COMPARATIVE STUDY OF THE ELECTROOXIDATION OF GRAPHITE AND Ti/RUO_2 ANODES FOR THE REMOVAL OF ORGANIC MATTER FROM SALINE WASTEWATER

NGHIÊN CỨU SO SÁNH XỬ LÝ OXY HÓA ĐIỆN HÓA CHẤT THẢI HỮU CƠ TRONG NƯỚC THẢI MẶN BẰNG ĐIỆN CỰC GRAPHITE VÀ Ti/RUO_2

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Đến Tòa soạn ngày 12/10/2022, chấp nhận đăng ngày 04/11/2022

Tóm tắt: In recent years, clean water is increasingly scarce due to increased human demand, untreated wastewater is the cause of water quality deterioration. The aquaculture industry brings benefits in terms of food for humans, but the water sourses can be easily polluted by decomposition of redundant aqua feed and organic waste. In this study, saline wastewater is treated by electrochemical oxidation with two types of Graphite and Ti/RuO_2 electrodes. Experiments were conducted to investigate the effect of reaction conditions such as salt concentration, current density, electrolysis time and pH on COD removal efficiency and electrode activity. Ti/RuO_2 electrode showed better handling ability than graphite electrode at the same reaction condition. For the optimal efficiency of COD removal and anode activity, the electrolysis of saline wastewater is set at 2% salt content, at 45 mA/cm^2 current density, in 60 minutes reaction , at 6 pH value. In this condition, COD treatment efficiency reached 87.7% (anode graphite) and 92.9% (anode Ti/RuO_2), electrode efficiency reached 0,208 kg/h.A.m^2 (anode graphite) and 0,22 kg/h.A.m^2 (anode Ti/RuO_2).

Từ khóa: Current density, electrode, environment, graphite, saline wastewater.

Abstract: Trong những năm gần đây, nguồn nước sạch ngày càng khan hiếm do nhu cầu sử dụng của con người tăng cao, nước thải chưa qua xử lý là nguyên nhân khiến chất lượng nước ngày càng suy giảm. Ngành nuôi trồng thủy sản mang lại lợi ích về thực phẩm cho con người, nhưng đi kèm với đó là ô nhiễm nguồn nước do thức ăn bị phân hủy, rác thải hữu cơ. Trong bài báo này, nước thải nhiễm mặn được xử lý bằng phương pháp oxy hóa điện hóa với hai loại điện cực Graphit và Ti / RuO_2. Các thí nghiệm được tiến hành để khảo sát ảnh hưởng của các điều kiện phản ứng như nồng độ muối, mật độ dòng điện, thời gian điện phân và pH đến hiệu suất khử COD và hiệu suất điện cực. Điện cực Ti/RuO_2 cho thấy khả năng xử lý tốt hơn điện cực graphit ở cùng điều kiện phản ứng. Để đạt hiệu suất xử lý COD và hiệu suất điện cực tối ưu, quá trình điện phân nước thải mặn được ưu tiên ở điều kiện hàm lượng muối 2%, mật độ dòng điện 45 mA/cm^2, thời gian phản ứng 60 phút, pH 6. Ở điều kiện phản ứng này, hiệu suất xử lý COD đạt 87,7% (cực dương graphit) và 92,9% (cực dương Ti/RuO_2), hiệu suất điện cực đạt 0,208 kg/h.A.m^2 (cực dương graphit) và 0,22 kg/h.A.m^2 (cực dương Ti/RuO_2).

Keywords: Mật độ dòng điện, điện cực, môi trường, graphit, nước thải mặn.

1. INTRODUCTION

In recent years, the aquaculture industry has grown rapidly, contributing to supplementing the essential food source, so aquaculture in brackish and saline water has been bringing great benefits to the people. However, the water quality in coastal aquaculture areas, especially in industrial models, has shown signs of organic pollution (BOD, COD, nitrogen, phosphorus). As reported by Unesco, about 80% of untreated wastewater has been being discharged into the environment [1], causing great harm to human health and agricultural production.

