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Removal of C.I. Acid Red 114 Dye from Wastewater by Using Ozonation and Electrocoagulation

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Abstract

This study was performed to investigate the removal ability of dyeing wastewater containing C.I. Acid Red 114 by ozonation and electrocoagulation in batch mode. In ozonation, the effects of some parameters: ozone gas flowrate, pH, temperature and initial dye concentration on color, dye and COD removal efficiencies were evaluated. And the gas holdup by ozone gas, volumetric mass transfer coefficient of ozone, enhancement factor and energy consumption were determined. In electrocoagulation, the effects of current density, initial dye concentration, pH and conductivity on color, dye and COD removal efficiencies were determined. Energy consumption and sludge production were evaluated. The results showed that the removal efficiencies of color and dye were higher than 95% with 50 min ozonation and 90% with 20 min electrocoagulation. The COD removal efficiencies were 79% and 89.3% in ozonation and electrocoagulation, respectively. In ozonation, the removal efficiency was affected by the ozone gas flow rate, pH, temperature and initial dye concentration. And in electrocoagulation, the treatment performance was significantly affected by current density and initial dye concentration. Ozonation consumed more energy than electrocoagulation, but it produces no sludge. Both methods are feasible for application in the treatment of dyeing wastewater containing C.I. Acid Red 114.

Keywords: C.I. Acid Red 114; Electrocoagulation; Dyeing Wastewater; Aluminum Electrode; Ozonation

Introduction

The dyeing wastewater is the most serious pollution in textile industry because it not only affects the receiving environment but also strongly affects the heath of humans and animals due to large amounts of wastewater containing the highly colourful, toxic, carcinogenic dyes and their breakdown products [1-3]. Therefore, the removal of dyes in such wastewater is always concerned. C.I. Acid Red 114 (AR114) dye is evaluated as a carcinogen to humans and animals [4]. In previous studies, the AR114 dye was treated by the adsorption [5-7], biological [8-10] and photochemical oxidation methods [11, 12]. Although these methods had high removal efficiency, there are still some limitations as: long treatment time, difficult to operate, produce a large amount of secondary solid waste and high operating cost. In addition, these methods do not suit the high capacity treatment and high pollution wastewater. Therefore, we need to find out other methods that can overcome these disadvantages.

Ozone can decompose the aromatic rings of some textile dyes, azo dyes and other organic pollutants in the wastewater. The advantages include the absence of increasing volume of wastewater and the secondary waste generation [13, 14].

In recent years, many studies showed that the electrocoagulation (EC) using of aluminum and/or iron electrodes can remove various types of dye. Most studies indicated that the color removal efficiency was high, from 83% to 100% [15-25]. More noticeable advantages of this technology, including less sludge generation and good adaptation to different volume and pollution loads wastewater.

In this study, ozonation and EC methods were investigated to remove AR114 (C37H28N4O10S3.2Na) in the dyeing wastewater with batch operating mode. The effect of operating parameters in ozonation and EC were deterninated. Gas holdup, volumetric mass transfer coefficient, enhancement factor, reaction rate and energy consumption were determined in ozonation treatment. In EC, reaction rate, energy consumption and sludge production were evaluated as well.

Materials and Methods

Material

The synthetic wastewater was prepared by dissolving AR114 dyestuff powder (purchased from Chemical Industry Co. Ltd., Tokyo, Japan) into the tap water. To same as the characteristics of actual wastewater, pH and electrical conductivity were controlled by NaOH/H_2SO_4 and NaCl (Samchun Pure Chemical Co., Ltd., South Korea), respectively.

Experimental Procedures

In the ozonation process, the bubble column reactor made of polyacrylic having a working volume of 10 liters. A ceramic diffuser (ø60 mm) was installed at the bottom of reactor. Gaseous zone was supplied into bubble column by an ozone generator PC – 57 (Ozonetech Co., Ltd, Korea) that can adjust ozone gas flow rate by flow meter.

The gaseous and soluble ozone concentrations were monitored. Schematic diagram of the ozonation process was set up as Figure 1.

In the EC process, 2.5 liters of the wastewater was supplied into a polyacrylic reaction tank containing a pair of aluminum cylindrical electrodes. The dimensions of electrodes are OD: ID: H = 50 mm: 95 mm: 100 mm. The gap between the electrodes is 2.25 cm. The total geometric surface area is 455.3 cm^2. The electrical current was directly supplied from a laboratory DC power supply (SC15-30A, Sunchang Electronic Co.,Ltd., South Korea). The 15 mL sample was taken and removal of deposited sludge by settling 90 min and centrifuging at 400 rpm for 5 min. Schematic diagram of electrocoagulation process was set up as Figure 2.

