume of reactor (L)

RESULTS AND DISCUSSION

The key operating parameters of the EC, ozonation and the combined system are summarized in Table 1.

The Electrocoagulation System

Fig. 2 shows the treatment performances and the remaining contaminants in the solution after treatment by the EC system corresponding to different HRT. It was observed that the reaction rates in this treatment followed the saturation rate law. With 5.12 min HRT, the colour, dye and COD removal efficiencies were 92.6%, 92.7% and 94.08%, respectively.

Volume and mass of generated sludge rates were observed and determined as linear functions of HRT:

$$V_{sludge} = 21.054\ HRT + 2.0172,\ \text{L/m}^3,\ R^2 = 0.9979 \quad ...(5)$$

$$M_{sludge} = 0.088\ HRT - 0.0094,\ \text{kg/m}^3,\ R^2 = 0.9949 \quad ...(6)$$

Energy consumption observed in this system was also proportional to HRT for all the colour, dye and COD removal:

$$E_{color} = 0.465\ HRT + 0.029,\ \text{Wh/Pt-Co},\ R^2 = 0.999 \quad ...(7)$$

$$E_{dye} = 3.6\ HRT + 0.267,\ \text{Wh/g},\ R^2 = 0.999 \quad ...(8)$$

$$E_{COD} = 4.569\ HRT + 0.271,\ \text{Wh/g},\ R^2 = 0.999 \quad ...(9)$$

The pH increased during the EC process due to OH^- generated at cathode. pH rapidly reached 8.47 with HRT of 1.28 min, after that it slowly augmented when increasing HRT from 1.28 to 2.56 and 5.12 (pH = 8.55 and 8.65, respectively). This result occurred because when pH of solution

Table 1: Summary of key operating parameters in operation of EC, Ozonation and combined systems.

No.	Parameters	Average		
		EC	Ozonation	Combined system
1	Initial dye concentration, mg/L		100 ± 1	
2	COD of effluent flow, mg/L		78 ± 0.5	
3	Colour of effluent flow, Pt-Co		770 ± 10	
4	pH of effluent flow		7 ± 0.2	
5	Electrical conductivity (μS.cm^{-1})		1500 ± 5	
6	Current density (mA m^{-2})	2.2	-	2.2
7	Ozone gas velocity (L.min^{-1})	-	0.7	0.7
8	Ozone gas concentration (mg.L^{-1})	-	64.167	64.167
9	Temperature of wastewater, °C	20.5	20.5	20.5

