

Pollutants Removal from Synthetic Wastewater by the Combined Electrochemical Sequencing Batch Reactor

Amin Mojiri, Akiyoshi Ohashi, Tomonori Kindaichi

Abstract—Synthetic domestic wastewater was treated via combining treatment methods, including electrochemical oxidation, adsorption, and sequencing batch reactor (SBR). In the upper part of the reactor, an anode and a cathode (Ti/RuO₂-IrO₂) were organized in parallel for the electrochemical oxidation procedure. Sodium sulfate (Na₂SO₄) with a concentration of 2.5 g/L was applied as the electrolyte. The voltage and current were fixed on 7.50 V and 0.40 A, respectively. Then, 15% working value of the reactor was filled by activated sludge, and 85% working value of the reactor was added with synthetic wastewater. Powdered cockleshell, 1.5 g/L, was added in the reactor to do ion-exchange. Response surface methodology was employed for statistical analysis. Reaction time (h) and pH were considered as independent factors. A total of 97.0% biochemical oxygen demand, 99.9% phosphorous and 88.6% cadmium were eliminated at the optimum reaction time (80.0 min) and pH (6.4).

Keywords—Adsorption, electrochemical oxidation, metals, sequencing batch reactor.

I. INTRODUCTION

ONE of the chief environmental problems is water pollution, which rises from several sources. Using of water resources is considered one of the world's critical environment issues. Wastewater treatment from human activities in several fields, such as agriculture, industries, and shipping, is considered a solution to water shortage [1]. These wastewaters comprise numerous kinds of contaminants such as heavy metals, phosphorous, and chemical oxygen demand (COD). Several physical/chemical and biological techniques are applied to treat wastewaters [2]. SBR is one of the biological treatment methods.

SBR is one of the biological processes employed to eliminate several pollutants [3]. SBR performance may be affected with heavy metals, low biodegradability, and concentration of high organic and inorganic contaminants in wastewaters [4]. So, researchers [5] have suggested the combined physical/chemical and biological treatment techniques to reach optimum elimination efficacies. One of the physical/chemical treatment techniques is electrochemical oxidation (EO).

In the other words, EO is an excellent alternative for wastewater treatment in order to eliminate organic compounds that resist biological degradation. EO depends chiefly on the generation of hydroxyl radicals ([•]OH) on the surface of the

anode, being capable of totally mineralizing organic compounds to CO₂, water and organic ions, or at least, converting them into more biodegradable organic compounds, reduce TOC, coloration and COD [6]. Barrera-Díaz et al. [7] expressed that contamination removal in high polluted wastewaters may not be done by EO individually due to needing high amount of energy. So, in literature [8], [9], EO has been combined with biological and other physical/chemical methods. Adsorption is one of the attractive treatment methods.

Adsorption is an amount transmission process by which a substance is moved from the liquid phase to the surface of a solid, and then bound via physical interactions, chemical interactions, or both [10]. Some of the most effective adsorbents are ash, activated carbon, cement, limestone and cockleshell, which have been applied by researchers [11], [12]. In literature [4], adsorbent has been added to the SBR to improve its performance.

This study chiefly intended to treat synthetic wastewater by combining electrochemical and powdered cockleshell (PCS) supplemented SBR. The researchers designed a combined wastewater treatment technique that has optimum performance. In this study, three kinds of treatments, namely, electrochemical, ion exchange/adsorption, and SBR, were applied to improve the efficiency of contaminant elimination in the same time.

II. MATERIALS AND METHODS

A. Producing Domestic Wastewater

In current research, tap water was contaminated with three pollutants including COD, phosphorous, and cadmium. The contaminants were prepared by dissolving their chemical grade in water. To reach phosphorous concentration, KH₂PO₄ was dissolved in water [13]. To reach COD, different carbon sources, including peptone, Na-acetate, starch, yeast, and milk powder were added to the tap water [14]. For Cd concentrations, cadmium was achieved by dissolving CdCl₂ in tap water, respectively [15].