The dye concentration was measured by a spectrophotometer (DR 2800, USA) with a calibration curve made at λ = 500 nm. Color, COD and mass of sludge were determined according to the Standard Method [26]. Removal rate based on volume of generated sludge (L) was evaluated by settling 1 liter treated water in cylinder in 90 min. The pH values, temperature and conductivity were measured by using the pH meter (Denver/UB-10, Germany), Okaya Handy Thermo (T200, Japan) and conductivity meter (Orion Model 130, Germany), respectively. Each experiment was repeated 3 times and the collected data was analyzed by ANOVA with α = 0.05.

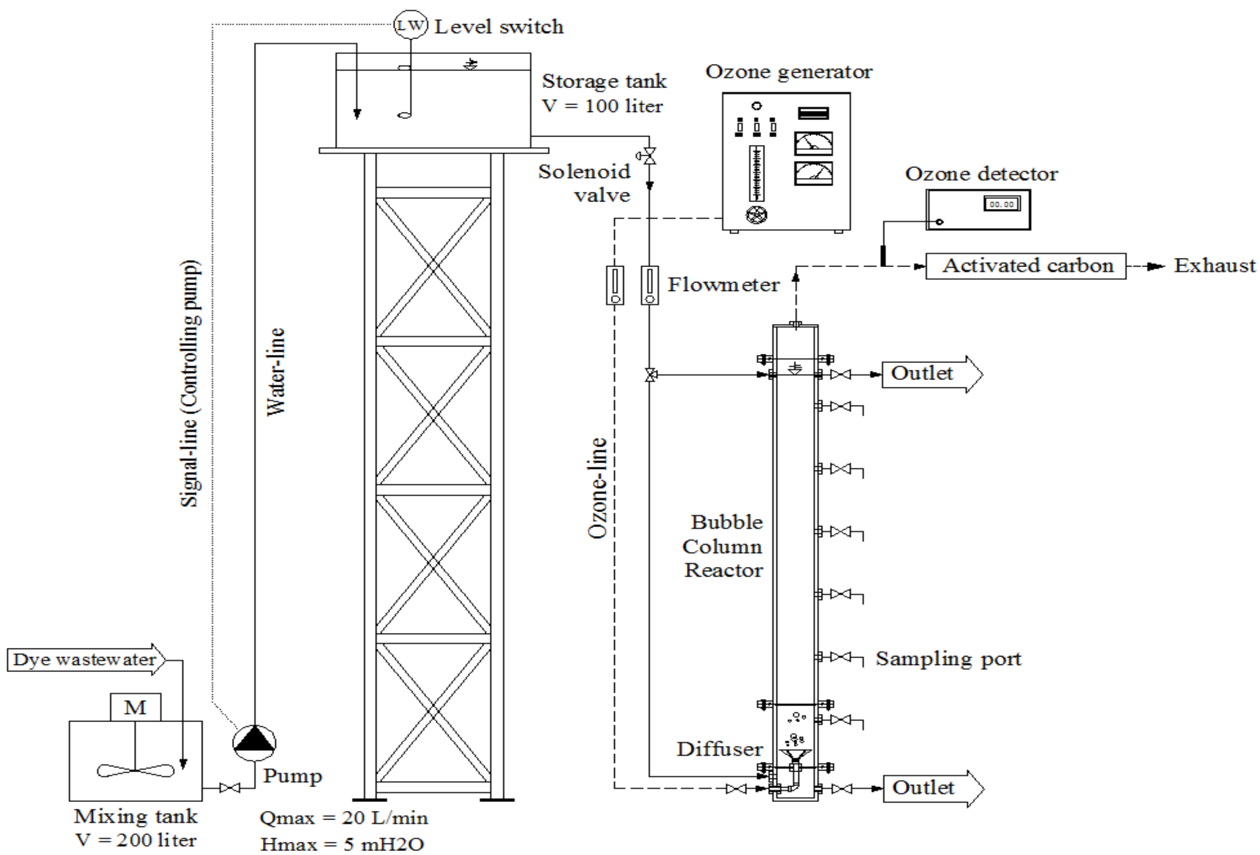

Figure 1. Schematic diagram of ozonation.