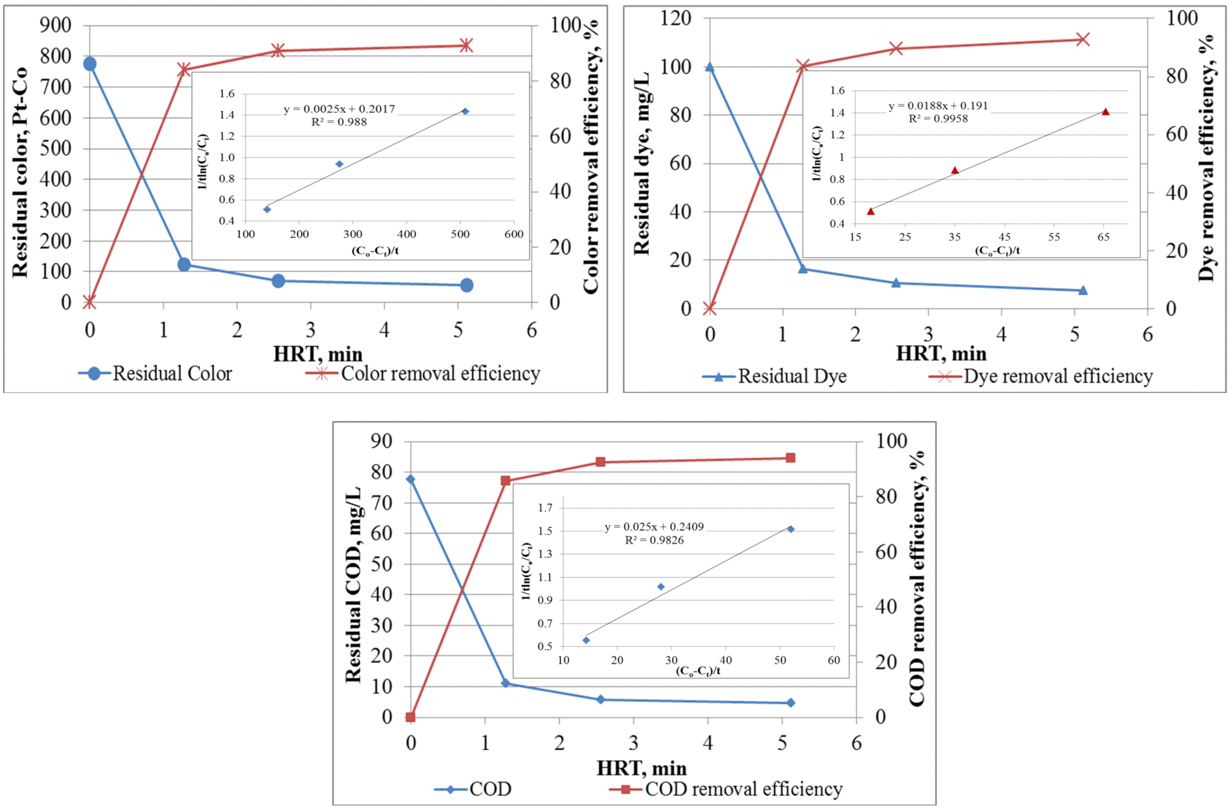

Fig. 2: The treatment efficiency by the electrocoagulation system.

was higher than 8, one Al ion was able to combine with 4 OH^- ions to form $Al(OH)^{4-}$ (Hem & Roberson 1967).

Electrical conductivity in solution reduced from 1500 μS.cm^{-1} to 1400 μS.cm-1 during this process but it was not too much. This result was caused by the adsorption of AR 114 molecules and dissolved ions on Al flocs.

The Ozonation System

The treatment performance by ozonation was assessed in the continuous reactor with co-current and counter current flows. The results are presented in Fig. 3. It shows that ozonation had good effectiveness in the removal of AR 114 dye with both cocurrent and counter flows. Reaction of ozone and AR 114 dye in these cases were near the first order reaction. The removal efficiency by ozonation with counter current flow was slightly higher than the other, but it is not remarkable. With HRT of 40 min, the residual colour, dye concentration and COD were 57 Pt-Co, 4.9 mg/L

