RESEARCH ARTICLE

Effect of salt concentration on the properties of electrolyzed reducing water (ERW) and electrolyzed oxidizing water (EOW): an empirical correlation study

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OBJECTIVES This research aimed to examine the effect of NaCl concentration on the pH and Oxidation Reduction Potential (ORP) values of both EOW and ERW products. METHODS The experiment was conducted using distilled water. The electrolysis apparatus consisted of anode and cathode chambers. The chambers were connected by a tube filled with a cotton (or a fabric). Both electrodes (anode and cathode) were made of titanium and formed as a spiral. Electrolysis was performed for 780 minutes, and the pH and ORP values of both EOW and ERW were measured every time. Sodium chloride concentration was varied for 0, 100, and 200 ppm. RESULTS Experimental results revealed that the higher the NaCl concentration, the higher ERW's pH rise and the lower the EOW's pH. Similar results were found for ORP. ERW's ORP was lowered while EOW's ORP rose with the increase in NaCl concentration. CONCLUSIONS This study could also generate a mathematical model that correlates pH and time during the electrolysis process. The model was developed by connecting with a simple polynomial. A similar approach was used to develop the model that correlates pH and ORP value.

1. INTRODUCTION

Electrolysis is considered one of the electrochemical processes that have many applications. The process is carried out in a chamber using a positive electrode (anode) and a negative electrode (cathode). Redox reaction, which takes place in the reactor, is influenced by several factors, including applied voltage, electrodes material, ion content, electrolyte, etc (Moore et al. 2001; Chakik et al. 2017). Electrolyzed water (EW) is usually produced by electrolyzing water with dissolved NaCl. To produce EW, it is needed to use two chambers due to the generation of two products, which are electrolyzed oxidizing water (EOW) and electrolyzed reducing water (ERW).

Electrolyzed reducing water (ERW), which has a benefit for health is also one of the forms of functional water (Shirahata et al. 2012). The definition of functional water itself, which The Functional Water Association of Japan defines, refers to the water that exhibits a specific function after it has been activated by a certain method, such as electrolysis, magnetic field treatment, etc (Shirahata et al. 2012). Moreover, the application of ERW as health-beneficial water has been studied by the Ministry of Health, Labour and Welfare of Japan for several years. In addition, reduced water intake has also shown a positive effect on radiation-induce oxidative stresses with the presence of oxidative stress which is induced by radiation treatment (Kang et al. 2011). Another study also reported that reduced water was also able to increase antioxidant capacity, which led to the reduction of inflammatory response in adults (Sim et al. 2020). Furthermore, reduced water consumption may also enhance the detoxification process (Yao et al. 2019).

Electrolyzed oxidizing water (EOW) has attracted attention for sanitizing purposes due to its vast application. Several reasons that make EOW pretty popular are due to its ease

in the making process, does not contain harmful chemicals, and applicable for many fields (agriculture, medical sterilization, food stock, etc) (Al-Haq et al. 2005; Liu et al. 2021; Rahman et al. 2016). This correlates with the properties of EW that can be prepared in various pH values, allowing multipurpose usage (Al-Haq et al. 2005; Liu et al. 2021; Rahman et al. 2016). There is also the opinion in regards to the application of EOW for drinking purposes, such as the regulation from the European Union (EU) and the United States (Rahman et al. 2016).

For both EOW and ERW, pH and ORP are among the important parameters that should be considered. The reduced water has a pH of around 11 while the oxidized water has a pH of around 2.5 (Su et al. 2007). The basic properties of ERW can reduce free radical in a biological environment, while the acidic properties of EOW had the main role for bactericidal purposes (Su et al. 2007). In addition, bacteria also only live in an environment with a particular range of oxidation-reduction potential (ORP). As EOW and ERW have a very positive and negative ORP, the metabolism of the bacteria is also affected (Fukuzaki 2006; Rahman et al. 2016). Sanitizing properties or germicidal effect of electrolyzed water are mainly caused by chlorine species present in the solution such as Cl_2, HClO, and ClO^- (Fukuzaki 2006; Rahman et al. 2016). The previous study stated that only HClO can penetrate the microorganism cell wall leading to deactivate deactivation it (Fukuzaki 2006). The ClO^- is only able to destroy the outer part of the cell, thus less effective compared to HClO (Fukuzaki 2006; Rahman et al. 2016).