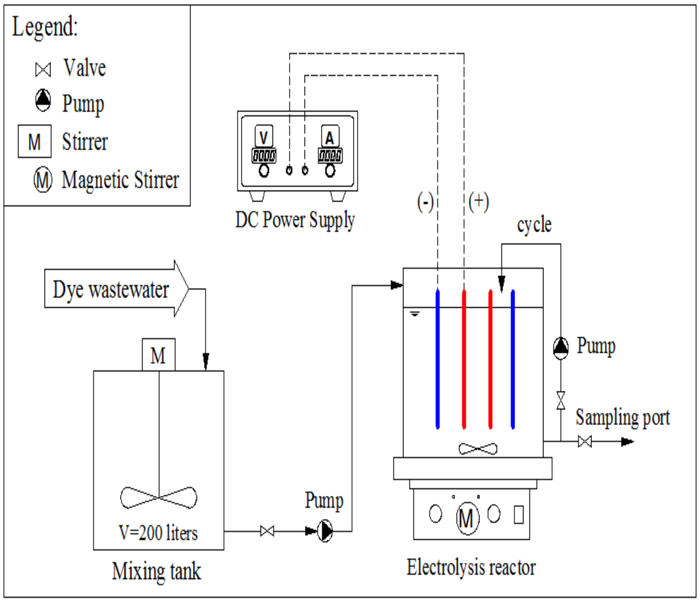

Figure 2. Schematic diagram of electrocoagulation.

Calculation of experimental parameters methods

The removal efficiency was calculated as function

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

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

Ozonation

Ozone volumetric mass transfer coefficient (k_La)

At low pressure, ozone is assumed as ideal gas. Partial pressure of ozone (P_{O_3}) can be calculated as function

$$P_{O_3} = \frac{[O_3]_g \times R \times T}{M_{O_3}} \quad (2)$$

$[O_3]$g is O_3 concentration in the inlet gas flow (g/L). R is the gas constant. T is temperature (K). And M_{03} is molecular mass of O_3 (g).

Equilibrium ozone concentration (C^*_{03}) in water can be used Henry's law

$$C^*_{O_3} = \frac{55.56 \times P_{O_3}}{H_e} \quad (3)$$

Henry's constant (*He*) was calculated by [27]:

$$He(atm/mol/mol) = 3.84 \times 10^7 \times \left(10^{pH-14}\right)^{0.035} \times \exp\left(-\frac{2428}{T}\right) \quad (4)$$

If assumed that ozone decomposition is neglected, the volumetric mass transfer coefficient can be determined by graphical analysis when plot $\ln\left(\frac{C^*_{O_3} - C_t}{C^*_{O_3}}\right)$ versus time t, slope is $-k_La$ [28] with C_t is ozone concentration in liquid at time *t*.

Gas holdup

The expansion method was used to measure the gas holdup in this study. Gas holdup was calculated by [27]

$$\varepsilon_g = \frac{\Delta h}{H + \Delta h} \quad (5)$$

Where: εg is the gas holdup. H is the height of water level before bubbling (m). Δh is the height difference (m).

Enhancement factor

In irreversible reaction of absorbed ozone with the dye solution, the ozone adsorption rate can be expressed by equation $N_A a = k_L a \times C^*_A \times E$ with E is the enhancement factor. The E factor can be determined from practical data by this expression [29].

$$E_{pr} = \frac{(n_i - n_0) \times Q_g}{k_L \times a \times C^*_{O_3} \times V} \quad (6)$$

Where: E_{pr} is the practical enhancement factor. n_i and n_o are the ozone concentration in the inlet and outlet gas flows (mg/L). Q_g is gas flow rate (L/min). V is the liquid volume (L).

Energy consumption in ozonation

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

$$E_{O_3} = \frac{P \times t}{3.6 \times V} \quad (7)$$

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

Electrocoagulation

The current density was calculated through the equation [18]:

$$CD = \frac{I}{S} \quad (8)$$

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

Electrical energy consumption [21, 30]:

$$E_{EC} = \frac{E_{cell} \times I \times t}{3.6 \times V} \quad (9)$$

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

Results and discussion

Ozonation

Gas holdup, mass transfer coefficient and enhancement factor

In this study, the ozone gas holdup was determined with the ozone gas flow rate range of 0.3 ~ 1.1 L/min (gas velocity range of 0.106 ~ 0.39 m/s, in a range of homogeneous regime) [31]. The ozone gas holdup was a linear function of the ozone gas flow rate (Figure 3).

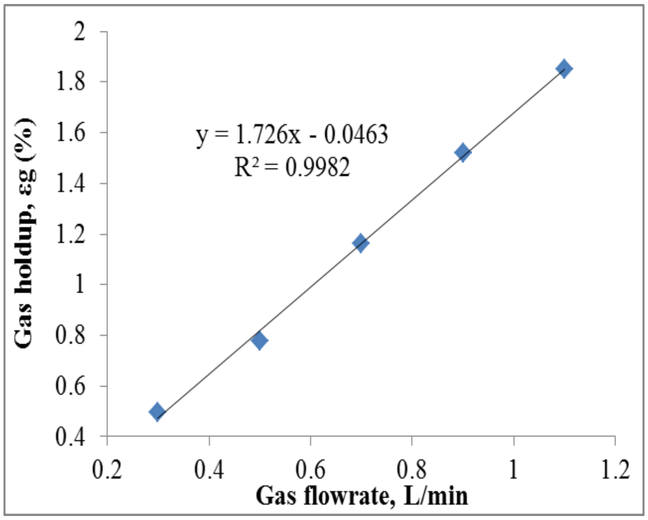

Figure 3. Gas holdup as a function of gas flowrate with initial Acid Red 114 dye concentration of 100 mg/L, pH 7, average temperature of 16.5 degree Celsius, conductivity of 1500 µS/cm.