Many solutions have been applied to reduce the pollution caused by this process, including: adsorption, flotation [2], electrocoagulation (EC) [3], electrodeposition, nanofiltration [4]. However, each of these methods has certain disadvantages such as: expensive, energy consuming and time consuming …

Electrochemical process (EC) is one of the new methods applied to industrial wastewater and saline wastewater treatment. They have some advantages comparing with other methods like: high efficiency, felixibility, energy-saving, environmental compatibility [5-6]. There are many types of anode electrodes used in other studies for the treatment of saline wastewater from different waste sources [7]. In different types of active electrodes, Ti-based electrode and various oxide coatings such as Ti/RhOx–TiO_2, Ti/PdO–Co_3O_4, Ti/PbO_2 and Ti/Pt–Ir, have been used as anodes for electrochemical oxidation of organic waste [8]. The results showed that method was highly effective at decomposing organic pollutants. In particular, the Ti/RuO_2 anode has the advantage of size stability and high overpotential of 2.0 V, which is the dominant anode in the oxidation reactions of saline wastewater [9]. In the part of inactive electrodes, graphite in electrochemical treatment of saline wastewater has advantage of low cost [10]. It has large surface area and may result better in the attenuation of pollution through the combination of adsorption and electrochemical degradation. [7].

In the electrochemical oxidation reactions, there are two types of oxidation processes: direct and indirect. The direct oxidation takes place on the surface of the electrode. The indirect one, with the NaCl presence, the decomposion of organic pollutants also occurs as described in the reaction equation below:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (2)$$

$$HOCl \leftrightarrow H^+ + OCl^- \quad (3)$$

The generated hypochlorite ions act as main oxidizing agent for the pollutant decomposion. The COD test is used to evaluate the efficiency of wastewater treatment. [11-13]. Finding the right reaction conditions, in order to obtain high processing efficiency, consume less energy, and reduce reaction time is necessary. In order to optimize the treatment process, the different anode materials and reaction conditions were investigated. We used two types of graphite and Ti/RuO_2 electrodes combine with reaction conditions: salt concentration, current density, pH, the electrolyse time for the COD removal.

2. MATERIALS AND METHODS

2.1. Chemicals

- Kalibicromate and Silver sulphate from Merck (Germany).
- Mercury sulfate, Sulfuric acid, Methylene blue, Sodium chloride salt from China.

2.2. Electro-oxidation process and reaction conditions

The reactions are carried out in a beaker with a solution of 40 (mL), the anode (Ti/RuO_2 or graphite) and the cathode (stainless steel) are spaced 1 cm apart (Fig 1), with working area of 6 cm^2.

The electric power supply was provided by D.C. power source with equipped current–voltage monitoring and it has a maximum amperage 5A. The assumed wastewater used is a methylene blue solution with an initial COD content of 200 mg/L. The pH was adjusted by NaOH (0.1 M) or HCl (0.1 M) aliquots by using HACH-HI2211 equipment.

The effect of the investigated reaction conditions are:

- NaCl concentration (from 0.5-3%), with the constant conditions of: current density - 45 mA/cm^2; pH 6; electrolyse time 60 minutes;
- Current density (from 15-55 mA/cm^2), the other conditions are kept constant: NaCl 2%; pH 6; electrolyse time 60 minutes.

$$H_{COD(\%)} = \frac{M_{CODb} - M_{CODa}}{M_{CODb}} \times 100 \qquad (4)$$

- pH (from 3-12), with the constant conditions of: NaCl 2%; current density 45 mA/cm^2; electrolyse time 60 minutes;
- Electrolyse time (from 30- 120 minutes), with the constant conditions of: NaCl 2%; current density 45 mA/cm^2; pH 6

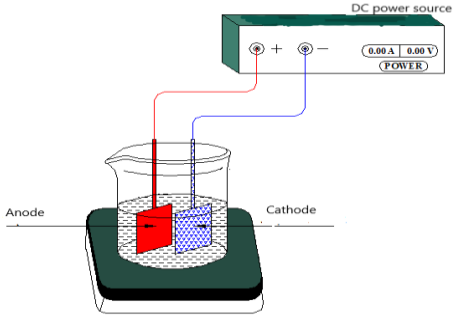

Figure 1. Diagram electrochemical oxidation

2.3. Calculations

Samples before and after the reaction were determined COD (chemical oxygen demand) according to section 5220D of *Standard Methods for the Examination of Water and Wastewater*. The efficiency of the reaction is calculated by the formula below:

- COD treatment performance was assessed according to the formula:

Inside:

M_{CODb} : Initial COD concentration (mg/L)

M_{CODa} : Concentration of COD after treatment (mg/L)

- Anode effiency is calculated by the formula:

$$H = \frac{M}{T.I.S} \qquad (5)$$

Inside:

H: electrode efficiency (kg/h.A.m^2);

M: amount of COD removed (kg);

T: electrolyse time- hours (h);

I: current (A);

S: anode working area (m^2).

