CHEMICAL ENGINEERING TRANSACTIONS

VOL. 81, 2020

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Qiuwang Wang, Min Zeng, Panos Seferlis, Ting Ma, Jiří J. Klemeš

ISBN 978-88-95608-79-2; **ISSN** 2283-9216

DOI: 10.3303/CET2081023

Treatment of Methyl Blue Dye Wastewater Solution by Three-Dimensional Electrolysis

Ben Wang[a], Yan Sun[a], Shengnan Yu[a], Qinghao Wu[b], Jinhua Yin[a,*]

[a]Qingdao University of Science and Technology, No.53 Zhengzhou Rd, Qingdao, Shandong, P.R. China, 266042
[b]Qingdao Q.K.L.Y.S&T Consulting Development Co.Ltd, No.51-2 Wuyang Rd, Qingdao, Shandong, P.R. China, 266042
yinjinhua@126.com

Dye wastewater has complex structures and is difficult to be biodegraded. Three-dimensional electrolysis is advantageous in mass transfer and oxidation degradation ability. In this paper, a continuous flow three-dimensional electrolytic reactor with coconut shell activated carbon as the filling material is established to treat methyl blue dye wastewater. The influence on the dye wastewater treatment by the pH value of the system, the impressed voltage, the concentration of electrolyte, the aeration rate, the electrolysis time and the interactions of the five factors on COD degradation are investigated in the experimental part, and the optimal degradation condition is finally determined. Results show that it not only improved the degradation efficiency of dye wastewater, but also help to energy conservation, emission reduction and sustainable development.

1. Introduction

The remediation of dye wastewater has been an urgent environment problem for every nation. Over the world, about 10^9 people are exposed to unsafe drinking water due to poor source water quality and lack of adequate water treatment (Han et al., 2009). The survey found that about 15 % of the total global production of dyes is lost during the dyeing process and released into the environment as textile effluent (Weber et al., 1993). Triphenylmethane dyes (TPM dyes) have the advantages of many systems and various, so it has been widely used. TPM dyes also have great harm to the environment and biology. In this paper, methyl blue was studied. There are various conventional methods used to treat methyl blue dye wastewater including biochemical method (Cui et al., 2016), photocatalytic method (Han et al., 2009), electrolytic method (Liu et al., 2020), hydrogel method (Chirag et al., 2020), adsorption method (Luo et al., 2019) and Novel bio-electro-Fenton Technology (Li et al., 2017). Recently, electrochemical methods have attracted more attention due to some advantages such as ease of operation, high efficiency and environmental compatibility (Pulkka et al., 2014). It has been found that the effect of three-dimensional electrolysis is about 15 % higher than that of two-dimensional electrolysis (Reza et al., 2020). Three-dimensional electrode water treatment technology can effectively increase the specific surface area of the working electrode and improve the mass transfer rate, effectively improving the degradation efficiency of organic matter (Gao et al., 2008). The selection of electrode materials determines the effect of wastewater treatment, so the appropriate electrode should be selected. Biocathode-electrocatalytic Reactor (BECR) successfully started up at 0.7 and 1 V and substantially improved MB and total organic carbon (TOC) removal compared with the electrocatalytic reactor with SS cathode (ECR-SS); less energy consumption, but still low efficiency of wastewater treatment (Mo et al., 2020). Fe/Cu, Fe/Al/Cu, Fe/Cu/C and Fe/Al/Cu/C internal electrolysis systems (IESS) were constructed and used to treat methylene blue dye (MB) wastewater. The degradation effect is good, but the energy saving is not realized (Liu et al., 2020). IrO_2/Ti and RuO_2/ Ti (DSA) can produce strong oxidizing groups and react with organics in wastewater (Song, 2008). DSA is used as anode material in this paper. The cathode material is graphite electrode, the price is low, and the COD removal rate is higher, so it is used as cathode material in this paper (Zhao, 2012). The continuous-flow three-dimensional electrode reactor could effectively remove the refractory organic pollutants in a secondary industrial effluent (Xu et al., 2008). However, as one of the most common types of industrial wastewater, the treatment of methyl blue dye wastewater by the continuous-flow three-