In the bubble reactor, mass transfer parameters are important. The volumetric mass transfer coefficient is the key parameter in the characterization and design of reactor [31]. In this study, it was determined by experimental data as guided by Stanley [28]. These experiments were carried out with tap water, at pH 7 and temperature of 14.3°C. The k_La was $0.021s^{-1}$ with assumed that ozone auto decomposition was negligible.

The practical enhancement factor (E_{pr}), the ratio of the absorption rate with and without the reaction the same process conditions, was determined by experimental data according to Eq. 6. Experiments were performed with the synthetic wastewater containing 100 mg/L AR114 dye, the gas flow rate of 0.7 L/min, pH 7, temperature of 14 ~ 15°C. The practical E factors decreased from 10.93 to 10.22 during 30 min reaction time due to the reduction of dye concentration in the liquid phase.

Effect of ozone gas flow rate

Decolorization ability and treatment of dye, COD by ozonation were evaluated with the ozone gas flowrate in a range of 0.3 L/min ~ 0.9 L/min. The results of ANOVA analysis showed that the ozone gas flow rate had a significant effect on the removal efficiencies. AR114 dye was destroyed the best at the flow rate 0.7 L/min. When increasing the ozone gas flow rate in a range of 0.3 ~ 0.7 L/min, the removal efficiencies increased due to ascending of intersurface area between ozone bubbles and wastewater. However, the ozone gas flow rate increased to 0.9 L/min, the removal efficiencies slightly decreased. Although the gas holdup was higher, the bigger bubble size and the faster velocity of ozone bubbles led to reducing the contact time between ozone bubbles with pollutants.

Effect of pH

pH value may affect the AR114 removal efficiency by ozonation. In alkaline medium, the ozone decomposition generates radical species that are stronger oxidants and may improve the removal rate [14, 32-34]. For example, according to Kusvuran et al. [32], the color removal efficiency of Basic Yellow 28, Reactive Black 5 and Reactive Red 198 dye were strongly affected by changes of pH value in a range of 3~10. The decolorization of Basic Yellow 28 decreased from 90% to 50% when increasing pH value from 3 to 10. However, with Reactive Black 5 and Reactive Red 198, pH 10 was optimal. In study of Tizaoui et al. [14], the pH value also had significant effect on the decolorization efficiency in the treatment of RO16 dye by the ozonation process when increased pH from 7 to 11. The removal percentage was 86% at all pH in a range of 2~7 and 95% at pH 11. However, in the study of Tehrani-Bagha et al. [33], the rate of decolorization of organic dye in the colored textile wastewater in alkaline condition was almost same as neutral and acidic mediums. Thus, it needs to be checked the effect of pH value on the AR114 dye removal. In this study, the changes of pH values (4, 7, 10) remarkably affected the treatment performance by ozonation. The removal efficiencies of color, dye, and COD increased when pH increased from 4 to 10. In acidic, ozone was the dominant reactant and interested in reaction with dye molecules more than intermediate products. In other hand, ozone was decomposed to form the radical species at alkaline high that prioritized to react with intermediate products more than dye molecules [14]. In this case, after ozone decomposed dye molecules into intermediate products which were rapidly degraded by radical species. Therefore, the removal efficiencies in alkaline was higher than in acidic.

Effect of temperature

Temperature is also an important factor that affects the reaction rate and ozone solubility. Temperature is especially concerned in countries, where have much fluctuations of temperature between seasons. In this research, the effect of temperature in a range of 10 ~ 30°C was investigated. Increasing of temperature led to slightly increasing the treatment performances that were less than 5%. So, it can be ignored in the practical condition to make operating easier. This result may be explained as following: rising temperature drags on the increase of reaction rate between ozone and pollutants. But, simultaneously, it makes a reduction of dissolved ozone concentration in solution and surface tension that can cause bigger bubbles formation and faster velocity of bubbles. The total contact surface and contact time between ozone bubbles and liquid phases are reduced. Thus, finally total removal efficiency increased but not too much.

