JOURNAL
of VIETNAMESE
ENVIRONMENT

Decolorizationof Reactive Red 195 solution by electrocoagulation process

Nghiên cứu khử màu nước thải nhuộm hoạt tính Red 195 bằng keo tụ điện hóa

Research article

Perng, Yuan-Shing; Bui, Ha-Manh*

Department of Environmental Engineering, Dayeh University, No.168, University Rd., Dacun, Changhua-51591, Taiwan, Republic of China

In this study, the application of bipolar electrocoagulation (EC) with iron electrode has been assessed for color removal of simulated wastewater containing Reactive Red 195. The influence of initial pH, sodium sulfate concentration, initial dye concentration, electrolysis time, and electric current were examined. The optimum operational parameters were found to be pH =11, concentration of dye = 50 mg L^{-1}, sodium sulfate concentration = 1200 mg L^{-1}, electrolysis time = 5 min, and electric current = 4 A. In such condition, color removal efficiency achieved over 99%. This result indicates that EC can be used as an efficient and "green" method for color removal from reactive dye solution.

Trong nghiên cứu này, quá trình khử màu nhuộm hoạt tính (Reactive Red 195) được khảo sát bằng hệ thống keo tụ điện hóa điện cực kép, với vật liệu sắt. Các yếu tố ảnh hưởng đến quá trình khử màu như pH, nồng độ màu nhuộm, nồng độ muối Na_2SO_4, thời gian phản ứng và cường độ dòng được lựa chọn nghiên cứu. Kết quả cho thấy hệ thống điện hóa trên loại gần như hoàn toàn màu nhuộm với hiệu suất đạt trên 99 % tại pH 11, nồng độ màu 50 mgL^{-1} và nồng độ muối Na_2SO_4 1200 mgL^{-1} trong khoảng thời gian 5phút. Kết quả trên cho thấy keo tụ điện hóa có thể xem là một phương pháp xử lý hiệu quả và "xanh" trong việc loại bỏ hoàn toàn màu từ nước thải nhuộm hoạt tính.

Keywords: color removal, current efficiency, electrolysis, reactive red 195, dyeing wastewater

1. Introduction

Wastewater of dyeing industry has been considered as one of the most serioussource of pollution, not only because of its toxic organic compounds but also for its color, which is aesthetically displeasing. Among classified dyes, the reactive dye is the most noticeable due to its ability to resist biodegradation (Gottlieb et al., 2003; Sadhasivam et al., 2005).

In the last few years, various modern methods such as ozonation, sonication, ion exchange, membrane filtration, etc. have been successfully applied for color removal of dye-containing wastewater (Kim et al., 2005; Lee et al., 2006; Zou and Zhu, 2008). Nonetheless, most of these techniques are limited by engineering, costs or difficulties in operation. Hence, they could not be employed for real dyeing wastewater treatment.

Coagulation and flocculation are traditional techniques using inorganic coagulant (alum, ferric chloride, poly aluminium chloride, etc.) or organic polymers (poly-acrylamide, polydiallyl-dimethyl-ammonium chloride, polyacrylic-acid-coacrylamide, etc.) to alter the physical state of pollutant particles and facilitate their removal by sedimentation. These techniqueshave been successfully used for color removal of textile wastewater overmany years (Verma et al., 2012). However, the coagulation process seems to be inefficient in the removal of some soluble dyes (Anjaneyulu et al., 2005) and produces a large quantity of highly putrescible sludge.

Recent studies focused on electrocoagulation (a new technique based on coagulation process), which completely removes color from dyeing wastewater (Daneshvar et al., 2007, and 2006; Şengil and Özacar, 2009).

In electrocoagulation (EC), directed current is used to dissolve metal electrode (mostly iron and aluminium) forming a range of coagulant species and metal hydroxides, whose adsorption efficiency is 100 times greater than pre-precipitated hydroxides of conventional coagulant (coagulation process) (Mollah et al., 2004).