Paper Received: 26/03/2020; Revised: 17/05/2020; Accepted: 21/05/2020
Please cite this article as: Wang B., Sun Y., Yu S., Wu Q., Yin J., 2020, Treatment of Methyl Blue Dye Wastewater Solution by Three-Dimensional Electrolysis, Chemical Engineering Transactions, 81, 133-138 DOI:10.3303/CET2081023

dimensional electrode reactor has not been studied. In this paper, a continuous flow three-dimensional electrolytic reactor with coconut shell activated carbon as the filling material was established to treat methyl blue dye wastewater, and the effect of COD degradation by changing the applied voltage, electrolyte concentration, electrolytic time, pH, and aeration conditions were analyzed by controlling single variable and orthogonal. This study also provides a basis for the continuous treatment of dye wastewater in the future.

2. Experiments

COD was taken as the index in the experiment. Single variable experiment and orthogonal experiment considering interaction were carried out. According to the extremum of orthogonal experiment results, the influence degree of each factor is determined.

2.1 Experimental Set-up

In this experiment, electrode material: graphite plate was used as cathode (Hamidi et al., 2004); DSA electrode was used as anode, and oconut shell activated carbon was used as a filling material. The cell volume was designed as: Xu et al. (2008) : "anode and cathode were 7 cm × 5 cm in size and were situated 3 cm from each other."

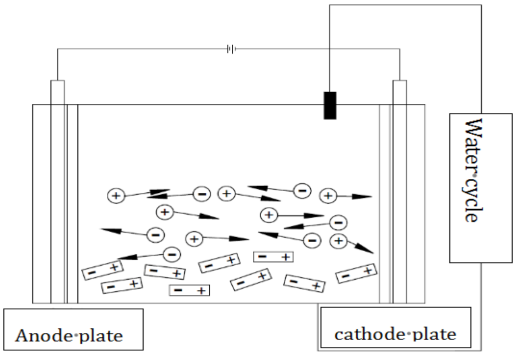


Figure 1:Structure of Three-dimensional electrode reactor

Paidar et al. (2002) studied the influence of the flow form of fluid in the three-dimensional electrolytic reactor on the degradation rate and current efficiency of pollutants in wastewater. The results showed that the current efficiency and pollutant removal rate of the flow plate electrolytic cell are higher, so a continuous flow three-dimensional electrolytic reactor with coconut shell activated carbon as the filling material was established in this paper.

2.2 Analytical method

Potassium hydrogen phthalate was used as the reference material for COD standard curve calibration (Liang et al., 2017), and the catalyst was H_2SO_4 solution of Ag_2SO_4. According to the determination method of COD_{Cr} in national standard, $K_2Cr_2O_7$ solution was used as the disinfectant, and the light transmittance data was measured by spectrophotometer at 445 nm.

3. Influence of single factor on the electrolysis process

In this experiment, methyl blue simulated wastewater was used as the treatment object. A continuous flow three-dimensional electrolytic reactor with coconut shell activated carbon as the filling material was established to treat methyl blue dye wastewater. The Standard condition of the experiment was set as below: the initial concentration was set to 200 mg/L, the volume was 250 mL, aeration rate was 30 L/h, the electrolysis was 120 min, the Na_2SO_4 concentration was 0.1 mol/L, the pH value was 5, and the electrolytic voltage was set to 14 V. The effects of various factors on the degradation of methyl blue simulated wastewater by three-dimensional electrodes was investigated.

3.1 Effect of the applied voltage

In this series of experiments, the applied voltage was taken as the operating variables and the other parameters were kept. The degradation rate of COD and current in the methyl blue wastewater were measured under different voltage conditions (Yan et al., 2011).