Effect of initial dye concentration

The initial dye concentration plays a significant role in treatment by ozone [14, 35, 36]. In this study, the different initial concentration wastewater samples were investigated (100 mg/L, 80 mg/L, 60 mg/L and 40 mg/L). The initial concentration of AR114 dye had a significant effect on the removal efficiencies. The removal efficiencies decreased with the higher initial dye concentration because of increasing demand of ozone consumption. The results showed that the influence of concentration of dye increased to 20 mg/L, lead to 9%, 7% and 3 % removal efficiency of color, dye and COD, respectively.

The removal efficiency by ozonation

To determine the treatment efficiency of synthetic wastewater containing AR114 dye treatment by ozonation, the experiment was performed by supplying ozone with ozone gas flowrate of 0.7 L/min, and maintained the initial conditions at pH~7, concentration of dye about 100 mg/L and reaction time about 50 min.

The observed data is depicted in Figure. 4. Reaction rate was highest at the first 5 min. After that it was diminutival follow the increasing of reaction time. The remaining of color, dye and COD in treated wastewater were 32 Pt-Co, 2.5 mg/L and 16.4 mg/L, with 50 min ozonation. The color, dye and COD removal efficiency reached 95.9%, 97.5% and 79%, respectively. The energy consumption was evaluated about 2666.7 Wh/m^3 for 50 min ozonation. Reaction of ozone and AR114 dye followed the first-order rate law. This result is similar with previous studies on ozonation [13, 35, 36]. pH value decreased during ozonation due to intermediate products have acidic groups.

Electrocoagulation

Effect of pH

pH value may have a positive or negative effect on the removal efficiency in EC treatment depending on particular pollutant [21]. Desired pH value of wastewater samples was adjusted before electrical current supply. In the experiments, pH of 4, 6 and 8 were used. The results of ANOVA analysis indicated that pH insignificantly affected the color, dye and COD removal efficiencies. In case of pH 4, the removal efficiency of color, was slightly higher than others in the first 10 min and equal when increasing reaction time. The dye and COD removal are shown the same trend as well. It may be caused by in this case, pH of solutions rapidly increases in the first 10 min of electrolysis and in a range of 5~7 that is the optimal for $Al(OH)_3$ formation with aluminum ions (Figure. 5) [37]. In addition, the concentration of CO_3^{2-}, HCO_3- was decreased in the acidic medium. So the removal efficiency was enhanced by generating .OH via oxidation process [36, 38- 41]. After 10 min reaction time, pH of solution increased over 7.5, and was nearly equal with pH value of the other samples. So, the removal efficiency of all samples was not much different. So it is no need to control pH before treating by EC that reduces the operating cost and makes the operation easier.