Three proposed mechanisms for dye removal in EC (iron anode) are precipitation, floatation and adsorption. They are illustrated in Figure 1 (Daneshvar et al., 2006).
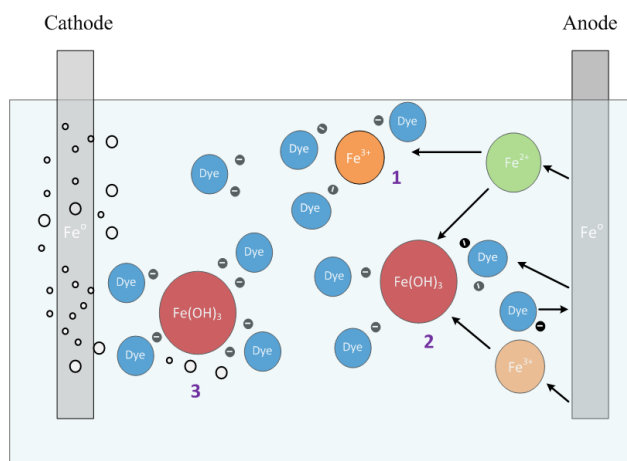
1. Precipitation; 2. Adsorption; 3. Flotation

Figure 1. Schematics of dye removal mechanism of electrocoagulation process with iron electrode (Daneshvar et al., 2006)

Although EC is based on coagulation process, it is simple, produces less sludge and does not require addition of chemical as a "clean reagent". Therefore, EC has attracted a great deal of attention. However, only a few reports on application of EC for the removal of color from dye-containing wastewater have been published in Vietnam (Hai, 2008; Huong, 2009). Thus, the focus of the present study is to assess the potential of EC for removal of Reactive Red 195 (R195) from aqueous solutions. EC studies were carried out under various parameters such as: electrolysis time, initial pH, initial dye concentration, electric current, and Na_2SO_4 (sodium sulfate) concentration.

2. Materials and methods

2.1. Materials

2.1.1. Reactive dye stock

The commercially available Reactive Red195 PAC was obtained from Oh-Young (a Korean company) with a molecular structure and characteristic as summarized in Table 1.

The dye stock solution (1000 mgL^{-1}) was achieved by completely dissolving 1.00 g dye powder into 1000 mL distilled hot waterat pH 11 for an hour to get the dye stock in the "hydrolyzed" form, and the solution was diluted to appropriate concentrations (30-140 mgL^{-1}) before using.

Table 1. Characteristics of Reactive Red 195

Chemical structure	
CAS No.	93050-79-4
Chromophore	Monoazo
M_w (g mole^{-1})	1136.30
λ_{max}	542

2.1.2. Experimental apparatus

The experiments were performed in a bipolar batch reactor (Figure 2), with four iron electrodes (Fe: 99.25% - CT2), dimensions of $146 \times 150 \times 4$ mm connected in parallel (bipolar mode). Only the outer electrodes were connected to the self-build digital DC power supply (220 V and 30 A) whose poles automatically switch every 30 sec. The electrocoagulator was made of plexiglas with the dimensions $160 \times 160 \times 250$ mm including an Imhoff sedimentation tank. The active area and the distance of each electrode were 19.6 cm^2 (140×140 mm) and 15 mm, respectively.
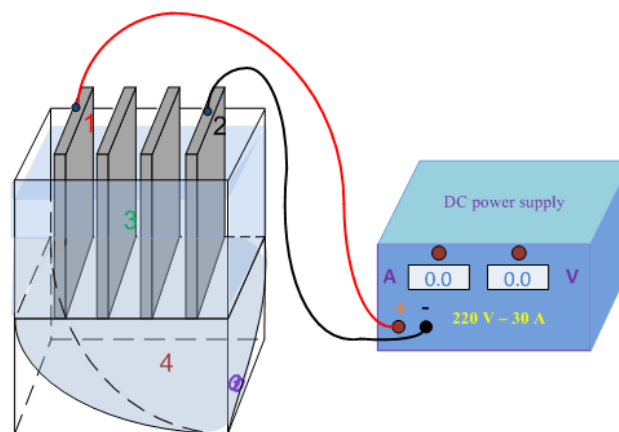
1. Anode; 2. Cathode; 3. Electrocoagulation zone
4. Baffled Settling zone