To achieve that certain value of pH and ORP, another compound, which is chlorine salt, must be added. Among several types of chlorine salt, NaCl is preferred due to its availability and economic feasibility. During the process, the components (both NaCl and water) are present in its ions. The positively charged ion (Na^+ and H^+) will move to the cathode in which NaOH and hydrogen gas are generated. On the other hand, the negatively charged ion will migrate to the anode to form HClO, ClO^-, HCl, O_2, and Cl_2 (Al-Haq et al. 2005; Rahman et al. 2016; Su et al. 2007). The pH value is very important for performing the disinfecting as it influences the formation of various chlorine substances, which will be favorable in the form of HClO (pH 5–6.5) (Cao et al. 2009).

To produce EOW and ERW with specified properties, electrolysis process must be carried out using suitable conditions. The electrolysis process is generally affected by several factors, such as NaCl concentration in the water. It is because those parameters can affect the reaction that takes place during electrolysis, which in turn changes the properties of EW. Even though studies of the application of EOW and ERW are quite extensive (Rahman et al. 2016), to provide a comprehensive viewpoint, it is necessary to develop a mathematical correlation. This mathematical correlation so far has not been systematically developed in previous studies related to electrolyzed water.

2. RESEARCH METHODOLOGY

2.1 Materials

The material used in this research were distilled water and sodium chloride (NaCl). The distilled water used had pH, TDS, and ORP of 7.6, 52 ppm, and 190 mV respectively. Sodium
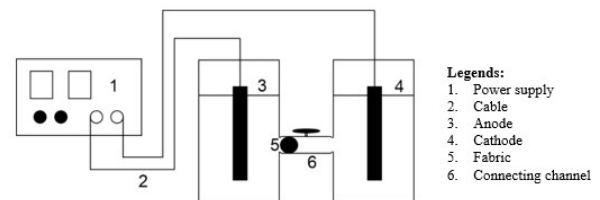

FIGURE 1. Electrolysis apparatus schematic.

chloride was obtained from Merck with a purity of 97%. Titanium wire having a diameter of 1.5 mm and length of 6.5 m was formed into a spiral (with a surface area of 0.031 m^2) and were used as electrodes both in anode and cathode chambers.

2.2 Procedures

This experiment was conducted in 2 food-grade plastic containers acting as an anode chamber and cathode chamber, respectively. Both chambers were filled with 1500 mL distilled water. The two chambers were connected by a tube/channel filled with cotton (or fabric) acting as a membrane, to facilitate the counter-ion migration. The selection of the electrode material was based on the potential reduction data to make sure that the electrode is not consumed during the process (Moore et al. 2001). The electrodes were connected to a constant power source having a DC voltage of 110 Volt. The experiment was carried out for 780 minutes. The pH, ORP, and TDS in each chamber were measured in situ from time to time. The measurement was conducted every 5 minutes for the first 60 minutes. The time increment for measurement was longer from the minute of 60 up to the minute of 780. The experiments were repeated for 3 different NaCl concentrations, which were 0, 100, and 200 ppm. The measurement of pH, ORP, and TDS were conducted using a pH meter, ORP meter, and TDS meter.
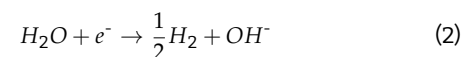
2.3 Mathematical modelling
2.3.1 Correlation of pH and time

During electrolysis, there are several reactions that take a place. However, since water is the main component, it can be assumed that the main reactions of the water electrolysis are as follows:
Anode:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad (1)$$

Cathode:

$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \qquad (2)$$
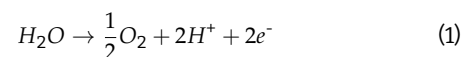
It is implied that the H^+ concentration will be influenced by the initial H^+ concentration and the one generated from the anode reaction. This correlation can be written as follows:

$$[H^+]_{\text{total}} = [H^+]_0 + [H^+]_{\text{reaction}} \qquad (3)$$

With $[H^+]_{\text{total}}$, $[H^+]_0$, and $[H^+]_{\text{reaction}}$ are H^+ total, initial present in water and from reaction respectively. The H^+ concentration produced from the reaction is always chang-
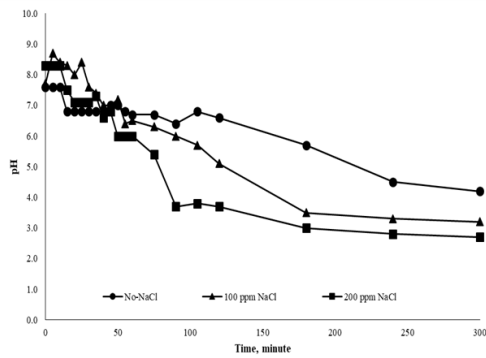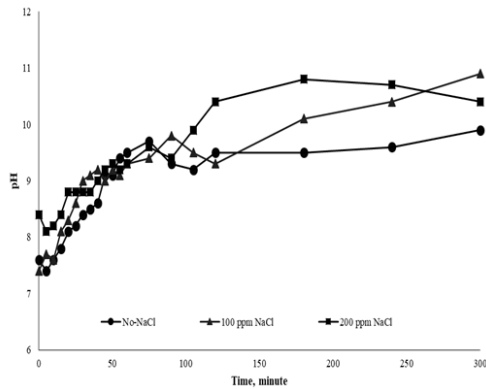
FIGURE 2. pH values of: (a) EOW and (b) ERW for different NaCl concentration.

FIGURE 3. ORP values of EOW and ERW for different NaCl concentration: (a) Anode side; (b) Cathode side.

ing as the reaction occurs. Since the reaction is also time-dependent, it is also logical to assume that the change of H^+ is also time-dependent. However, such a correlation is still unknown. To approach the phenomenon, firstly, it is considered that:
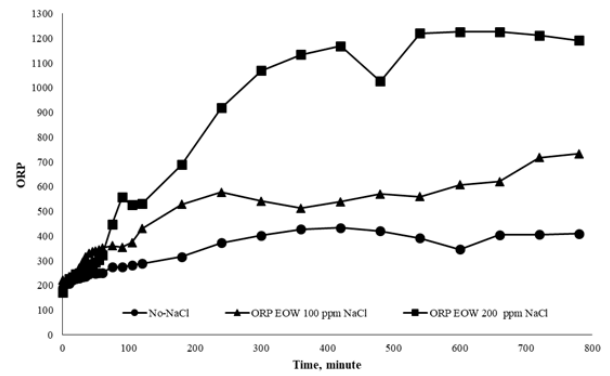
$$[H^+] \propto e^-_{anode} \qquad (4)$$

With e^-_{anode} corresponds to the number of electrons involved in $[H^+]$ production reaction. Basic electrochemistry provides that the coulomb is the number of electrons that passes at a certain point at a certain time. Since it is known that to produce 1 coulomb of charges (Q) requires 6.24×10^{18} electrons, it is possible to estimate the number of electrons that are involved during by Equation 5:

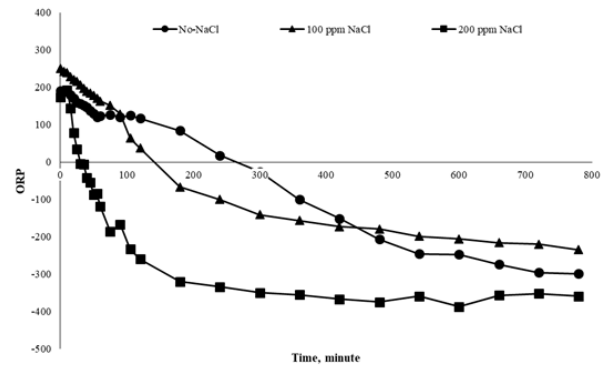$$e^-_{total} = \frac{Q}{6.24 \times 10^{18}} \qquad (5)$$