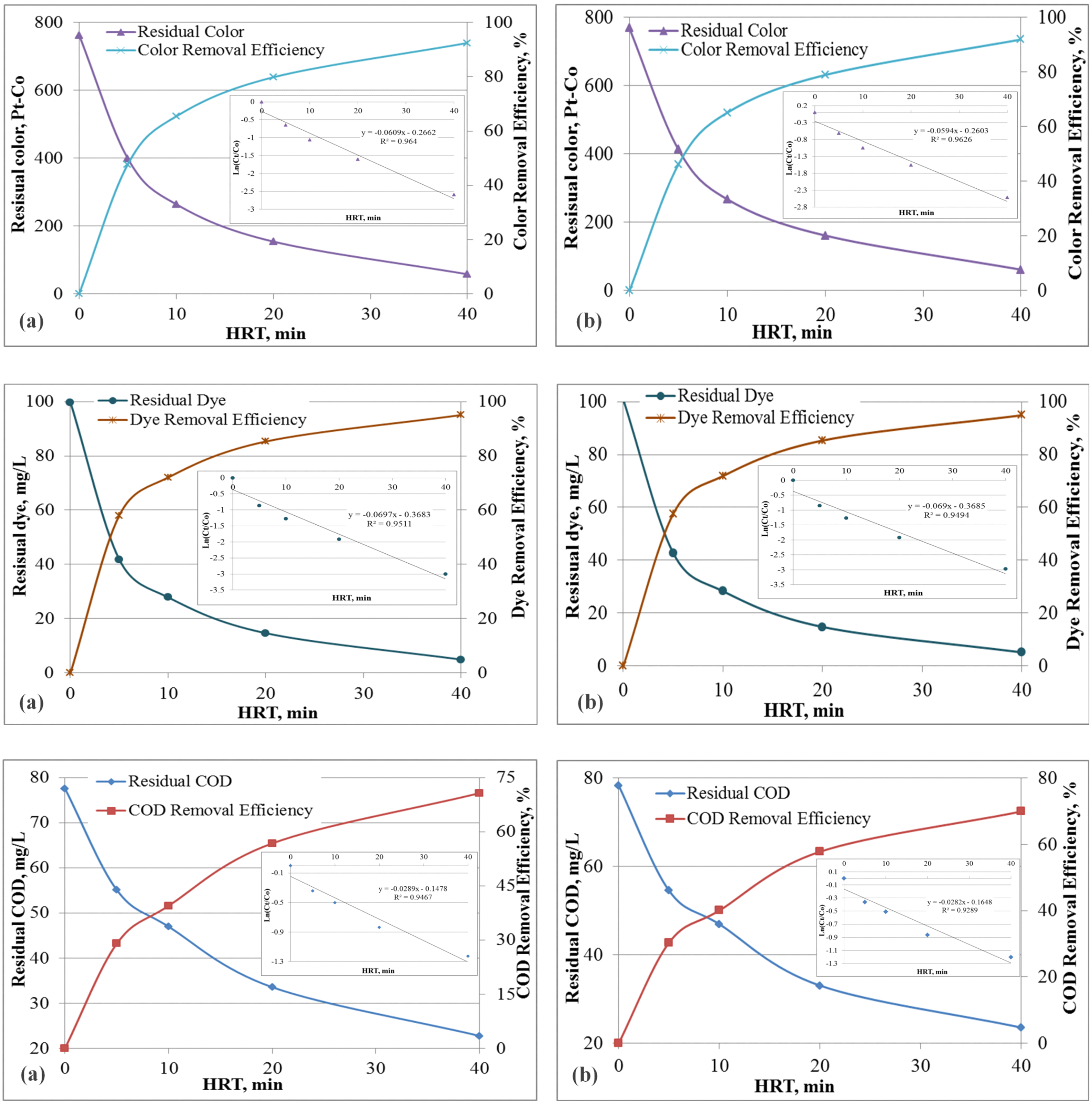

Fig. 3: The removal efficiency by ozonation with counter current (a), cocurrent (b).

and 22.74 mg/L with counter current. The colour, dye and COD removal efficiencies were approximately 92%, 95% and 70%, respectively.

The reaction rate coefficients in counter current and cocurrent cases are equivalent. The pH value decreased during ozonation time due to intermediate products containing acidic groups. In this experimental condition, HRT of 20 min was enough and residual colour, dye and COD were less than 155 Pt-Co, 15 mg/L and 34 mg/L, respectively. It requires about 1066.7 Wh for 1 m^3 wastewater.

The Combined System

Determination of HRT of each reactor: To determine HRT of each reactor in the system, the ozonation process occurred with HRT alternately changed with 2 min, 2.5 min and 3.33 min. After that the treated water was led to the EC reactor with different HRT of 0.85 min, 1.024 min, 1.28 min and 1.7 min. It was then mixed in the mixing tank to en-