Figure 2. Bench scale of the EC reactor

2.2. Procedures and analysis

In each run, 4.0 L of the constant dye solution with concentrations (IDC) of 30, 50, 80, 100 and 140 mgL^{-1} were placed into the electrolytic cell. The pH of solution was set to suitable value (3, 5, 6, 7, 8, 9, 10, 11, and 12) using HCl and NaOH 0.1 N. The sulfate concentration varied from 1000 mgL^{-1} to 2000 mgL^{-1} in steps of 200 mgL^{-1}. The current (i) was adjusted to the desired value (2, 3, 4, and 5 A). After 30 min settling at the end of each run, 25 ml of the treated samples were collected, filtered and determined the absorbance at 542 nm, λ_{max}, using a spectrophotometer (Thermo UV-Vis GENESYS 10). Furthermore, to avoid electrode passivation, at the end of each run, the electrodes were washed thoroughly with water and dipped in HCl solution (10% v/v) for at least 15 min. All analyses were conducted in duplicate for reproducibility of data, and all of the data in results was the average value.

3. Results and discussion

3.1. pH influence

As reported by other researchers (Alinsafi et al., 2005, Daneshvar et al., 2007), pH plays a key role on the performance of EC on dye removal process as it determines the iron and dye speciation in solution. Hence, it would have a significant influence on the decolourization mechanism. To examine effect of pH, a series of experiments were performed by adjusting the initial pH in the interval from 3 to 12.

The effect of pH on EC is presented in Figure 3, which indicates that the poorest color removal was obtained between pH 3-6, with removal efficiencies below 18%. However, when pH of the dye solutions increased from 6 to 11 the decolorization rised significantly and reached a peak at pH 11 then significantly dropped in the strong basic zone (pH 12).
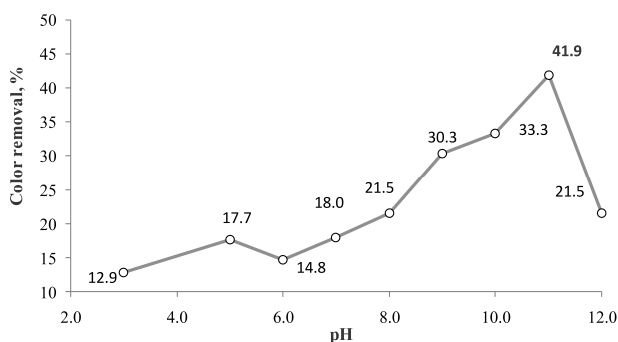

Figure 3. Effect of initial pH on color removal efficiency (IDC 50 mgL^{-1}, SO$_4^{2-}$ 1200 mgL^{-1}, i3 A, and t 4 min)

This result may be due to the formation of Fe(OH)$_2$(s) flocs which have large surface areas. These flocs are useful for a rapid adsorption of soluble dye as described in Figure 4 (Barrera-Díaz et al., 2003). At other pH, the complexes of formed hydrolysis products caused the decrease of the removal efficiency. It confirmed that, for electrocoagulation of R195, the key mechanism is adsorption, which correlates well with the decolorization process

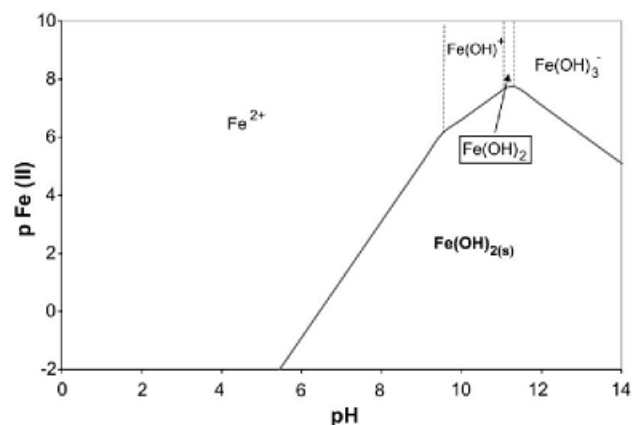of Reactive Black 5 reported by Şengil and Özacar (2009).