B. Designed Reactor

One beaker (height = 25 cm and diameter = 10 cm) with a working value of 1500 mL was employed in this contemporary study (Fig. 1). In the upper part of the reactor, anode and cathode plates (Ti/RuO₂-IrO₂, 8 cm × 4 cm) were employed for the EO procedure. The plates were prepared parallel (distance was 3 cm) to each other and were dipped in water. Na₂SO₄ with a concentration of 2.5 g/L was added as electrolyte to the reactor before each experiment. Electronic power (digital DC power supply) was applied as the power source. Air was

A. Mojiri is with the Department of Civil and Environmental Engineering, Hiroshima University, Japan (e-mail: amojiri@hiroshima-u.ac.jp).

A. Ohashi is with the Department of Civil and Environmental Engineering, Hiroshima University, Japan (e-mail: ecoakiyo@hiroshima-u.ac.jp).

T. Kindaichi is with the Department of Civil and Environmental Engineering, Hiroshima University, Japan (e-mail: tomokin@hiroshima-u.ac.jp).

supplied from the bottom of the reactor by using an air pump because it was an SBR-based reactor. Aeration rate was set to 1.5 L/min. The periods of fill (10 min), settle (45 min), and draw and idle (10 min) were fixed based on preliminary experiments. In addition, 1.50 g/L of powdered cockleshell (PCS) was added in the SBR for adsorption.

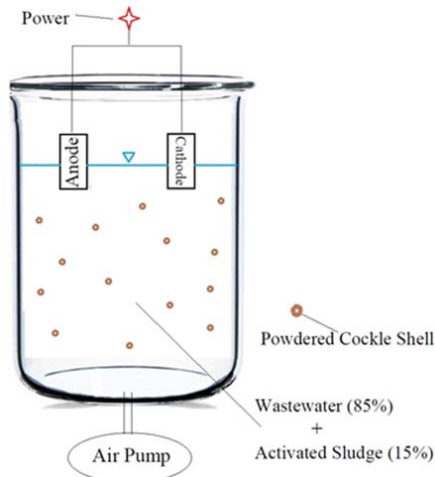


Fig. 1 Schematic of the reactor

C. Experimental Procedure

A 1500 mL reactor was used in current study. The reactor was filled with 1275 mL synthetic wastewater, representing the 85% working value of the reactor. A total of 225 mL activated sludge from domestic WWTP (wastewater treatment plant) was added in the reactor, representing the 15% working value of the reactor. Mojiri et al. [4] applied activated sludge from domestic WWTP in SBR as 10% working value to supply bacteria and improve biodegradability in treating landfill leachate. The voltage and current in the preliminary experiments were set to 7.50 V and 0.40 A, respectively. In the contemporary study, two independent factors, including contact time (reaction time; 30 min to 120 min) and pH (5.50 to 7.50), were investigated. COD and phosphorous concentrations were set to 2500 mg/L. Cd concentrations was set to 100 mg/L. Chemical, physical, and biological analyses for the wastewater were carried out in order to standard methods [16]. P, Cd, and COD were tested by using spectrophotometry in accordance with Standard DR/2800 HACH.

D. Statistical Analysis

The elimination effectiveness is computed based on (1).

$$\text{Removal (\%)} = \frac{(C_i - C_f)}{C_i} \cdot 100, \quad (1)$$

where C_i and C_f are the preliminary and final concentrations of the features, respectively.

Response surface methodology (RSM) was applied for statistical analysis. RSM is a mathematical and statistical method used in designing experiments, building models, and evaluating the effect of process variables. The responses can be

linked to the factors by using linear or quadratic models in RSM. The quadratic model, which also comprises the linear model, is used in (2).

$$Y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{j=1}^k \beta_{jj} X_j^2 + \sum_i \sum_{j=2}^k \beta_{ij} X_i X_j + e_i, \quad (2)$$

where Y is the response; X_i and X_j are the variables; β_0 is a fixed coefficient; β_j , β_{jj} , and β_{ij} denote the interface coefficients of the linear, quadratic, and second-order terms, respectively; k denotes the quantity of considered factors; and e denotes the error.