While Q is the charge that occurs during the process, it is also known that:

$$e^-_{total} = \frac{\varphi \cdot i \cdot t}{6.24 \times 10^{18}} \qquad (6)$$

With φ, i, and t are constant, current and electrolysis time, respectively. If the constant part of the equation is combined into another constant α, Equation 3 is changed into Equation 7. Notice that the current "i" is also changed into "f(t)" to emphasize that current will change with time with a certain trend. In this experiment, electrical current was not measured due to its value that keeps changing due to the change of ionic composition in the system. As in this experiment, the value of the current is not measured, it is then approached

that the current follows Equation 8.

$$[H^+] \propto a \cdot t \cdot f(t) \qquad (7)$$

$$\cdot f(t) = a + b \cdot t \cdot \qquad (8)$$

Modifying Equation 3 with previous equations will result in:

$$[H^+]_{total} = [H^+]_0 + \alpha(a + b \cdot t) \cdot t \qquad (9)$$

Correlating Equation 9 with the definition of pH will produce Equation 10:

$$pH = -log[H^+]_0 + \alpha(a + b \cdot t) \cdot t \qquad (10)$$

Expansion of Equation 10 will produce polynomial as follows:

$$pH = a' + b't + c't^2 \qquad (11)$$

This equation will then be analyzed with experimental data to determine its constant. In addition, Equation 11 is also valid for the cathode side as there is a correlation between pH and pOH.

2.3.2 Correlation of pH and ORP

As ORP is also an important parameter for EOW, it is also interesting to study the correlation of ORP with another water characteristic, which in this case is pH. Using a similar approach as in 2.3.1, it is known that pH correlates with O_2 and H^+ in the system. The following are the equations at anode and cathode chambers:
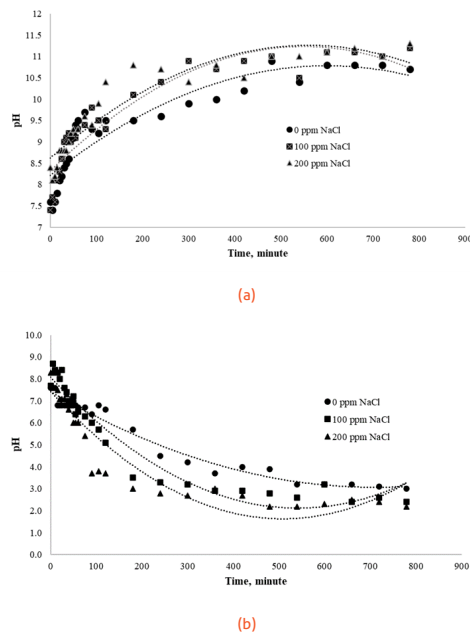
FIGURE 4. Curve-Fitting of pH-time correlation equation with experimental data: (a) Cathode side (ERW); (b) Anode side (EOW).

At anode chamber

Based on Equation 1, Equation 12 can be developed as follows:

$$(ORP)_{\text{anode}} \propto [O_2] \, and \, [H^+] \quad (12)$$

Because $[O_2] = \frac{1}{4}[H^+]$
Then:

$$(ORP)_{\text{anode}} \propto [H^+] \quad (13)$$

Using a similar approach, Equation 13 can be changed into:

$$(ORP) \propto pH \quad (14)$$

or

$$(ORP) = a + b \cdot pH + c \cdot pH^2 \quad (15)$$

At cathode chamber

$$(ORP)_{\text{cathode}} \propto [H_2] \, and \, [OH^-] \quad (16)$$

Then:

$$(ORP)_{\text{cathode}} = f[OH^-] \quad (17)$$

Because:

$$[OH^-] = \frac{K_w}{[H^+]} = K_W[H^+]^{-1} \quad (18)$$

Then:

$$(ORP)_{\text{cathode}} = f\left\{K_W[H^+]^{-1}\right\} = g\{[H^+]\} \quad (19)$$