Figure 4. Predominance zone diagram for Fe(II) chemical species in aqueous solution (Barrera-Díaz et al., 2003)

Moreover, pH value of raw reactive textile effluents normally was around 11.0 (Racyte et al., 2009). Thus, there is no requirement to adjust pH value of dye solution and pH 11 was selected for the subsequent experiments.

3.2. Effect of sulfate salt concentration

During dyeing process, Glauber's salt (sodium sulfate) was added to the dye bath to help the dye drive onto the fiber and form dye-fiber bonding. Furthermore, this salt concentration could affect operational parameters in EC such as voltage, current efficiency, and electrical energy (Daneshvar et al., 2006). In order to investigate this effect on decolorization, the sodium sulfate concentration was varied from 1000 mgL^{-1} to 2000 mgL^{-1} with interval 200 mgL^{-1} to evaluate its impact on EC process.
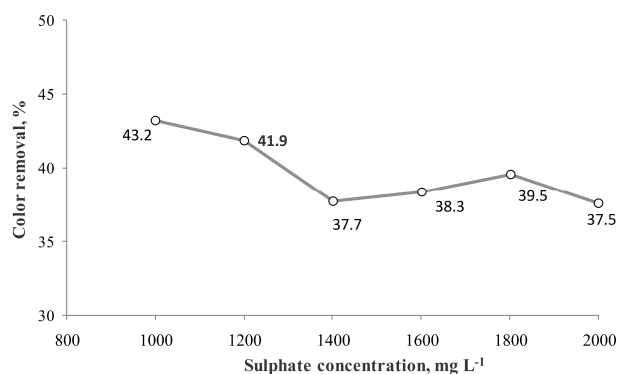

Figure 5. Influence of sodium sulfate concentration on dye color removal (IDC 50 mgL^{-1}, pH 11, i3 A, and t 4 min)

According to the results (Figure 5), in this decolorization process sodium sulphate had little impact. The maximum removal efficiency was around 40%. Among them, sulfate concentration of 1200 mgL^{-1} got the suitable result (41.9 %). Thus, the salt concentration of 1200 mgL^{-1} was chosen for the next study.

3.3. Effect of initial dye concentration

Figure 6 indicates the effect of initial dye concentration (IDC) on color removal and shows that by varying the IDC from 30 mgL^{-1} to 140 mgL^{-1}, the removal efficiency significantly drops. When IDCs were less than 50 mgL^{-1}, the efficiencies were above 40%, but with its increase to 140 mgL^{-1}, the efficiencies fell down immediately around 24%. After this point, the IDC 50 mgL^{-1} corresponding to 41.9% dye removal was chosen for further studies.
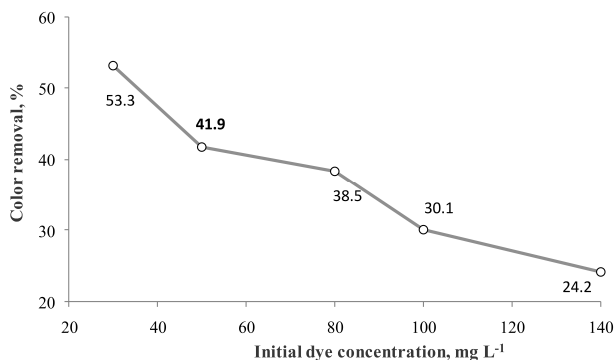