III. RESULTS AND DISCUSSION

In current research, concentrated synthetic wastewater was treated via using the combined system. The combined system comprised EO, adsorption, and SBR. The 3D surface plots of COD, P and Cd elimination are displayed in Fig. 2. Tables I and II show the response values for different experimental conditions and the ANOVA results for response parameters, respectively.

TABLE I
EXPERIMENTAL VARIABLES AND RESULTS

Run	Reaction Time (h)	pH	COD rem. (%)	P rem. (%)	Cd rem. (%)
1	6.5	75	98.2	99.9	86.3
2	7.5	75	97.7	99.9	79.1
3	5.5	30	76.2	94.3	98.1
4	7.0	75	98.1	99.9	82.7
5	7.5	30	94.9	97.1	79.2
6	6.5	30	95.5	97.5	92.1
7	5.5	75	78.4	94.2	97.7
8	7.0	30	96.4	99.9	82.5
9	5.5	30	79.1	93.1	98.2
10	6.5	75	96.4	99.9	87.7
11	7.5	30	95.9	98.2	79.8
12	5.5	120	77.9	94.5	97.3
13	7.0	120	96.1	99.9	83.3
14	7.5	120	97.0	99.9	77.7
15	7.0	75	97.9	99.9	85.3
16	5.5	75	80.7	96.1	98.8
17	6.5	75	98.0	99.9	86.2
18	7.5	75	95.8	99.9	79.0
19	6.5	75	96.9	99.9	86.7
20	5.5	120	79.3	95.2	97.2
21	7.5	120	95.7	99.9	78.5
22	6.5	120	97.2	99.9	85.6

TABLE II
ANOVA RESULTS FOR RESPONSE PARAMETERS

Responses	R ²	Adj. R ²	Adec. P.	SD	CV
COD	0.984	0.979	33.63	1.21	1.32
P	0.948	0.932	20.20	0.63	0.64
Cd	0.972	0.969	42.71	1.31	1.50

R²: Coefficient of determination; Adj. R²: Adjusted R²; Adec. P.: Adequate precision; SD: Standard deviation; CV: Coefficient of variance.

A. COD Removal

In current research, COD elimination varied from 76.2% (pH= 5.5 and reaction time = 30 min) to 98.1% (pH= 7 and

reaction time= 75 min) by using the current combined treatment system. COD diminished by 98.5% at optimum pH= 7.2 and reaction time= 80.5 min (Fig. 2 (A)).

Vilar et al. [6] could remove 64% of COD via combined biological–EO treatment. Markou et al. [17] could reduce COD from 4000 mg/L to around 2000 mg/L (efficiency around 50%) in 120 min reaction time during electrochemical treatment of biologically pre-treated dairy wastewater. In this contemporary study, COD removal efficiency was more than in literature review, since three kind of treatment methods were applied in a same time.

B. Phosphorous Removal

In current study, P elimination varied from 93.1% (pH= 5.5 and reaction time = 30 min) to 99.9% (pH= 7 and reaction time= 75 min) by using the current combined treatment system. P diminished by 100% at optimum pH= 6.6 and reaction time= 90.2 min (Fig. 2 (B)).

Tejedor-Sanz et al. [18] reported 98% P removal via microbial electrochemical system. Huang et al. [19] reported 23.6 of P removal in voltage of 20 V, NaCl dosage of 6 g/L, and a dolomite dosage of 10 g/L for 270 min by dolomite application for the removal of nutrients from synthetic swine wastewater by a novel combined electrochemical process. They could improve the removal efficiency to 95% by aeration rate of 4 L/min for 120 min.

In this contemporary study, P could be removed completely in a short time, since three kind of treatment methods were applied in a same time.