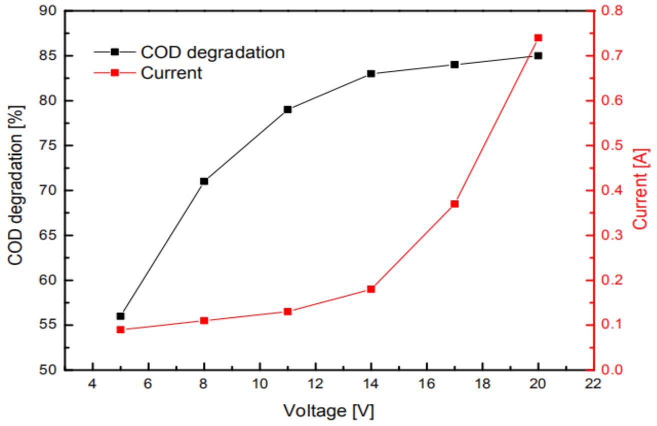


Figure 2: Effects of the applied voltage on electrolytic process

Figure 2 shows that as the applied voltage increase, the COD degradation degree and current in methyl blue simulate wastewater both increase. Before the applied voltage reach 14 V, the COD degradation rate increase faster and the current increase slowly. After the applied voltage of 14 V, the COD degradation rate increase slowly and the current increase faster. With the increasing of applied voltage, the current increase rapidly, while the removal rate of COD does not increase significantly, resulting in energy waste. Comprehensively, the optimal voltage is 14 V.

3.2 Effect of the electrolysis time

In this part, the electrolysis time was taken as the operating variables in a set of experiments and the other parameters were kept. Samples were taken every 10 min to analyze the degradation of COD in methyl blue simulated wastewater at different times.

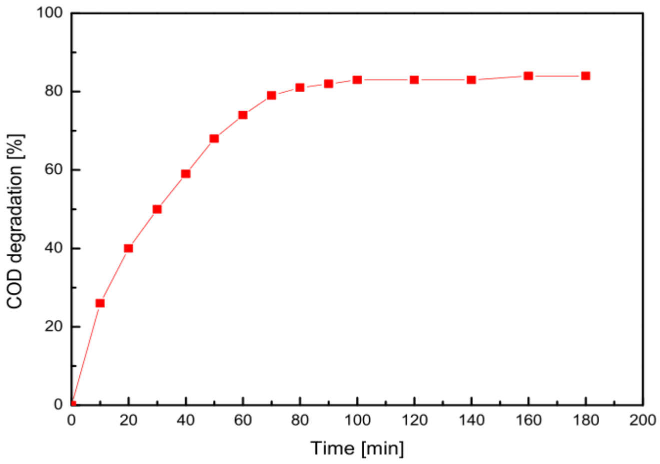


Figure 3: Effects of the electrode time on electrolytic process

Figure 3 shows that with the increasing of the electrolysis time, the degradation rate of COD of methyl blue dye wastewater increases. As the reaction time goes on, the slope of the curve of COD shows a downward trend, because the content of COD in the system is less and less. According to the slope of 80 ~ 120 min, we can know that it is an obvious increasing trend than 120 - 140 min. Although the growth trend slowed down between 80 min and 120 min, in order to achieve 83 % degradation rate, combined with the experimental results, we used 120 min.

3.3 Effect of the pH

In this part, pH was taken as the operating variables and the other parameters were kept. The degradation experiments of methyl blue simulated wastewater were carried out under different pH conditions.