Figure 6. Effect of dye concentration on EC of the dye (SO$_4^{2-}$ 1200 mgL^{-1}, pH 11, *i*3 A, and t 4 min)

3.4. Effect of electric current

Electric current (*i*) is a critical operational parameter in EC due to its effect to coagulant dosage rate, bubble production rate, size and growth of the flocs. Generally, with an increase in the power of the current, the dissolution rate of the anode enhances due to the increase in the number of iron hydroxide flocs (Alinsafi et al., 2005, Mollah et al., 2004). The following experiments were carried out at constant conditions: suitable pH 11, IDC 50 mgL^{-1}, sodium sulfate concentration1200 mgL^{-1}, and electrolysis time 4 min with difference in electric current (*i*): 2-5 A.
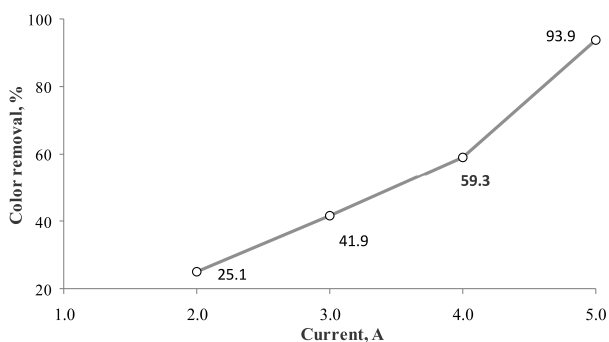

Figure 7. Effect of electric current on color removal efficiency (SO$_4^{2-}$ 1200 mgL^{-1}, pH 11, IDC 50 mgL^{-1}, and t 4 min)

As noted in Figure 7, the increasing *i* had a significant impact on the accomplished decolorization. With increasing of *i* up to 5 A, the color almost disappeared (removal efficiency >93 %). However, for optimization purpose, value *i* of 4 A with the yield 59.3 % was fixed for next EC experiments.

3.5. Effect of electrolysis time

At this stage, the effect of electrolysis time (t) was performed by varying times (2-13 min) under constant parameters at equilibrium condition.

The effect of electrolysis time (t) on color removal is indicated in Figure 8, which showes that by varying t from 2 min to 13 min, the removal efficiencies were significantly enhanced. In particular, between 2 min and 5 min, it reached over 99%. Nevertheless, beyond this time, the yields were almost unchanged. A possible explanation of these results might be that with an increasing electrolysis time, there will be more iron hydroxide (flocs) in solution, and that leads to a better result in removal efficiency. However, beyond the optimal electrolysis time, the removal efficiencies were relatively constant.
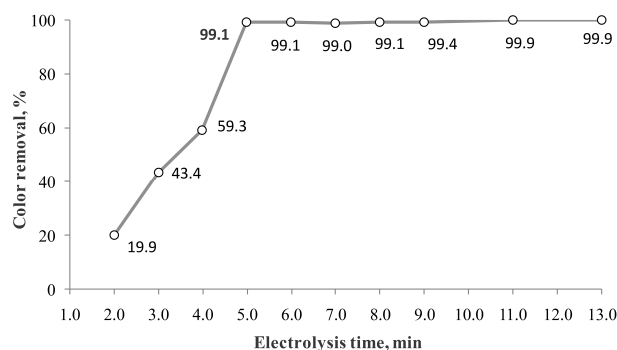

Figure 8. Effect of electric current on color removal efficiency (SO$_4^{2-}$ 1200 mgL^{-1}, pH 11, IDC 50 mgL^{-1}, and *i* 4 A)

4. Conclusions

EC was demonstrated to be a simple and efficient method for color removal of simulated wastewater from Reactive Red 195. Parameters such as pH, IDC, electrolysis time and electric current seem to be the main effective factors, whereas salt concentration was insignificant for decolorization process. The best removal of the dye was 99.1% at pH 11, IDC 50 mgL^{-1}, sodium sulfate concentration 1200 mgL^{-1}, electrolysis time 5 min, and electric current 4 A.