C. Cadmium Removal

In current research, Cd elimination varied from 77.7% (pH= 7.5 and reaction time = 120 min) to 98.8% (pH= 5.5 and reaction time= 75 min) by using the current combined treatment system. Cd diminished by 98.9% at optimum pH= 5.5 and reaction time= 30.0 min (Fig. 2 (C)).

Qian et al. [20] stated 71% Cr elimination from wastewater via using electrochemical way. Tran et al. [21] described 22.5% metal ion removal from wastewater via electrochemical treatment. Peng et al. [22] eliminated 65% Ni with coated titanium mesh and graphite as cathode and anode at pH = 5 and V (voltage) = 4 for 120 min. Mojiri et al. [4] stated 76.9% to 79.5% metal removal via adsorbent augmented SBR at original pH and contact time = 11 h.

In this contemporary study, COD removal efficiency was more than in literature review, since three kind of treatment methods were applied in a same time.

Final equation in terms of actual factor for COD removal, P elimination and Cd removal are presented as (3)-(5), respectively. They are significant in 0.05.

$$-332.06 + 121.93A - 8.71A^2 - 0.0006B^2 \quad (3)$$

$$-16.03 + 32.59A + 0.05B - 2.35A^2 - 0.0004B^2 \quad (4)$$

$$151.15 - 9.48A - 0.01B \quad (5)$$

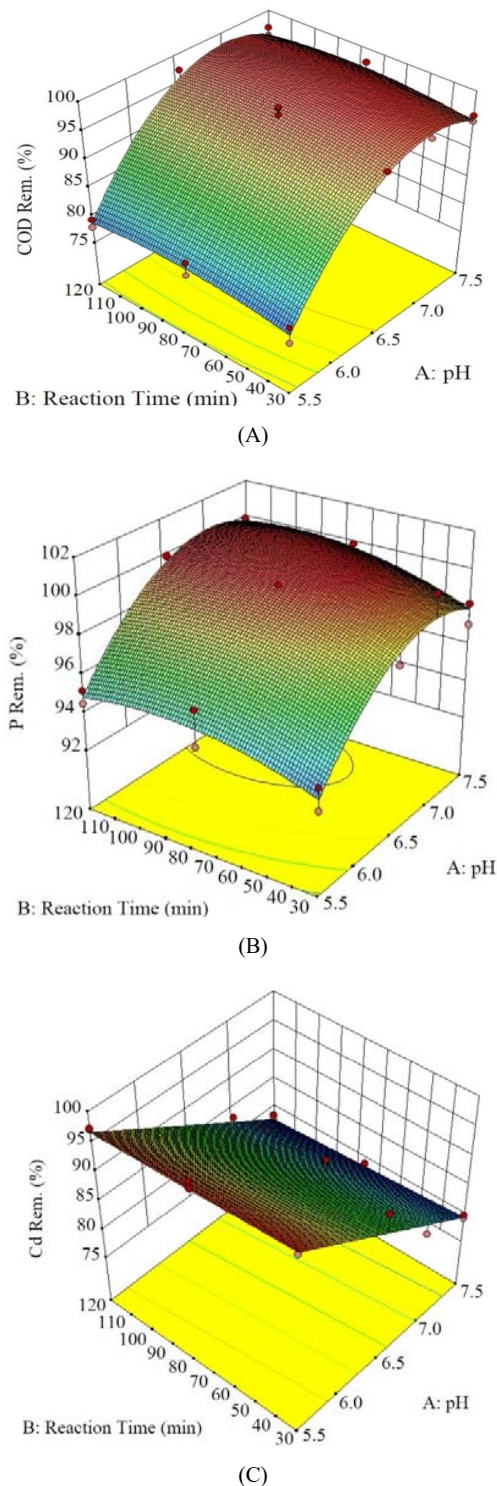


Fig. 2 The 3D surface plots of (A) COD, (B) phosphorous and (C) Cd removal

IV. CONCLUSION

Water pollution is a very vital environmental problem because of overpopulation, industrialization and urbanization.