$$(ORP) \propto g\{[H^+]\} \quad (20)$$

$$(ORP) = a' + b' \cdot pH + c' \cdot pH^2 \quad (21)$$

3. RESULTS AND DISCUSSION

3.1 Experimental result

The change of pH as the function of NaCl concentration and time is shown in Figure 2. Based on Figure 2, it can be observed that insignificant change occurred during the first 100 minutes of the process before showing a clearer effect and progressing steadily. Based on Figure 2, it was observed a distinct region of pH changes both for EOW and ERW. However, the effect of NaCl concentration was more clearly observed for EOW. In EOW, the low value of pH is caused by various Cl-based acids due to the reaction between Cl_2^- in the anode with water, forming Cl^-, ClO^-, and H^+ as expressed in Equation 3 (Rahman et al. 2016). The contribution of these acidic substances caused the pH to drop even further as the process took place. On the other hand, the formation of OH^-, followed by the reaction of Na^+ with OH^- to form NaOH increased the pH of ERW, producing alkaline water. Since there is an only a base constituent in the ERW, the increase in pH did not significantly occur. In addition, it can be seen that higher salt concentration will result in lower pH in EOW and the other way around for ERW. This result was similar to previous work by Kim et al. (2019) and Pangloli and Hung (2013) which reported that increasing water hardness produced a lower pH value for EOW.

As for pH, Figure 3 showed that the ORP values of EOW and ERW were located in a different regions. Based on Figure 2 and 3 comparisons, ORP correlates with the value of pH oppositely. It can be seen that ERW which has higher pH had the ORP value in the lower region, indicating its stronger reductive properties. A similar trend was found for EOW, where the lower the pH, the ORP of EOW was higher, indicating higher oxidative properties. Further changes in ORP values also corresponded to NaCl concentration, in which higher NaCl concentration produced a more negative ORP for ERW and a more positive for EOW. This correlation between higher salt concentration and ORP value was also found by Ampiaw et al. (2021). Other studies presented that the value of ORP for EOW is ≥1100 mV while it is ≤800 mV for ERW (Al-Haq et al. 2005; Hsu 2005). Although the ORP of EOW was already similar to the previous value, the result is quite different from the ORP of ERW. This corresponds also to the pH of ERW which is less than 11 as mentioned in several studies (Hsu 2005; Su et al. 2007). That phenomenon might indicate that the added salt concentration is still relatively low.

3.2 Mathematical correlation

To give a more comprehensive result to the study, experimental data was also plotted using the aforementioned model. This will provide information on whether the model suits ex-
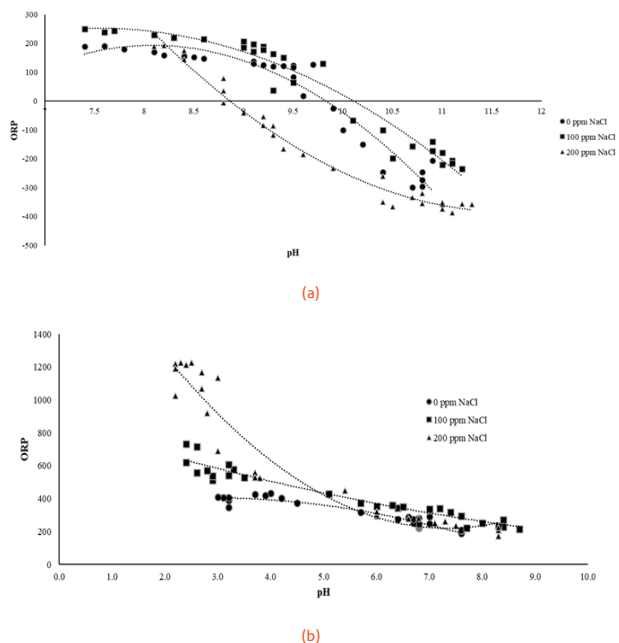
(a)

(b)

FIGURE 5. Curve-Fitting of ORP-pH correlation equation with experimental data: (a) Cathode side (ERW); (b) Anode side (EOW).

perimental data. Based on Figure 5a and 5b, it is revealed that the second-order polynomial model produces relatively fit data for both the anode and cathode sides. Previous study by Syaichurrozi et al. (2021) also revealed that the second-order polynomial fit with experimental data. However, there was no other discussion of the theoretical background of the model development.