5. References

[1] Alinsafi, A., Khemis, M., Pons, M.N., Leclerc, J.P., Yaacoubi, A., Benhammou, A., Nejmeddine, A. 2005. Electro-coagulation of reactive textile dyes and textile wastewater. Chemical Engineering and Processing: Process Intensification 44(4): 461-470

[2] Anjaneyulu, Y., Sreedhara Chary, N., Samuel Suman Raj, D. 2005. Decolourization of Industrial Effluents – Available Methods and Emerging Technologies – A Review. Reviews in Environmental Science and Bio/Technology 4(4): 245-273

[3] Barrera-Díaz, C., Palomar-Pardavé, M., Romero-Romo, M., Martínez, S. 2003. Chemical and electro-chemical considerations on the removal process of hexavalent chromium from aqueous media. J. Appl. Electrochem. 33(1): 61-71

[4] Daneshvar, N., Khataee, A.R., Amani Ghadim, A.R., Rasoulifard, M.H. 2007. Decolorization of C.I. Acid Yellow 23 solution by electrocoagulation process: Investigation of operational parameters and evaluation of specific electrical energy consumption (SEEC). J. Hazard. Mater. 148(3): 566-572

[5] Daneshvar, N., Oladegaragoze, A., Djafarzadeh, N., 2006. Decolorization of basic dye solutions by electrocoagulation: An investigation of the effect of operational parameters. J. Hazard. Mater. 129(1–3): 116-122

[6] Gottlieb, A., Shaw, C., Smith, A., Wheatley, A., Forsythe, S. 2003. The toxicity of textile reactive azo dyes after hydrolysis and decolourisation. J. Biotechnol. 110(1): 49-56

[7] Hai, L.T. 2008. A study on the decolourization of Dye-containing solutions by Electrocoagulation. UD's J. Sci. Technol. 31(4): 78-83

[8] Huong, N.T. 2009. The efficiencies of Textile wastewater treatment by Electrocoagulation and oxidation with Fenton agent. UD's J. Sci. Technol. 35(6): 102-106

[9] Kim, T.-H., Park, C., Kim, S. 2005. Water recycling from desalination and purification process of reactive dye manufacturing industry by combined membrane filtration. Journal of Cleaner Production 13(8): 779-786

[10] Lee, J.-W., Choi, S.-P., Thiruvenkatachari, R., Shim, W.-G., Moon, H. 2006. Submerged microfiltration membrane coupled with alum coagulation/powdered activated carbon adsorption for complete decolorization of reactive dyes. Water Res. 40(3): 435-444

[11] Mollah, M.Y.A., Morkovsky, P., Gomes, J.A.G., Kesmez, M., Parga, J., Cocke, D.L. 2004. Fundamentals, present and future perspectives of electrocoagulation. J. Hazard. Mater. 114(1–3): 199-210

[12] Racyte, J., Rimeika, M., Bruning, H. 2009. pH effect on decolorization of raw textile wastewater polluted with Reactive dyes by Advanced oxidation with UV/H_2O_2. Environ. Prot. Eng. 35(3): 167-178

[13] Sadhasivam, S., Saritha, E., Savitha, S., Swaminathan, K. 2005. Comparison of the Efficacy of Live and Autoclaved Mycelium of Trichoderm harzianum on the Removal of Trypan Blue. Bull. Environ. Contam. Toxicol. 75(5): 1046-1053

[14] Şengil, İ.A., Özacar, M. 2009. The decolorization of C.I. Reactive Black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes. J. Hazard. Mater. 161(2–3): 1369-1376

[15] Verma, A.K., Dash, R.R., Bhunia, P. 2012. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. J. Environ. Manage. 93(1): 154-168

[16] Zou, L., Zhu, B. 2008. The synergistic effect of ozonation and photocatalysis on color removal from reused water. J. Photochem. Photobiol. A: Chem. 196(1): 24-32