A combined treatment system comprising EO, adsorption and SBR was applied to treat wastewater during in current study. The designed electrochemical and cockleshell-SBR could remove 97.0%, 99.9% and 88.6% of COD, P, and Cd, respectively at the optimum of pH (6.4) and reaction time (80.0 min).

ACKNOWLEDGMENT

Authors would like to express their gratitude to JSPS (Japan Society for the Promotion of Science) for providing fellowship with the reference number "P17375". This work was supported by JSPS KAKENHI Grant Number JP17F17375.

REFERENCES

- [1] A. E. Burakov, E. V. Galunin, I. V. Burakova, A. E. Kucheroa, S. Agarwal, A. G. Tkachev, and V. K. Gupta, "Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review," *Ecotoxicology and Environmental Safety*, vol. 148, pp. 702-712, 2018.
- [2] A. Latif, S. Noor, Q. M. Sharif, and M. Najeebullah, "Different techniques recently used for the treatment of textile dyeing effluents: A review," *Journal Chemical Society of Pakistan*, vol. 32, pp. 115-124, 2010.
- [3] S. Q. Aziz, H. A. Aziz, and M. S. Yusoff, "Optimum process parameters for the treatment of landfill leachate using powdered activated carbon augmented sequencing batch reactor (SBR) technology," *Sep. Sci. Technol.*, vol. 46, pp. 1-12, 2011.
- [4] A. Mojiri, H. A. Aziz, N. Q. Zaman, S. Q. Aziz, and M. A. Zahed, "Powdered ZELIAC augmented sequencing batch reactors (SBR) process for co-treatment of landfill leachate and domestic wastewater," *J. Environ. Manag.*, vol. 139, pp. 1-14, 2014.
- [5] A. Mojiri, H. A. Aziz, N. Q. Zaman, S. Q. Aziz, and M. A. Zahed, "Metals removal from municipal landfill leachate and wastewater using adsorbents combined with biological method," *Desalin. Water Treat.*, vol. 57, pp. 2819-2833, 2016.
- [6] D. S. Vilar, G. O. Carvalho, M. M. S. Pupo, M. M. Aguiar, N. H. Torres, J. H. P. Américo, E. B. Cavalcanti, K. I. B. Eguiluz, G. R. Salazar-Banda, M. S. Leite, and L. F. R. Ferreira, "Vinsasse degradation using Pleurotus sajor-caju in a combined biological – Electrochemical oxidation treatment," *Sep. Purif. Technol.*, vol. 192, pp. 287-296, 2018.
- [7] C. Barrera-Diaz, P. Canizares, F. J. Fernandez, R. Natividad, M. A. Rodrigo, "electrochemical Advanced Oxidation Processes: An Overview of the Current Applications to Actual Industrial Effluents," *J. Mex. Chem. Soc.*, vol. 58, pp. 256-275, 2014.
- [8] S. Tejedor-Sanz, J. M. Ortiz, and A. Esteve-Núñez, "Merging microbial electrochemical systems with electrocoagulation pretreatment for achieving a complete treatment of brewery wastewater," *Chem. Eng. J.*, vol. 330, pp. 1068-1074, 2017.
- [9] A. Baiju, R. Gandhimathi, S. T. Ramesh, and P. V. Nidheesh, "Combined heterogeneous Electro-Fenton and biological process for the treatment of stabilized landfill leachate," *J. Environ. Manag.*, vol. 210, pp. 328-337, 2018.
- [10] A. Mojiri, H. A. Aziz, and S. Q. Aziz, "Trends in physical-chemical methods for landfill leachate treatment," *J. Sci. Res. Environ. Sci.*, vol. 1, pp. 16-25, 2013.
- [11] A. K. Basumatary, R. V. Kumar, K. Pakshirajan, and G. Pugazhenthir, "Iron(III) removal from aqueous solution using MCM-41 ceramic composite membrane," *Membr. Water Treat.*, vol. 7, pp. 495-505, 2016.
- [12] M. A. Khan, M. I. Khan, and S. Zafar, "Removal of different anionic dyes from aqueous solution by anion exchange membrane," *Membr. Water Treat.*, vol. 8, pp. 259-277, 2017.
