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Effect of pH on electrochemical treatment using platinum coated titanium mesh electrodes for post treatment of anaerobically treated sugarcane vinasses

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Abstract

This study examines electrochemical post treatment to remove COD, SS, K+ and Cl- from anaerobically treated sugarcane molasses vinasse (ASMV). A platinum coated titanium mesh was used as an electrode material for both the cathode and anode, with 843.18 cm2 of working area. The effects of pH on removal efficiency, as well as energy and electrode consumption, were investigated. Influent ASMV was diluted 10 times and its initial pH was adjusted by addition of HCl and NaOH. The electrolysis experiment was performed at a current density of 94.88 A/m2 with 15 minutes of reaction time, and the effluent was collected after settling for 90 minutes. The results showed that the treatment efficiency was influenced by the initial pH value. A maximal COD removal efficiency (49.25%) was obtained at a pH of 5.0. For SS removal, the maximal efficiency (46.27%) was obtained at a pH of 10.0, and the lowest level of removal occurred at neutral pH conditions. The maximal efficiency of Cl- removal (17.59%) was obtained at a pH of 8.2 (non-adjusted), and its efficiency was lower when influent was adjusted to acidic and neutral pH conditions using HCl. Maximal efficiency of K+ removal (7.23%) occurred at neutral pH conditions and did not occur at alkaline pH values. Energy consumption was lower under pH-adjusted conditions than under non-adjusted conditions, and electrode consumption was higher in both acidic and alkaline conditions relative to neutral pH conditions.

Keywords: Pt-Ti electrode, Sugarcane vinasse, Electrochemical treatment, pH

1. Introduction

Vinasse, or distillery spent wash, is the wastewater discharged from the distillation process of ethanol production.Most ethanol production in Thailand uses sugarcane molasses as a raw material. For every liter of sugarcane molasses, ethanol production generates 7-9 liters of raw vinasses [1]. The chemical oxygen demand (COD) of sugarcane molasses vinasse (SMV) is extremely high, in the range of 100,000-170,000 mg/l [2]. Anaerobic treatment (methane fermentation process) is usually installed for energy recovery in ethanol plants in Thailand but is limited, as COD removal efficiency performs at a limited 40 – 62%, with the high concentration of inhibitors for methanogens, such as potassium (K^+) and chloride (Cl^-), being problematic for treatment [2]. The treated vinasses with recalcitrant constituents results in a low BOD/COD ratio of 0.11, for which biological treatment as post treatment is difficult [3]. Ethanol plants must have substantial land area reserved for storing anaerobically treated vinasse before distributing it to surrounding farmers for agricultural land use [2].

Electrochemical treatment is fascinating for its advantageous capability to degrade recalcitrant constituents, as well as its advantages of being easy to operate and requiring a short reaction time [4]. Recent studies have reported on the use of electrochemical treatment for alcohol distillery wastewater, especially for SMV [5-9]. Krishna et al. [7] applied aluminum electrode electrochemical treatment to SMV from an anaerobic lagoon at a current density of 0.03 A/cm^2 and a pH of 3, and the COD removal was 72.3%. Manisankar et al. [8] investigated the use of graphite electrode materials and sodium halide electrolytes with 10 times diluted SMV and achieved maximum removal efficiencies of 93.5% BOD and 85.2% COD and 98.0% absorbance reduction. These studies show that the electrochemical pretreatment process results in a high fraction of organic substance removal; and biogas energy, which in using the anaerobic process is targeted for wastewater treatment in ethanol plants, is decreased.

For the electrochemical treatment process, key success factors include: electrode material, pH, electrolyte, temperature, and current density [4]. Platinum modified titanium is one of the more efficient and stable electrode materials [10], yet there has been no research using platinum coated titanium mesh electrodes (Pt-Ti mesh) for electrochemical treatment of SMV. This study aimed to

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conduct preliminary testing of Pt-Ti mesh electrode use in post treatment in order to collect the effluent from the anaerobic process for anaerobic inhibitor removal before feeding it back through the anaerobic circulation process. The study focused on the effect of pH on the removal of chloride (Cl^-) and potassium (K^+), along with COD and suspended solids (SS) removal.