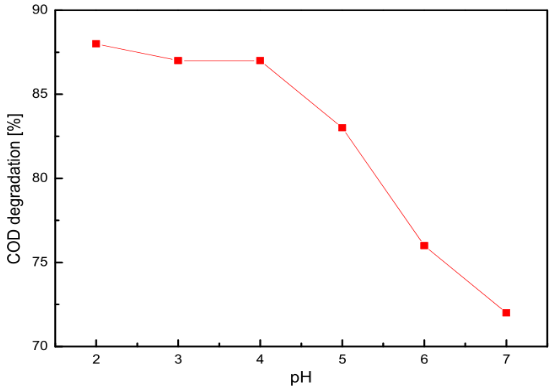
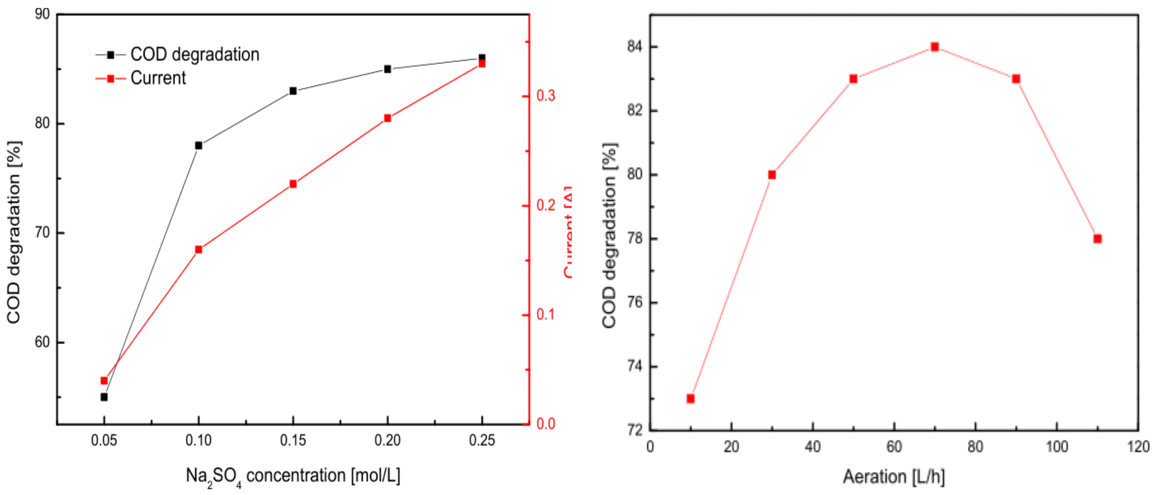


Figure 4: Effect of the pH on the electrolytic process

It can be seen from Figure 4 that the degradation rate of COD decreases with the increasing of pH value. When the pH is between 2 to 4, the degradation rate of COD is higher and does not change much, about 88 %. When the pH is between 4 to 7, the degradation rate of COD decreases sharply. With the decreasing of pH value, the conductivity of the methyl blue wastewater system would inevitably increase, which would lead to increasing reaction current and the consumption of electric energy. The pH value that the neutral electric energy is closer, the waste is less. Considering the treatment cost of the methyl blue wastewater, the pH is taken as 4.

3.4 Effect of the electrolyte concentration

Methyl blue simulated wastewater containing different Na_2SO_4 concentrations was prepared, and electrolyte concentration was changed with other parameters remained. The effect of electrolyte concentration on the COD degradation and reactor current in methyl blue simulated wastewater was investigated.



(a) (b)

Figure 5: Effects of (a) the electrolyte concentration and (b) the aeration rate on electrolytic process

As can be seen from Figure 5 (a), with the electrolyte concentration increasing, the COD degradation and current both show an upward trend. The COD degradation and current increase rapidly from 0.05 mol/L to 0.10 mol/L, while the degradation rate of COD and the current between 0.10 mol/L and 0.20 mol/L both increase slowly. When the concentration is larger than 0.2 mol/L, the COD degradation rate does not increase, but the current still maintain the previous growth trend. Considering the waste of energy, the electrolyte concentration is taken as 0.2 mol/L.

3.5 Effect of the aeration rate

In this part, the aeration rate was taken as the operating variables and the other parameters were kept. The degradation experiments of methyl blue simulated wastewater were carried out under different the aeration rate pH conditions.

It can be seen from Figure 5 (b) that with the increasing of aeration, the COD degradation increase first and then decrease. When the aeration rate is 70 L/h, the COD degradation rate reached the maximum of 84 %. when the aeration is 50 L/h, the COD degradation rate reached 83 %. At 50 ~ 70 L/h, COD degradation rate has little change. Comprehensive consideration, aeration rate of 50 L/h is selected.