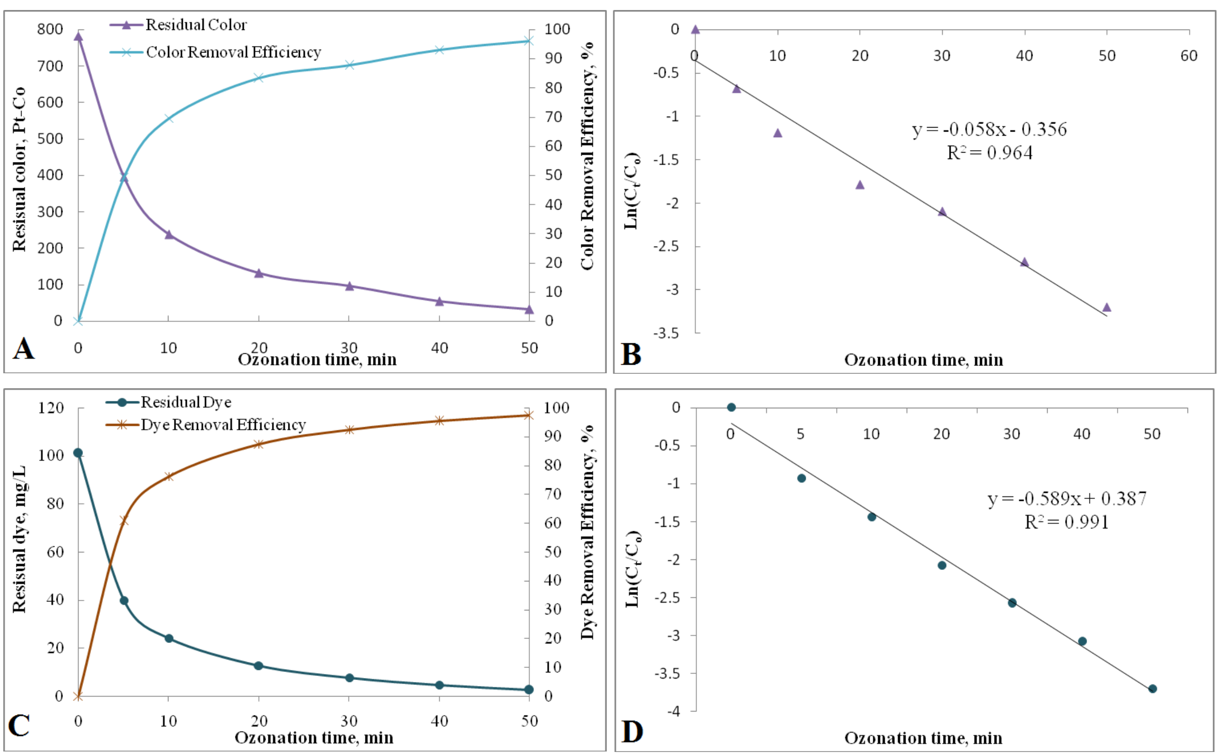

Figure 4. Residual color and color removal efficiency by ozonation (A) and color removal rate by ozone (B). Residual AR114 dye and dye removal efficiency by ozonation (C) and reaction rate between AR114 dye with ozone (D), with initial AR114 dye concentration of 100 mg/L, ozone gas flowrate of 0.7 L/min, pH 7, reaction time 50 min.

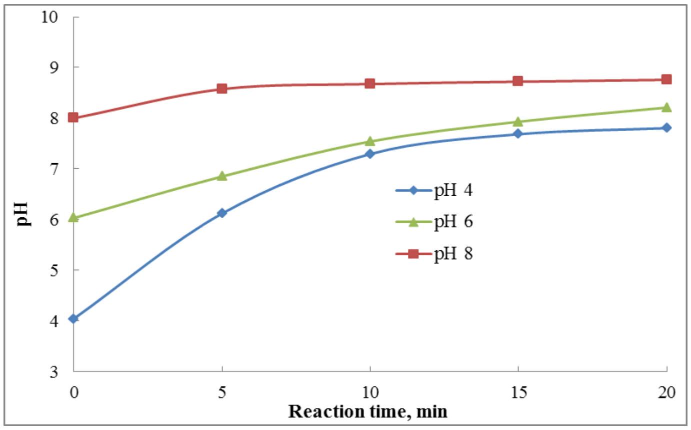

Figure 5. Variation of pH during with different initial pH values in Electrocoagulation, initial AR114 dye concentration of 100 mg/L, current density 2.2 mA/cm^2, conductivity of 1500 µS/cm.

Effect of current density

It is well known that the applied current density directly affects the removal efficiency and energy consumption in the EC treatment. In this study, the current density was changed in a range of 1.1 ~ 4.4 mA/cm^2. The result indicated that increasing the current density improved the removal efficiency of color, dye and COD. The result was as the same with one in studies of Daneshvar et al. [18] and Kobya et al. [42]. Remarkable removal efficiencies increased when the current density ascended from 1.1 ~ 2.2 mA/cm^2 and slightly increased if the current density increased from 2.2 ~ 4.4 mA/cm^2. Namely, the color, dye and COD removal efficiencies increased from 75.8%, 68.7% and 77.1% to 82%, 79% and 86%, respectively with 5 min reaction time when increasing current density from 1.1 mA/cm^2 to 2.2 mA/cm^2.

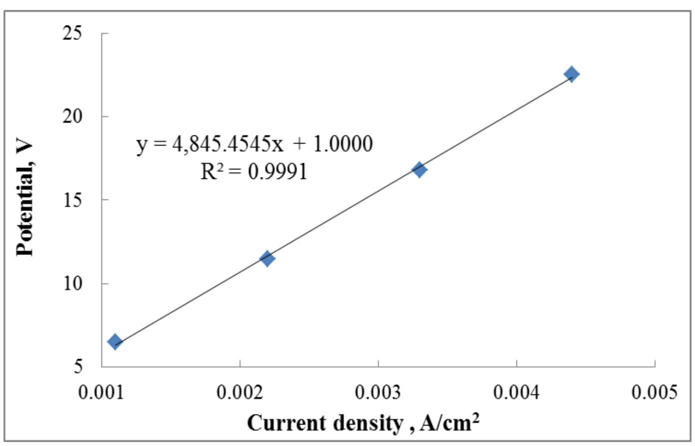

Figure 6. Potential as a function of current density with conductivity of 1500 µS/cm, pH 7.

Whereas, the color, dye and COD removal efficiencies were 86%, 83% and 87.8% in case of 4.4 mA/cm^2. Increasing current density enhanced the treatment performance due to an increase in generated aluminum ion and flocs formation. However, when increasing current density, will lead to rise the applied potential (V) as well. The applied voltage was a linear function of the applied current density, Figure. 6. The voltage increase is synonymous with rising in energy costs. Therefore, we need to limit the current density to get suitable operating costs and avoid heat generation [43]. With this treatment condition, the applied current density of 2.2 mA/cm^2 was reasonable.