2. Materials and methods

2.1 Characteristics of anaerobically treated SMV

The anaerobically treated SMV (ASMV) used in this study was obtained from a local alcohol distillery plant in Khon Kaen Province, Thailand. Its characteristics are described in Table 1.

Table 1 Characteristics of anaerobically treated sugarcane molasses vinasse (ASMV) used in this study

Parameters (Unit)	Value
pH	7.92
Conductivity (mS/cm)	32.6
ORP (mV)	-219.2
Total COD (mg/l)	57,600
SS (mg/l)	7,583
Cl^-(mg/l)	5,070
K^+(mg/l)	7,800

2.2 Electrochemical reactor setup

Figure 1 depicts the experimental setup of the batch. The electrochemical reactor consisted of a clear, rectangular-shaped PVC plastic tank with 1 L of working volume. Six sheets of Pt-Ti mesh (as shown in Figure 2) were used as electrodes. Electrode dimensions were 70 mm x 150 mm with 1 mm thickness. Electrodes were placed with monopolar electrodes in parallel connections with15 mm electrode gaps. The total immersed area (working area) of electrodes was 843.18 cm^2. A direct current power supply was built specifically for the setup. Current was adjustable from 0 to 10 amperes, and in this experiment the current was fixed at 8 amperes.

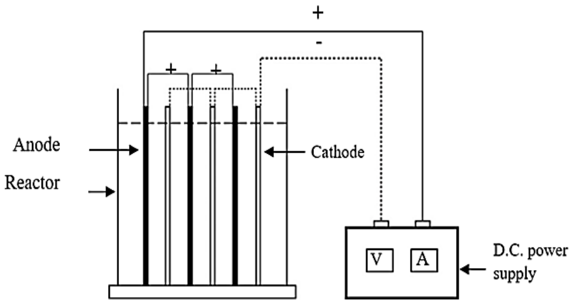

Figure 1 Experimental setup for electrochemical reactor

2.3 Analytical method

Measurements of pH and ORP were made using a microprocessor pH meter (pH 211 HANNA). Conductivity (EC) was measured with a conductivity meter (EZDO 7200). The COD, SS and Cl^- were analyzed following Standard Methods, 18th edition [11], namely, close reflux method, gravimetric method and mercuric method, respectively. An ion electrode method using a HORIBA compact ion meter was applied for K^+measurements.

2.4 Experimental conditions

The experiment was conducted using 10 times diluted ASMV with concentrations of COD, SS, Cl^- and K^+ at 6,096, 620, 490 and 780 mg/L, respectively. Test temperature was room temperature (27±2ºC). ORP and conductivity were 21.0 mV and 4.3 mS/cm, respectively. All test conditions were operated at a current density of 94.88 A/m^2 and given 15 minutes of reaction time. After each experiment and 90 minutes of settlement, effluent was collected from the middle of the reactor tank for quality analysis. The treatment efficiency, or % Removal, was calculated as

$$\% \text{ Removal} = (C_{inf} - C_{eff}) / C_{inf}, \quad (1)$$

Where C_{inf} is influent concentration (mg/L) and C_{eff} is effluent concentration (mg/L).
Energy consumption was calculated as

$$\text{Energy consumption } (kWh/m^3) = U \times I \times t / V, \quad (2)$$

Where U is electric potential difference (volt), I is current (A), t is electrolysis time (h) and V is wastewater volume (L).

2.5 Electrode consumption

All the electrodes before and after the experiment were weighed after drying at 105ºC and left in the desiccator. Electrode consumption was calculated as

$$\text{Electrode consumption } (g/m^3) = (W_1 - W_0) / V, \quad (3)$$

Where W_0 is initial weight of electrodes (g), W_1 is electrodes' weight after experimentation (g) and V is wastewater volume (m^3).

3. Results and discussion

Different initial pH values yielded influent and effluent with the characteristics displayed in Table 2, summarized in terms of pH, conductivity, total COD, SS, Cl^- and K^+.