3.6 Investigation of the interaction of electrolytic factors

Table 1: Orthogonal experiment of influence factors of electrolysis

Factor	pH	Voltage V	Electrolyte concentration mol/L	Time min	Aeration L/h	Degradation rate of COD %
Group 1	3	8	0.05	60	0	69
Group 2	3	11	0.1	90	20	76
Group 3	3	14	0.15	120	50	85
Group 4	3	17	0.2	150	100	88
Group 5	4	8	0.15	120	20	83
Group 6	4	11	0.2	60	0	75
Group 7	4	14	0.05	90	100	76
Group 8	4	17	0.15	150	50	73
Group 9	5	8	0.2	90	50	73
Group 10	5	11	0.15	60	100	65
Group 11	5	14	0.1	150	0	84
Group 12	5	17	0.05	120	20	78
Group 13	6	8	0.1	120	100	75
Group 14	6	11	0.05	150	50	72
Group 15	6	14	0.2	60	20	69
Group 16	6	17	0.1	90	0	74
Average 1	79.5	70.0	73.7	69.0	75.5	—
Average 2	77.7	72.0	77.0	74.7	76.5	—
Average 3	75.0	75.5	76.7	78.2	75.7	—
Average 4	72.5	76.2	76.2	79.7	76.0	—
Range	7.00	6.5	3.25	12.75	1.00	—

According to the range value in Table 1, the influence degree of each factor test is: electrolysis time > pH value > voltage > electrolyte concentration > aeration. Dye degradation increases with voltage, aeration, electrolyte concentration, time and acidity. When the electrolysis voltage is 17 V, pH is 3, aeration is 100 L/h, electrolyte concentration is 0.2 mol/L and time is 150 min, in methyl blue simulated wastewater has the highest degradation rate of COD of 88 %. Combined with the single variable experiment, considering the waste of energy, the optimal experimental electrolysis conditions for the treatment of methyl blue simulate wastewater by three-dimensional electrolysis are determined: pH is 4, voltage is 14 V, aeration rate is 50 L/h, electrolyte concentration of Na_2SO_4 is 0.15 mol/L, electrolysis time is 120 min.

4. Conclusions

In this paper, a continuous flow three-dimensional electrolytic reactor was established to treat methyl blue dye wastewater with coconut shell activated carbon as the filler. This method is not only simple and easy to operate but also environment friendly, and has high degradation efficiency. Through the extremum of orthogonal experiment, the influence degree of each factor is determined. The regular is: electrolysis time > pH value > applied voltage > electrolyte concentration > aeration amount. Combined with the results of single-factor experiments, the optimal combination conditions for the three-dimensional electrolytic treatment of methyl blue dye wastewater are determined: The operating parameters for treating methyl blue dye wastewater are that electrolytic voltage is 14 V, electrolytic time is 120 min, pH is 4, electrolyte concentration is 0.15 mol/L and the aeration amount is 50 L/h. Under this conditions, the content of COD in the wastewater of methyl blue dye is the lowest, so the purpose of energy saving and emission reduction is achieved, the utilization rate of water resources is improved. Because the continuous flow three-dimensional electrolytic reactor is used, this study provides a basis for the subsequent continuous treatment.

References

Chirag B.G., Xiao Y.H., Lu X.I., 2020, Amine Functionalized Sodium Alginate Hydrogel for Efficient and Rapid Removal of Methyl Blue in Water, International Journal of Biological Macromolecules.144, 671-681.

Cui M.H., Cui D., Gao L., Cheng H.Y., Wang A.J., 2016 Analysis of Electrode Microbial Communities in an Up-flow Bioelectrochemical System Treating Azo Dye Wastewater, Electrochimica Acta. 220, 252-257.

Cui Y.P., Yang C.Z., 2004, Study on the Treatment of Phenol Wastewater with Three-dimensional Electrode, Energy and Environmental Protection, 018 (001), 23-26.

Gao Y., Wu H., Chen S. 2008, Study of Highly Concentrated Organic Waste water Treatment by Electrolysis and Oxidation, Industrial Water Treatment, 28(5), 69-71.