2.4. Investigate the ability of the electrode to different initial COD content

Different concentrations of organic matter to be treated will affect the electrode's processing performance. Initial COD content with concentrations: 300, 400, 500 mg/L was oxidized under optimal conditions from previous experiments.

- Salt content: 2%;
- pH solution: 6;
- Current density: 45 mA/cm^2;
- Reaction time: 60 minutes.

3. RESULTS AND DISCUSSION

3.1. Effect of NaCl concentration

In this experiment, the concentration of NaCl was increased from 0.5 to 3,0 %. Other conditions are keept constant: pH 6; current density 45 mA/cm^2, electrolyse time 60 minutes. Data of figure 2 showed that both types of electrodes are able to decompose methylene blue even in the low NaCl concentration (0.5%), after 60 minutes of electrolysis the COD index has decreased from 200 mg/L to approximately 22 mg/L (for anode graphite) and 10 mg/L (for anode Ti/RuO_2). Amount of COD reduction was found to be directly proportional to the salt concentration. This trend probably could be attributed to the increased level of generation of chlorine and hypochlorite when the salt concentration is increased [14].

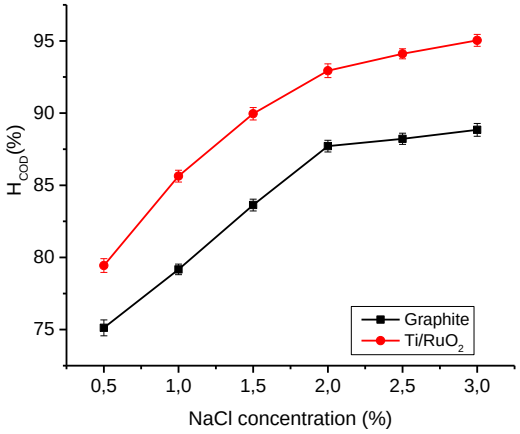

Figure 2. Effect of NaCl concentration on COD removal efficiency of electrode

During electrochemical oxidation, NaCl plays an important role in creating strong indirect oxidizing agents (Cl_2, ClO^- ...) from reactions on the anode electrode surface according to reaction equations 1-3. These oxidizing agents have a strong oxidizing effect on organic matter in wastewater [15].

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (2)$$

$$HOCl \leftrightarrow H^+ + OCl^- \quad (3)$$

Similarly, the electrode's efficiency at different salt concentrations are shown in figure 3. Its shows that, the electrode efficiency also increases as the NaCl concentration increases.

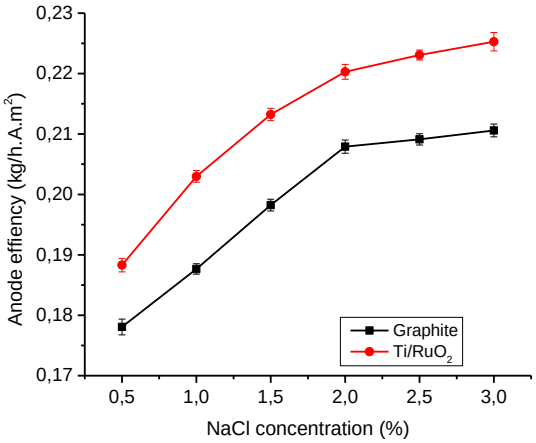

Figure 3. Effect of NaCl concentration on anode efficiency

Under research conditions, when increasing NaCl concentration from 0.5% to 2%, COD treatment efficiency and electrode efficiency both increase strongly, when NaCl concentration increases to 3%, COD treatment efficiency is only slight increase. Therefore, the 2% NaCl salt concentration was selected for the next experiments.

3.2. Effect of curent density

The investigative experiments are carried out under the following conditions: current density are varied from 15-55 mA/cm^2; other experimental conditions kept unchanged include NaCl concentration 2%, pH 6, and reaction time 60 minutes. Experimental results are shown in Figure 4-5.

The results obtained in Figure 4 show that for both electrodes, COD treatment efficiency increases with increasing current density,

which may explain the increasing electrolytic current increasing the number of effects oxidizing agents formed, such as Cl_2, HClO or OH• [7]. Increases in current density decreased the anode efficiency of both anode electrodes. From the above results, a current density of 45 mA/cm^2 was chosen as the most optimal condition for both electrodes.