Effect of conductivity

The conductivity is an important parameter in EC treatment [21]. It may affect the treatment performance via oxidation by generated OCl-, HOCl on anode [38]. In this study, conductivity was various at 1500 µS/cm, 2000 µS/cm and 2500 µS/cm. Although the results showed that the removal efficiency of color, dye and COD in with conductivity of 2500 µS/cm was slightly higher than the others, ANOVA analysis results indicated that the variation of conductivity did not significantly affect the treatment performance for all color, dye and COD removals.

However, the conductivity could affect the energy consumption. In the experiments, increasing the conductivity of wastewater by NaCl and then supplying a fixed current density, the supplied potential (V) proportionally decreased as seen Figure. 7 below. Thus, the higher conductivity gives, the lower energy consumption is.

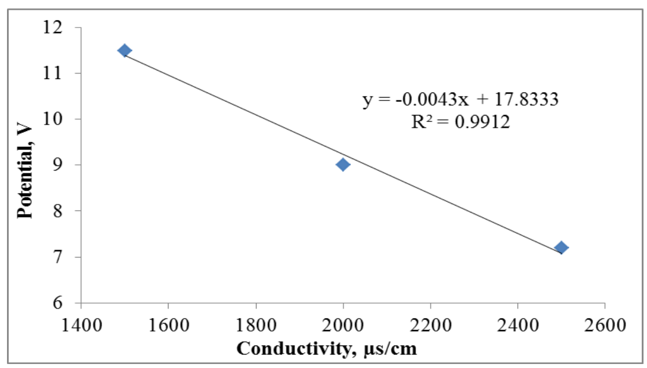

Figure 7. Potential as a function of conductivity with current density of 2.2 mA/cm^2, pH 7.

Effect of initial concentration

The initial concentration has direct effect on the removal efficiency [42, 44]. In this study, the effect of initial dye concentration was examined with various initial dye concentrations in a range of 40 ~ 100 mg/L. The EC was carried out at the current density of 2.2 mA/cm^2 and pH 7. Under this condition, the variation of initial dye concentration significantly affected the removal efficiency of color, dye and COD. The treatment performance markedly increased when raising the initial dye concentration. Because in high dye concentration samples, there were more contacting opportunities between dye molecules and aluminum hydroxides, it makes the flocculation to be easier and the adsorption of dye on flocs to be better.

The treatment efficiency by EC

The results showed that the EC could effectively treat the dyeing wastewater containing AR114 dye. With 5 min reaction time, removal of color, dye and COD treatments rapidly reached 80%, 77% and 82%, respectively, the wastewater sample contained 100 mg/L dye as shown in Figure. 8. With 20 min reaction time, the treatment efficiency was 90.3%, 89.3% and 92.5% corresponding to the color, dye and COD removal. The amount of generated aluminum in first 5 min was nearly enough to flocculate and adsorb the majority of dye. So, when increasing reaction time, generated aluminum ions increased but the removal efficiencies did not noticeably ascend. This treatment followed the saturation rate law.

Energy consumption for 1 m^3 treated water was around 1533.2 Wh/m^3 with 20 min reaction time. Volume and mass of generated sludge were functions of reaction time (Figure. 9). Increasing reaction time will lead to raising volume and mass of generated sludge. Choosing a reasonable reaction time is necessary to reduce the energy consumption and the treatment cost of secondary waste sludge.