3.1 pH and conductivity

Table 2 shows that the effluent pH increased from initial pH when initial pH values were 5.0, 7.0 and 8.2 (non-adjusted). In acidic conditions, or at an initial pH of 5.0, hydrogen gas was generated at the cathode according to equation 4. In neutral or alkaline conditions, or at initial pH values of 7.0 and 8.2, a reduction reaction produced hydrogen gas, as in equation 5 [4]. However, with the initial pH at 10.00, the concentration of OH^- increased, resulting in a reverse reaction, as in equation 5, and resulting in a pH decrease from 10.0 to 9.9.

$$2H^+_{(aq)} + 2e \rightarrow H_{2(g)} \quad (4)$$

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \quad (5)$$

The EC of the influent increased when the initial pH was adjusted using HCl and NaOH. This phenomenon occurred because H^+ and OH^- are strong electrolytes, causing these ions to move through solutions very rapidly, and resulting in a higher EC. Moreover, the addition of HCl to decrease pH also increased Cl^-, a support electrolyte effective in COD removal from ASMV [7].

Table 2 The characteristics of influent and effluent at different initial pH values

Parameters (unit)	Influent				Effluent			
	Initial pH							
	5.0	**7.0**	**8.2**	**10.0**	**5.0**	**7.0**	**8.2**	**10.0**
pH	5.0	7.0	8.2	10.0	6.6	8.6	8.9	9.9
Conductivity (mS/cm)	5.5	4.9	4.3	5.0	5.4	4.6	4.0	5.0
Total COD (mg/l)	5,990	6,170	6,080	6,080	3,040	3,580	4,690	4020
SS (mg/l)	560	600	680	670	320	380	400	360
Cl^-(mg/l)	1,390	730	510	550	1290	660	420	540
K^+(mg/l)	870	830	780	630	840	770	740	630

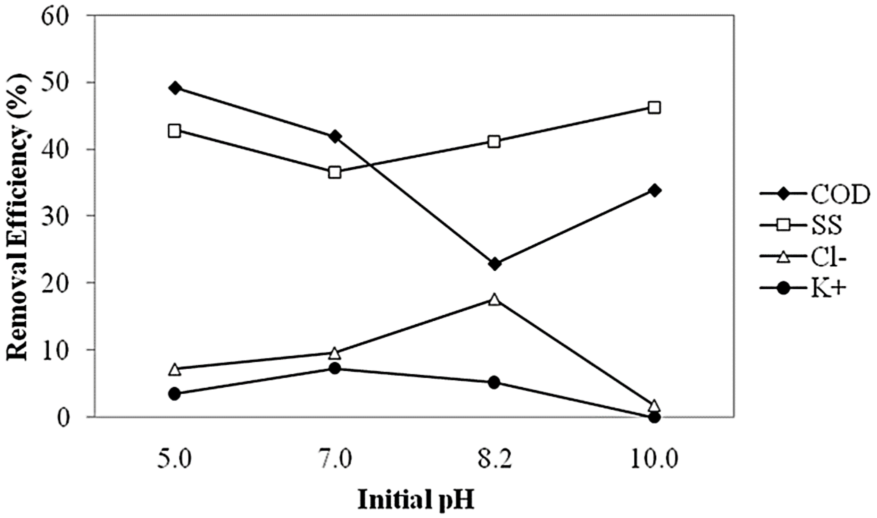

Figure 2 The removal efficiency of COD, SS, Cl^- and K^+

3.2 Efficiency

Figure 4 shows % removal efficiencies for COD, SS, Cl^- and K^+. Non-adjustment conditions, with the initial pH of 8.2, showed removal efficiencies of 22.86%, 41.18%, 17.59% and 5.13%, for COD, SS, Cl^- and K^+, respectively. When the initial pH was adjusted to 5.0, the removal efficiencies were 49.25%, 42.86%, 7.19% and 3.45% for COD, SS, Cl^- and K^+, respectively. At an initial pH of 7.0, the removal efficiencies were 41.98%, 36.67%, 9.59% and 7.23% for COD, SS, Cl^- and K^+, respectively. Finally, at an initial pH of 10.0, removal efficiencies were 33.88%, 46.27%, 1.82% and 0.00% for COD, SS, Cl^- and K^+, respectively.