- [13] K. Xu, T. Deng, J. Liu, and W. Peng, "Study on the phosphate removal from aqueous solution using modified fly ash," *Fuel*, vol. 89, pp. 3668-3674, 2010.
- [14] I. Nopens, C. Capalozza, and P. A. Vanrolleghem, "Stability analysis of a synthetic municipal Wastewater," *Department of Applied Mathematics, Biometrics and Process Control*, Universiteit Gent, 2001.
- [15] K. Parmar, "Removal of cadmium from aqueous solution using cobalt silicate precipitation tube (CoSPT) as adsorbent," *IJSIT*, vol. 2, pp. 204-215, 2013.
- [16] APHA, "Standard Methods for Examination of Water and Wastewater (20th ed.)," *American Public Health Association*, Washington, DC, USA, 2005.
- [17] V. Markou, M. C. Kontogianni, Z. Frontistis, A. G. Tekerlekopoulou, A. Katsaounis, and D. Vayenas, "Electrochemical treatment of biologically pre-treated dairy wastewater using dimensionally stable anodes," *J. Environ. Manag.*, vol. 202, pp. 217-224, 2017.
- [18] S. Tejedor-Sanza, J. M. Ortiz, and A. Esteve-Núñez, "Merging microbial electrochemical systems with electrocoagulation pretreatment for achieving a complete treatment of brewery wastewater," *Chem. Eng. J.*, vol. 330, pp. 1068-1074, 2017.
- [19] H. Huang, D. Zhang, G. Guo, Y. Jiang, M. Wang, and P. Zhang, "Dolomite application for the removal of nutrients from synthetic swine wastewater by a novel combined electrochemical process," *Chem. Eng. J.*, vol. 335, pp. 665-675, 2018.
- [20] A. Qian, P. Liao, S. Yuan, and M. Luo, "Efficient reduction of Cr(VI) in groundwater by a hybrid electro-Pd process," *Water Res.*, vol. 48, pp. 326-334, 2014.
- [21] T. K. Tran, H. J. Leu, K. F. Chiu, and C. Y. Lin, "Electrochemical Treatment for Wastewater Contained Heavy Metal the Removing of the COD and Heavy Metal Ions," *Inter. J. Eng. Res. Sci.*, vol. 1, pp. 96-101.
- [22] C. Peng, R. Jin, G. Li, F. Li, Q. Gu, "Recovery of nickel and water from wastewater with electrochemical combination process," *Sep. Purif. Technol.*, vol. 136, pp. 42-49, 2014.

Amin Mojiri is currently working as JSPS Research Fellow at Department of Civil and Environmental Engineering, Hiroshima University. He received his PhD in Environmental Engineering- Waste Management in 2015.

Before joining Hiroshima University, he was working as Postdoctoral Research Scholar in University Technology Mara-Malaysia from 2015 to 2017.

Dr. Mojiri could publish more than 40 papers in International Journals. His area of specialization is waste management, waste recycling, wastewater treatment, wastewater recycling, and soil pollutions.

Akiyoshi Ohashi is currently working as Professor at Department of Civil and Environmental Engineering, Hiroshima University. He received his PhD in Engineering and Environmental Engineering in 1994.

Dr. Ohashi published more than 100 papers in International Journals. His area of specialization is biological wastewater treatment, including energy recovery as methane and metals removal.

Tomonori Kindaichi is working as Assistant Professor at Department of Civil and Environmental Engineering, Hiroshima University. He received his PhD in Urban and Environmental Engineering in 2004.

Prof. Kindaichi could publish more than 50 papers in International Journals. His area of specialization is environmental microbiology, and biological wastewater treatment.