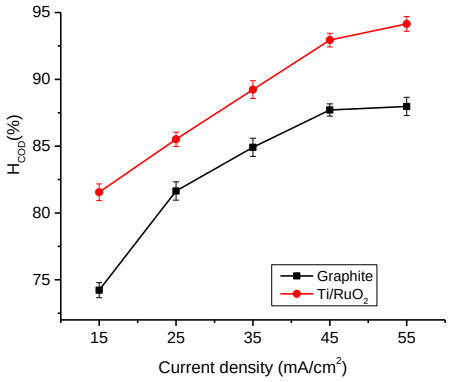

Figure 4. Effect of current density on COD treatment efficiency

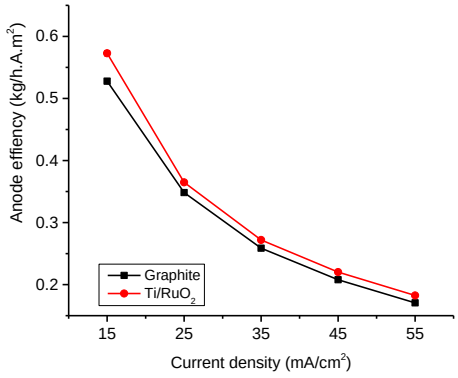

Figure 5. Effect of current density on the anode efficiency

3.3. Influence of initial pH

In this experiment, pH value changed from 3.0 to 12 with an increment of 3. NaCl concentration, current density and electrolyse time were kept constant at 2% of NaCl, 45 mA/cm^2 and 60 minute of reaction. The data are shown in the figure 6 and 7.

The pH at 3, main oxidizer was Cl_2. From 3-8, the dominant was HClO and the ClO^- increased if pH was above 8. Because HClO (E° = 1.49 V/SHE) and Cl_2 (E° = 1.36 V/SHE) showed a higher redox potential than ClO^- (E° = 0.89V/SHE), the process oxidizing organic matter in acidic environment was more effectively than in alkaline environment [14]. That explained why the COD treatment efficiency of graphite electrode decreased from 88.2% (pH 3) to 77.7% (pH 12). For Ti/RuO_2 electrodes, the treatment efficiency was 91.3% and 80.3%.

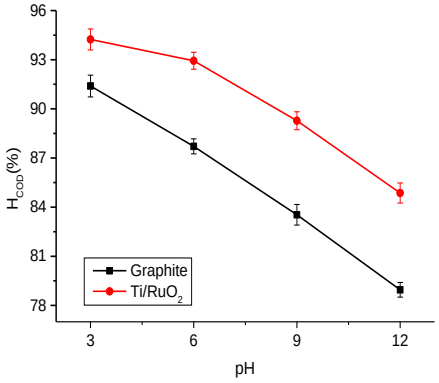

Figure 6. Effect of pH on COD treatment

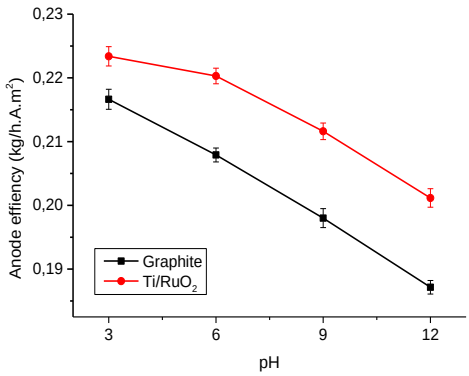

Figure 7. Effect of pH on electrode effiency

3.4. Influence of electrolyse time

The reactions are performed with reaction times of 30, 60, 90 and 120 minutes. Other conditions kept constant include salt concentration of 2.0%, current density 45 mA/cm^2, pH 6. The result of the reaction is shown in the figures 8 and 9.

From those graphs, the COD removal efficiency of both electrodes increased with

electrolyse time, while the electrode efficiency value decreased. After 120 minutes of electrolysis, COD removal efficiency reached 95.45% for graphite anodes and 98.82% for Ti/RuO_2 anodes.