The COD removal mechanisms in electrolysis are effective due to the presence of chlorides in the influent, as the chloride produces chlorine (Cl_2) (equation 6), and the Cl_2 reacts with water to form hypochloric acid (HOCl) (equation 7).Then, partial dissolution of HOCl produces a hypochlorite ion (OCl^-) (equation 8). The HOCl and OCl^-, as strong oxidants, can cause the oxidation of organic matter in the influent [7, 12]. The ratio of Cl_2, HOCl and OCl^- depends on pH. At a pH lower than 7 or in acidic conditions, Cl_2 is present in the form of HOCl, which possesses higher oxidation potential than that of OCl^-. As a result of these reactions, COD removal efficiencies when the initial pH was adjusted to pH 5.0 and 7.0 were higher relative to the non-adjusted influent, and the maximum COD removal was observed when influent pH was 5.0.

$$2Cl^- - 2e^- \rightarrow Cl_2 \quad (6)$$

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \quad (7)$$

$$HOCl \leftrightarrow OCl^- + H^+ \quad (8)$$

It was found that in acidic and alkaline conditions, hydrogen gas bubbles were more vigorously generated at the cathode during electrolysis than during neutral pH conditions. The bubble generation induced floatation of flocculated particles [12-13], causing SS removal at acidic and alkaline conditions to be slightly higher than in neutral pH conditions.

As for chloride removal, when the initial pH was adjusted to values of 5.0 or 7.0 using HCl, the concentration of Cl^- in the influent was increased to twice as much as in the non-adjusted influent, as shown in Table 2. Consequently, the Cl^- removal efficiency at acidic and neutral conditions was lower than in non-adjusted conditions. On the other hand, when initial pH was adjusted to 10.0, the initial Cl^- concentration had negligible change relative to the non-adjusted pH sample, but the chloride removal of the former was 16% lower than that of the latter. When pH is set at a higher pH, above 7.0, there is virtually no evolution of Cl_2 gas, and Cl_2 presents in the form of ClO^-, which has lower oxidation potential relative to HOCl. This may explain why at an initial pH of 10.0 there was lower Cl^- removal relative to the initial pH of 8.2 or non-adjusted pH conditions.

The performance of K^+ removal in all conditions was poor, with the initial pH at 10.0 showing the lowest results, and the initial pH at 7.0 showing the highest results. The difference in value between the lowest and highest removal was only 7.23%. It can be concluded that Cl^- and K^+ removal did not occur when using Pt-Ti mesh electrode.

3.3 Energy consumption and electrode consumption

Table 3 presents the energy consumption and electrode consumption required per one volume of the batch experiment at different initial pH values. Energy consumption was decreased when the initial pH was adjusted. The decrease was due to the addition of support electrolytes in the form of H^+, Cl^-, Na^+ and OH^- into the test ASMV, resulting in an increase in EC when the initial pH was adjusted. Consequently, the movement of ions was more fluid than in the non-adjusted pH sample, reducing electrolysis cell resistance. The voltage between electrodes was subsequently reduced, resulting in energy consumption calculated according to equation 2 [9].

As for electrode consumption, more fluid movement of ions in the electrolyte solution under acidic conditions led to higher electrode consumption, as shown in Table 3. Electrode consumption was highest with the initial pH of 5.0.