Hamidi A A., Mohd N A., Mohd S M., Zahari., Salina A., 2004, Removal of Ammoniacal Nitrogen (N–NH3) from Municipal Solid Waste Leachate by Using Activated Carbon and Limestone, Waste Management & Research the Journal of the International Solid Wastes & Public Cleansing Association Iswa, 22(5), 371-375.

Han F., Venkata S.R.K., Madapusi S., Dharmarajan R., Ravi N., 2009, Tailored Titanium Dioxide Photocatalysts for the Degradation of Organic Dyes in Wastewater Treatment: A Review, Applied Catalysis A: General, 359(1-2), 25-40.

Li C., Zhu Y., Mo D.Q., 2010, Color Removal Treatment of Dyeing Wastewater by Method of Three-dimensional Electrode, Environmental Science & Management. 703, 1674-6139.

Li X.H., Jin X.D., Zhao N.N., Angelidaki I., Zhang Y.F., 2017, Novel bio-electro-Fenton Technology for Azo Dye Waste water Treatment Using Microbial Reverse-electrodialysis Electrolysis Cell, Bioresource technology, 228, 322-329.

Liang H, Ren Y, Qiu Y, Cui M, Khim H, Sang-Hwan L 2017, Research on the Electrolytic Active Chlorine in the Process of Treating Chlorine-Containing Wastewater by Three-Dimensional Electrode Method, Industrial Water Treatment.

Liu L.H., He D.W., Pan F., Huang R., Lin H., Zhang X.H., 2020, Comparative Study on Treatment of Methylene Blue Dye Wastewater by Different Internal Electrolysis Systems and COD Removal Kinetics. Thermodynamics and Mechanism, Chemosphere. 238, 124-671.

Luo T.J., Liang H., Chen D., Ma Y.H., Yang W.T., 2019, Highly Enhanced Adsorption of Methyl Blue on Weakly Cross-linked Ammonium-functionalized Hollow Polymer Particles, Applied Surface Science, 505.

Mo Y.H., Du M.M., Yuan T.T., Liu M.X., Wang H., He B.Q., Li J.X., Zhao X., 2020, Enhanced Anodic Oxidation and Energy Saving for Dye Removal by Integrating O_2-reducing Biocathode into Electrocatalytic Reactor, Chemosphere, 252, 0045-6535.

Paidar M., Bouzek K., Bergmann H., 2002, Influence of Cell Construction on the Electrochemical Reduction of Nitrate, Chemical Engineering Journal, 85(2–3), 99-109.

Pulkka S., Martikainen M., Bhatnagar A., Sillanp M., 2014, Electrochemical Methods for the Removal of Anionic Contaminants from Water – A review, Sep. Purif. Technol. 132, 252–271.

Reza S., Davood N., Mohammad R. S., Ghasem A., Zahra L., 2020, Optimization of Three-dimensional Electrochemical Process for Degradation of Methylene Blue from Aqueous Environments Using Central Composite Design, Environmental Technology & Innovation, 18, 2352-1864.

Song G.J., 2012, Study on the Treatment of High Chlorine Organic Wastewater by Ti/IrO_2-RuO_2 Electrochemical Method, Beijing: Beijing Nonferrous Metals Research Institute.

Weber E.J., Stickney V.C., 1993, Hydrolysis Kinetics of Reactive Blue 19-Vinyl Sulfone. Water Res. 27(1),63-67.

Xu L.N., Zhao H.Z., Shi S.Y., Zhang G.Z., Ni J.R., 2008, Electrolytic Treatment of C.I. Acid Orange 7 in Aqueous Solution Using A Three-dimensional Electrode Reactor, Dyes and Pigments.

Yan L., Ma H.Z., Wang B., Wang Y.F., Chen Y.S., 2011, Electrochemical Treatment of Petroleum Refinery Wastewater with Three-dimensional Multi-phase Electrode, Desalination, 276, 397-402.

Zhao M., 2012, Study on Advanced Treatment of Pharmaceutical Wastewater by Three-dimensional Electrode Method, Zhengzhou University.