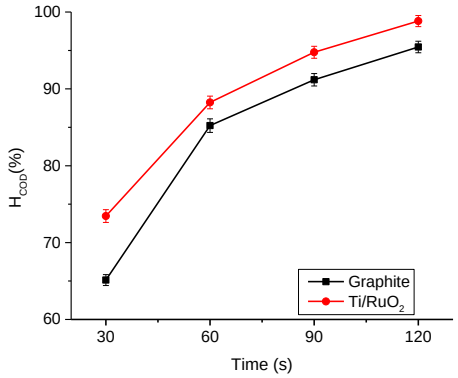

Figure 8. Effect of electrolyse time on COD treatment efficiency

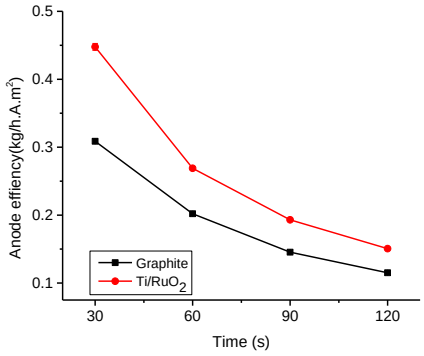

Figure 9. Effect of electrolyse time on electrode performance

The COD removal efficiency of both electrodes increased rapidly during the reaction time from 30-60 min. After that, continuing the reaction process, the COD treatment efficiency increased more slowly. While, the performance of both electrodes decreased with increasing reaction time.The experimental results show that: The best conditions for electrochemical oxidation to treat 40 mL of methylene blue solution with an initial COD of 200 mg/L are as follows:

- Salt concentration: 2%;
- pH solution: 6;
- Current density: 45 mA/cm^2;
- Reaction time: 60 minutes.

In this condition, COD treatment efficiency reached 87.7% (anode graphite) and 92.9% (anode Ti/RuO_2), electrode efficiency reached 0,208 kg/h.A.m^2 (anode graphite) and 0,22 kg/h.A.m^2 (anode Ti/RuO_2).

From the obtained results, the Ti/RuO_2 electrode for COD treatment was more efficient in comparison with the graphite electrode. In the indirect oxidation reactions, the Ti/RuO_2 electrode was able to produce number of highly reactive radicals like hydroxyl radicals ($OH^{\bullet}$) that help in-situ oxidation of organic pollutants [9].

3.5. Investigate the ability of the electrode to different initial COD content

From the results obtained in section above, further surveys were conducted with initial COD content of 300, 400 and 500 mg/L, the reactions were carried out under optimal conditions as follows:

- Salt concentration: 2%;
- pH solution: 6;
- Current density: 45 mA/cm^2;
- Reaction time: 60 minutes.

Experimental results are presented in Table1.

Table 1. COD treatment results of electrodes with different initial COD contents

COD initial (mg/L)	Graphite		Ti/RuO_2	
	COD (mg/L)	Anode effiency (kg/h.A.m^2)	COD (mg/L)	Anode effiency (kg/h.A.m^2)
300	46,791	0,234	87,102	0,266
400	63,446	0,208	78,185	0,238
500	81,840	0,180	70,362	0,214

In the treatment of saline wastewater with an initial COD content of 200 mg/L, the use of Ti/RuO_2 and Graphite electrodes for treatment

efficiency is almost equivalent. In particular, Graphite electrode is preferred because of its low cost, short time and lower current density than Ti/RuO_2 electrode.

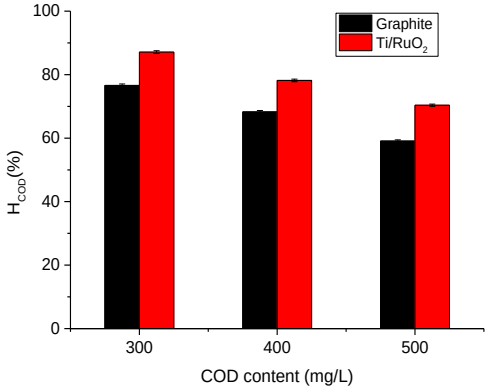

Figure 10. COD removal efficiency with the different of initial COD content

Reaction conditions for removal of organic pollutant current density of 45 mA/cm^2, salt concentration 2%, and electrolysis time of 60 minutes at neutral pH are believed to be better for reduced COD requirement and anode efficiency.