Table 3 Energy and electrode consumption

Initial pH	Energy consumption (kWh/m^3)	Electrode consumption (g/m^3)
5.0	19.13	2.500
7.0	20.40	0.300
8.2 (original pH)	21.62	1.400
10	19.73	1.000

4. Conclusion

Maximum COD removal efficiency achieved at an initial pH of 5.0, or acidic conditions, with 42.86% removal efficiency,and non-adjusted pH conditions (pH 8.2) resulted in the lowest efficiency. Maximum SS removal efficiency was attained at an initial pH of 10.0, and neutral pH conditions resulted in the lowest efficiency. At all adjusted initial pH values, Cl^- removal was lower than for non-adjusted conditions. Especially acid and neutral pH conditions adjusted using HCl solution resulted in increased Cl^- concentrations in the influent. In contrast, the maximum K^+ removal was attained in neutral pH conditions, with only **7**.23% removal efficiency, and K^+ removal did not occur in alkaline conditions. Energy consumption of treatment in pH-adjusted conditions was lower than non-adjusted conditions, because the electrical conductivity of the influent was increased when the initial pH was adjusted. Electrode consumption was higher in both acidic and alkaline conditions and lowest in neutral pH conditions.

5. Acknowledgements

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6. References

[1] Choeisai P. Anaerobic biodegradation of ethanol distillation plant wastewater. In: Suwannarat K, Wirojanagud W, Chaowakitchareon P, Pitayasoponkij M, Tangtrakarnpong D, Thongsanit P, editors. The proceeding of national environmental conference; 2007 March 7-9; Pitsanulok, Thailand. Thailand: Environmental Engineering Association of Thailand; 2005. p. 1-8.

[2] Mawangnutoon N, Choeisai P, Syutsubo K. Anaerobic wastewater treatment system applied for sugarcane molasses ethanolplants in Thailand. In: Wongratanacheewin S, Tattawasart U, Punratanasin P, Nethanomsak T, editors. The proceeding of national and international graduate conference; 2016 January 15; Khon Kaen, Thailand. Khon Kaen: Graduate School, Khon Kaen University; 2016. p. 96-101.

[3] Choeisai P, Jitkam N, Silapanoraset K, Yubolsai C, Yoochatchaval W, Yamaguchi T, et al. Sugarcane molasses-based bio-ethanol wastewater treatment by two-phase multi-staged up-flow anaerobic sludge blanket (UASB) combination with up-flow UASB and down-flow hanging sponge. Water Sci Tech. 2014; 69(6):1174-80.

[4] Chen G. Electrocoagulation technology in wastewater treatment. Separ Purif Tech. 2004;8:11-41.

[5] Kumar M, Ponselvan FIA, Malviya JR, Srivastava VC, Mall ID. Treatment of bio-digester effluent by electrocoagulation using iron electrodes. J Hazard Mater. 2009;165:345-52.

[6] Tsioptsias C, Petridis D, Athanasakis N, Lemonidis I, Deligiannis A, Sanaras P. Post-treatment of molasses wastewater by electrocoagulation and process optimization through response surface analysis. J Environ Manag. 2015;164:104-13.

[7] Krishna BM, Murthy UN, Kumar BM, Lokesh KS. Electrochemical of distillery wastewater using aluminum electrode. J Appl Electrochem. 2010;40: 663-73.

[8] Manisankar P, Rani C, Viswanathan S. Effect of halides in the electrochemical treatment of distillery effluent. Chemosphere. 2004;57:961-6.

[9] Asaithambi P, Sajjadi B, Aziz ARA, Daud EMABW. Performance evaluation of hybrid electrocoagulation process parameters for the treatment of distillery industrial effluent. Process Saf Environ Protect. 2016;104:406-12.

[10] Abdel Rahim MA, Hassan HB. Titanium and platinum modified titanium electrodes as catalysts for methanol electro-oxidation. Thin Solid Films. 2009;517:3362-9.

[11] American Public Health Association/American Water Works Association/Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. 18th ed. Washington DC, USA: American Public Health Association/American Water Works Association/Water Environment Federation; 1992.

[12] Bensadok K, Hanafi NEl, Lapicque F. Electrochemical treatment of dairy effluent using combined Al and Ti/Pt electrodes system. Desalination. 2011;280: 244-51.

[13] Zuo Q, Chen X, Li W, Chen G. Combined electrocoagulation and electroflotation for removal of fluoride from drinking water. J Hazard Mater. 2008;159:452-7.