The polynomial parameter for Figure 5 was then presented in Tables 1 and 2. The value of R-square which is in the range of 0.82–0.97 indicated that the polynomial approached was not perfectly representative of the phenomenon taking place. However, by examining the magnitude of the a' parameters, it is implied pH did not significantly change with the increase of time as the value of b' and c' (which correspond to the time variable) have very small values. On the other hand, Figure 4 has shown that it seems there is a quite significant pH increase in the first 100 minutes of the experiment. This

might be attributed to the increased mass transfer resistance as well as the depletion of reacting species in the system.

In addition, Table 1 also represented that the changing pH with NaCl concentration is not wide at the beginning of the process, then the gap starts to increase as the influence of time on b' rises. This is probably because at longer reaction time, there is not enough Cl^- to form other species that causes pH to change more, compared with another system with higher NaCl concentration. However, Table 2 shows that the change in NaCl concentration from 100 to 200 ppm is not as high as from 0 to 100 ppm, while this change is relatively similar to Table 1 (anode side). This is probably due to the generation of various Cl^- based substance that causes pH to decrease further as its presence in the water becomes high.

The second-order polynomial also worked well on the correlation between ORP and pH data as presented in Figure 5, which were then analyzed with R^2 calculation. Based on the calculation of Figure 5, it was found that the R^2 value is between 0.8–0.98 which corresponds to the fitness of the experimental data and model. This, in turn, will be useful to predict the time or salt concentration to achieve certain values of pH and ORP.

The polynomial parameters are presented in Tables 3 and 4. Scrutinizing the polynomial parameters will provide information that the ORP changes with pH as each parameters have comparable values. Moreover, a quite strong correlation was observed in Table 4 (for the anode side). This can be an indication that the change of ORP in the anode side was mainly caused by reactions that involve H^+ and the other way around for the cathode side. An interesting phenomenon is also recorded in Figure 5b or Table 4 as a significant change of ORP due to NaCl the increase of NaCl concentration was observed mainly in low pH value, while the presence of the substances will cause a high increase of ORP. The phenomenon can probably be caused by the increase of Cl-based substances in anode side as higher NaCl concentration is exhibited in the system. Figure 4 informs that higher NaCl concentration will lead to lower pH value.

TABLE 1. Polynomial parameters for pH-time correlation in the cathode side.

Conc. NaCl	Parameter			
	a'	b'	c'	R^2
0 ppm	8.2156	0.0086	-7.0.E-06	0.8256
100 ppm	8.3265	0.0106	-1.0.E-05	0.8922
200 ppm	8.621	0.0086	-8.0.E-06	0.8256

TABLE 2. Polynomial parameters for pH-time correlation in the anode side.

Conc. NaCl	Parameter			
	a'	b'	c'	R^2
0 ppm	7.4196	-0.0122	9.00E-06	0.9703
100 ppm	8.0763	-0.022	2.00E-05	0.9431
200 ppm	7.4399	-0.0228	2.00E-05	0.8895

TABLE 3. Polynomial parameters for ORP-pH correlation in the cathode side.

Conc. NaCl	Parameter			
	a'	b'	c'	R^2
0 ppm	-3955.8	1026.3	-63.473	0.931
100 ppm	-1918.4	576.02	-38.21	0.946
200 ppm	6220.3	-1131.1	48.428	0.981

TABLE 4. Polynomial parameters for ORP-pH correlation in the anode side.

Conc. NaCl	Parameter			
	a'	b'	c'	R^2
0 ppm	331.6	52.939	-9.418	0.911
100 ppm	857.81	-101.45	3.3692	c
200 ppm	2213.4	-543.43	37.04	0.935

4. CONCLUSIONS

In this research, the effect of NaCl concentration on the properties of electrolyzed water (EOW and ERW), which is represented by pH and ORP was studied. It was observed that pH will decrease along with the addition of NaCl in EOW, while it was the other way around for the ERW. The ORP value also varied as NaCl concentration increased. It caused the ORP of EOW to rise, indicating its stronger potential as an oxidizing agent. On the other side, it declined the ORP value of ERW, showing its potential as a reducing/anti-oxidizing agent. Moreover, it was also shown that the correlation of pH and time can be performed using the second-order polynomial. This approach also produced a good fit with experimental data between ORP and pH. Further examination of the polynomial parameters revealed that the change of pH was significantly correlated to NaCl concentration rather than time.

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