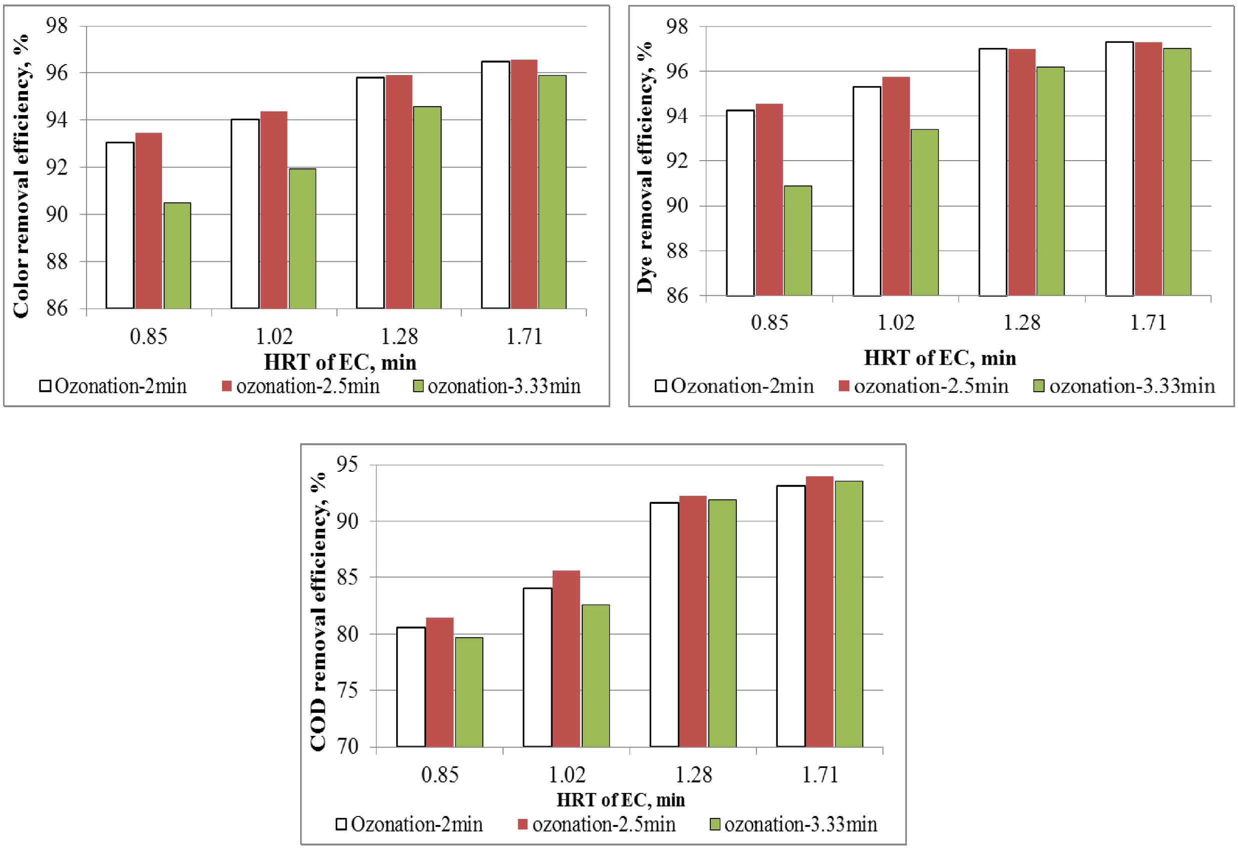

Fig. 4: The colour and dye removal efficiencies by the combined system.

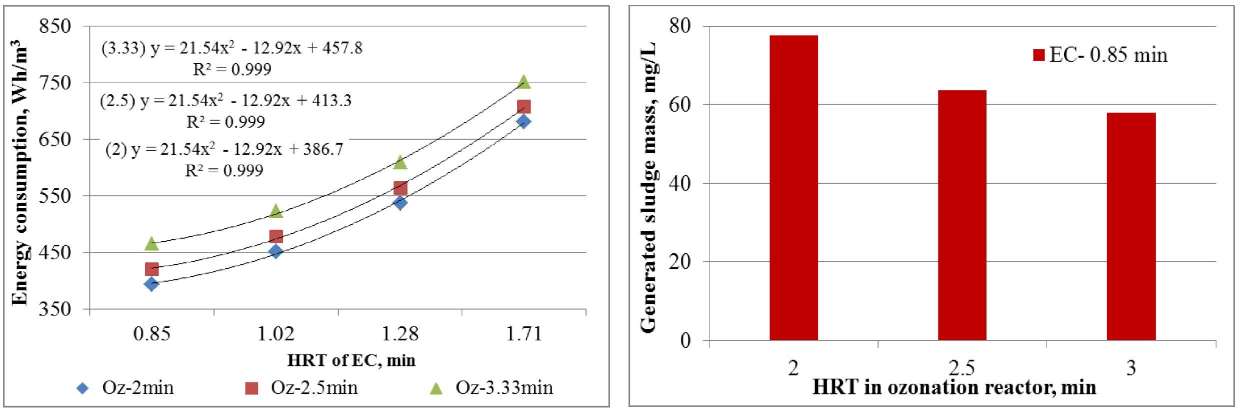

Fig. 5: Energy consumption and mass of generated sludge in the combined system.

hance the flocculation and flotation. The obtained results presented in Fig. 4 showed that the overall removal efficiency of the system with 2.5 min ozonation was higher than other cases, especially, in case of 2.5 min HRT in the ozonation reactor combined with 0.85 min and 1.02 min HRT in the EC reactor. The removal efficiency decreased when HRT was 3.33 min in the ozonation reactor due to dye concentration in the influent of EC reactor was less than other cases. It decreased the flocculation and flotation opportunities in the EC reactor. When increasing HRT in the EC reactor, the different removal performances of the system caused by the change of HRT in the ozonation reactor were

Table 2: Comparisons of the ozonation, EC and combined systems.