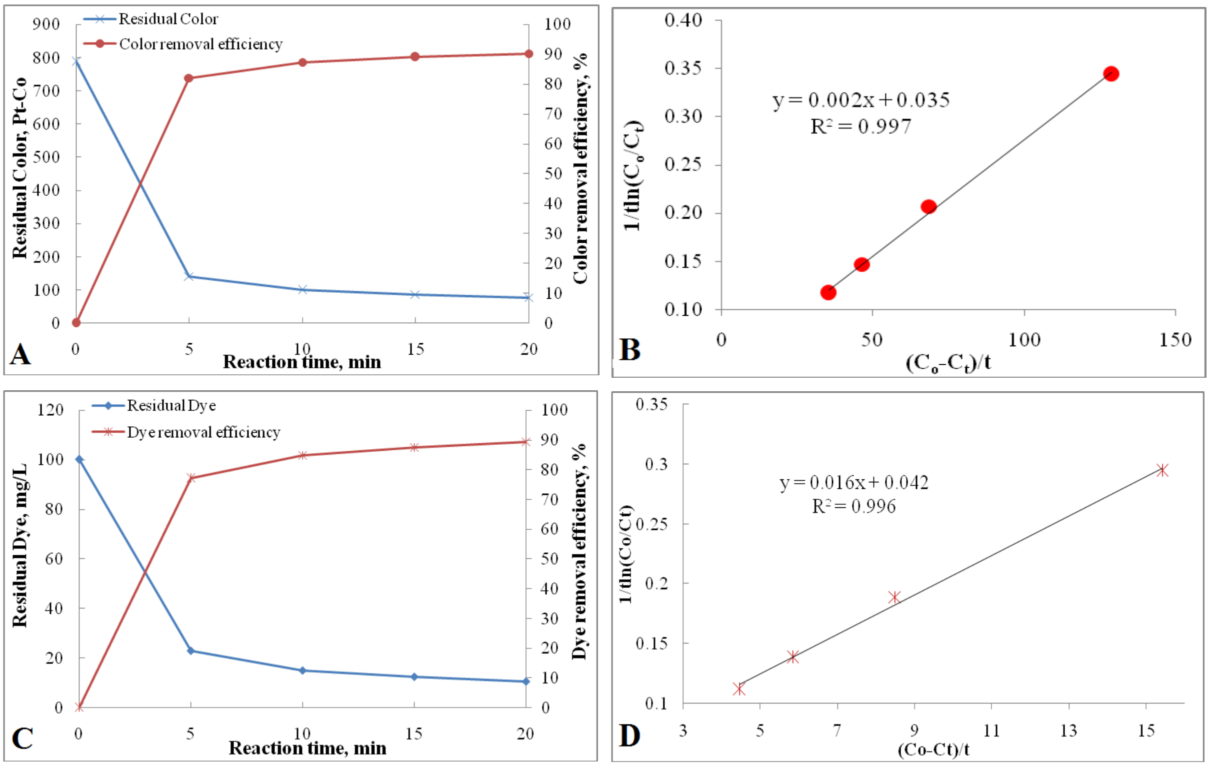

Figure 8. Residual color and color removal efficiency by EC (A). Color removal rate by EC (B). Residual AR114 dye and dye removal efficiency by EC (C). Dye removal rate by EC (D) with variation reaction time, initial AR114 dye concentration of 100 mg/L, current density of 2.2 mA/cm^2, conductivity of 1500 µS/cm, pH 7.

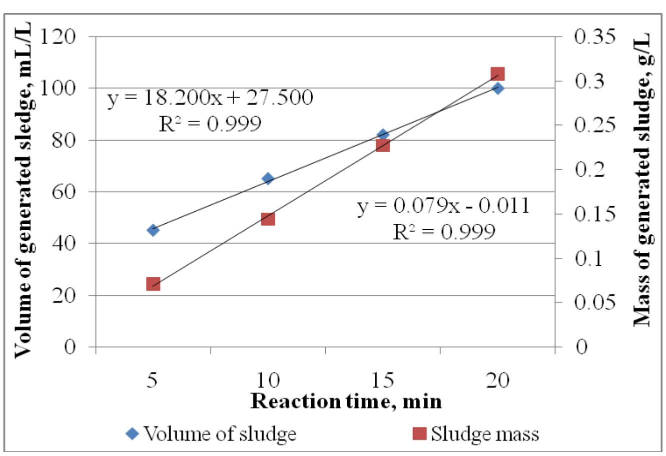

Figure 9. Sludge production in EC treatment with initial AR114 dye concentration of 100 mg/L, pH 7, current density of 2.2 mA/cm^2, conductivity of 1500 µS/cm.

Conclusion

The results of this study showed that both of the ozonation and EC were extremely feasible and effective in the treatment of wastewater containing AR114 dye. These methods can be applied for the dyeing wastewater treatment without pre-treatment requirement. In the comparison with the previous studies on AR114 dye removal, the ozonation and EC not only achieved high removal efficiency but also were shown shorter reaction time, no/less sludge production and easier operation. So these methods may be the promising techniques for the treatment of dyeing wastewater, especially containing AR114 dye.

When using ozonation method, some factors need to be considered such as:

• Gas diffuser and ozone gas flowrate are two most important factors that affect the treatment efficiency due to ozone solubility performance. Gas diffuser should be chosen a fine bubble type. Ozone gas flowrate must be in optimal range.

• pH and reaction time need to be carefully selected and adjusted to ensure the balance between the removal efficiency and operating cost; therefore, they should be optimized for a given reactor.

• Residual ozone in exhausted flow need to be controlled to prevent secondary pollution and effect on the human health.

With EC application, some parameters need to be concerned:

• Conductivity of wastewater should be high to reduce electrical energy consumption and may improve the removal efficiency.

• pH and reaction time need to be reasonably adjusted to fall into optimal pH region of aluminum precipitation and have a balance between of the treatment efficiency and cost of sludge treatment.

Acknowledgements

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