4. CONCLUSIONS

In the treatment of saline wastewater with an initial COD content of 200 mg/L, the use of Ti/RuO_2 and Graphite electrodes for treatment efficiency is almost equivalent. In particular, Graphite electrode is preferred because of its low cost, preferred reaction in the short time and lower current density than Ti/RuO_2 electrode. Reaction conditions for removal of organic pollutant current density of 45 mA/cm^2, salt concentration 2%, and electrolysis time of 60 minutes at neutral pH are believed to be better for reduced COD requirement and anode efficiency.

ACKNOWLEDGMENTS

This work was funded by the Vietnam Academy of Science and Technology (VAST) under the grant number TĐVLTT.01/21-23.

REFERENCES

[1] A. Adedoja Owodunni, Suzylawati Ismail, "Revolutionary technique for sustainable plant-based green coagulants in industrial wastewater treatment-A review", Journal of Water Process Engineering 42 102096 (2021).

[2] Kyzas, G.; Matis, K, "*Flotation in water and wastewater treatment".* Processes, 6, 116 (2018).

[3] A. A. Al-Raad, M. M. Hanafiah, A. S. Naje, M. A. Ajeel, A. O. Basheer, T. Ali Aljayashi and M. E. Toriman, "*Treatment of Saline Water Using Electrocoagulation with Combined Electrical Connection of Electrodes"*, Processes, 7, 242 (2019), doi:10.3390/pr7050242.

[4] Xiuzhen Wei, Xin Kong, Songxue Wang, Hai Xiang, Jiade Wang, and Jinyuan Chen, *"Removal of Heavy Metals from Electroplating Wastewater by ThinFilm Composite Nanofiltration Hollow-Fiber Membranes"*, Ind. Eng. Chem. Res. 52, 17583−17590 (2013).

[5] Han Yu, Ya Li, Min Zhao, Heng Dong, Hongbing Yu, Sihui Zhan, Linus Zhang, "Energy saving removal of methyl orange in high salinity wastewater by electrochemical oxidation via a novel Ti/SnO_2-Sb anode- air diffusion cathode system", Catalysis Today, 258, 156-161(2015).

[6] Bhatnagar, R., Joshi, H., Mall, I.D., Srivastava, V.C, "*Electrochemical treatment of acrylic dye bearing textile wastewater: optimization of operating parameters",* Desalination Water Treat. 52, 111–122 (2013).

[7] S. Sundarapandiyan, R. Chandrasekar, B. Ramanaiah, S. Krishnan, P. Saravanan, "*Electrochemical oxidation and reuse of tannery saline wastewater"*, Journal of Hazardous Materials 180 (1-3) 197–203 (2010).

[8] Lidia Szpyrkowicza, Santosh N. Kaulb, Rao N. Netib, Shanta Satyanarayan, *"Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater",* Water Research 39, 1601–1613 (2005).

[9] Parminder K., Jai Prakash K., Vikas Kumar S, "Evaluation and disposability study of actual textile wastewater treatment by electro- oxidation method using Ti/RuO_2 anode", Process safety and environment protection 111,13- 22 (2017).

[10] L. Szpyrkoicz, S.N. Kaul, R.N. Neti, S. Satyanarayan, "Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater", Water Res. 39 1601–1613 (2005).

[11] Kavoos Dindarloo1, Hamza Ali Jamali, Parvin Lakbala, Hamid Mahmoodi, Fatemeh Kazemi, *"Feasibility of electrochemical oxidation process for treatment of saline wastewater"*, Environmental Health Engineering and Management Journal, 2(3), 129–134 (2015)

[12] Umesh Ghimire, Min Jang, Sokhee P. Jung, Daeryong Park, Se Jin Park, Hanchao Yu and Sang-Eun Oh, "Electrochemical Removal of Ammonium Nitrogen and COD of Domestic Wastewater using Platinum Coated Titanium as an Anode Electrode", Energies, 12, 883 (2019); doi:10.3390/en12050883

[13] Bo Yang and Jie Tang, *"Electrochemical Oxidation Treatment of Wastewater Using Activated Carbon Electrode"*, Int. J. Electrochem. Sci., 13, 1096 – 1104 (2019), doi: 10.20964/2018.01.78

[14] Francisca C. Moreiraa, Rui A.R. Boaventuraa, Enric Brillas, Vítor J.P. Vilar, "*Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters"*, Applied Catalysis B: Environmental 202, 212-261(2017)

[15] Carlos A. Martinez- Huitle, Enric Brillat, "*Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review"*, Applied Catalysis B: Environmental 87 (3–4) 105-145(2009).

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