Parameters		Ozonation	Electrocoagulation	Combined system
HRT (min)		40	5.12	2 /0.85
Removal efficiency (%)	Colour	92.48	92.64	93.03
	Dye	95.05	92.68	94.25
	COD	70.68	94.08	80.59
Residual contaminants	Colour	57.3	57	56.3
	Dye	4.9	7.3	5.74
	COD	22.74	4.6	15.2
Volume of generated sludge (mL/L)		0	110	30
Mass of generated sludge (g/L)		0	0.4507	0.077
Energy consumption (Wh/m^3)		2133.3	1776.816	393.9

decreased and gradually became equal. Namely, when HRT of the EC reactor rose to 1.71 min, the removal efficiencies of colour, dye and COD were approximately equal for all the cases. These results could be explained as follows: The treatment performance of EC process in the combined system was very high. It was able to fill the difference between the removal efficiencies of the ozonation treatment caused by the change of HRT. However, increasing HRT of the EC reactor led to the rising of energy consumption and the increasing of sludge production. It means that the system will get the higher operating costs and the higher treatment cost of secondary waste sludge. In this combined system, HRT of 2 min or 2.5 min in ozonation reactor and HRT of 0.85 - 1 min in EC reactor were too enough for treatment of 100 mg/L Acid Red 114 dye wastewater.

Correlation of HRT in each reactor with the energy consumption and the secondary waste sludge are presented in Fig. 5.

The removal efficiency by the combined system: In this study, the combined system had impressive results. As seen in Fig. 4, the removal efficiency reached 93%, 94.25% and 80.6% respectively for colour, dye and COD treatment with only 2 min reaction time in the ozonation reactor and 0.85 min in the EC reactor. The remaining of colour, dye concentration and COD were 56.3 Pt-Co, 5.7 mg/L and 15.2 mg/L, respectively. The energy consumption in this system was calculated as total energy requirement for ozone generator and EC process. With 2 min in ozonation and 0.85 min in EC reactor, energy consumption was 393.9 Wh/m^3. Volume and mass of the generated sludge were 30 mL/L and 77 mg/L, respectively.

Comparison of the combined system, the ozonation and EC systems: Comparison of these systems is based on the parameters such as HRT, the removal efficiency, energy consumption, and volume and mass of the generated sludge. The colour removal efficiency was chosen as standard of comparisons. With the same colour removal efficiency, approximately 92%, the other criteria were compared and summarized in Table 2. The results showed that the combined system had remarkable achievements when compared with the others such as:

- HRT in the combined system was too much less than the others. It is nearly equal to one-fourteen HRT of the ozonation system and a half of HRT of the EC system. With the same colour removal efficiency (92%), the ozonation system needed 40 min reaction time, the EC system needed 5.12 min, whereas the combined system needed only 2 min in ozonation and 0.85 min in EC reactor. It has especially meaning when it will be applied in real condition because the area and construction costs requirements will be significantly reduced.
- The combined system could enhance 10% COD removal performance when compared with the ozonation system.
- Volume and mass of the generated sludge in the combined system were too much less than in the EC system (30 mL/L and 77 mg/L instead of 110 mL/L and 450.7 mg/L in the EC system). It is an impressive advantage of this combined system. It helps to reduce the treatment cost of waste sludge. It also matches the development trends of wastewater treatment technology as it is reducing or approaching no secondary waste.
- Energy consumption by the combined system was 393.9 Wh/m^3, nearly equal to 1/4.5 and 1/5.4 energy consumption in the EC and ozonation systems, respectively.

CONCLUSIONS

The combination of ozonation and EC in treatment system had more effectiveness on removal of AR 114 dye than the others. The advantages of ozonation and EC were accumulated in this combined system and mutually supported to improve their disadvantages. The combined system not only had high removal efficiency, but also it could reduce HRT, energy consumption and generated waste sludge. This study introduced a new way for dyeing wastewater treatment that suit to the developing trend in wastewater treatment technology.

The next step is the study on removal of some different dye stuffs by this combined system to get more design and operating information. The authors believe that this combined system will also have good results on other dye stuff treatment. In addition, scaling up this combined system to pilot and test with real dyeing wastewater or other wastewaters is needed to continuously develop and apply this study in wastewater treatment.

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