Removal of bromide from raw water in drinking industry by electrochemical method with horizontal rotating anode reactor

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A B S T R A C T

Drinking water industries in Indonesia generally use the ozonation method as a disinfection process (more than 90%). However, it has a negative effect in oxidizing bromide (Br–) into bromate, which is a carcinogenic compound associated with several clinical symptoms, such as nausea, vomit and even kidney failure. Meanwhile, bromide anion is thermodynamically easy to be oxidized into bromine (E°: 1.074 V), resulting in an effective removal of bromide. A double-chamber electrocatalytic reactor with a working volume of 100 L was made with platinum-doped carbon cloth, copper, and proton exchange membrane as anode, cathode, and separator, respectively. The reactor was designed as a horizontal rotating drum electrocatalytic reactor which will accelerate the oxidation of Br–/Br2 and enhance the transfer rate of Br2 from liquid to gas phase. Potential, flowrate, anode rotation speed and salt concentration were chosen as evaluated parameters. Bromide concentration of 0.3858 mg/L was significantly reduced (93%) at 8.7 L/min flowrate, 7 V potential, 2.3 A current, and 100 mg/L salt concentration. Raw water containing 0.3858 mg/L of bromide, which resulted in 0.3 mg/L bromate after ozonation and reduced to 0.002 mg/L and was able to meet the requirements of SNI 3553 or 6241. Total energy consumption to remove bromide was about 8.17 kJ/g Br or 1.2 IDR/L raw water.

Keywords: Bromide; Bromate; Microporous layer carbon cloth; Pt-carbon cloth; Horizontal rotating drum electrocatalytic reactor reactor

1. Introduction

Freshwater is the main requirement for the human body because it contains no calories, diuretics, preservatives and dyes. Teens and adults generally need 8 glasses of water per day, though it is highly varied and depending on age, weight, existing disease, and climate. There are approximately 700 drinking water industries in Indonesia, published in more than 2,000 brands. Most of those industries use ozonation as a sterilization method, as it is an established and low-cost method. Several researchers reported that ozonation contributed to the formation of halogen compounds, such as bromate, as ozone (O3) reacted with bromide (Br–) [1–3]. Naumov and von Sonntag [4] also reported a mechanism of bromate formation based on bromide and ozone, that is, [4]:

\[ \text{Br}^- + \text{O}_3 \rightleftharpoons \text{BrOOO}^- \]  

(1)

\[ \text{BrOOO}^- \rightarrow \text{BrO}^- + \text{O}_2 \]  

(2)

\[ \text{BrO}^- + \text{O}_3 \rightarrow \text{BrO}_2 + \text{O}_2 \]  

(3)

\[ \text{BrO}_2 + \text{O}_3 \rightarrow \text{BrO}_3 + \text{O}_2 \]  

(4)

Furthermore, the Indonesian government has determined a maximum standard of bromate, that is, less than...
0.01 mg/L for mineral and demineralized water, as mentioned in SNI 3553:2015 and 6241:2015, respectively.

One of the testing laboratories mentioned that approximately 11% of drinking water industries in Indonesia still contain more than 0.01 mg/L of bromide in their products. This report indicates that raw water used in their process potentially contains bromide. Furthermore, a report described an analysis of several water springs in Indonesia which contain bromide, ranging from 0.0147 to 0.15 mg/L. Quite significant contents of bromide (<0.05–3 mg/L) were detected in groundwater and surface water in Perth, Australia. The presence of bromide in water was possibly caused by the specific characteristic of rocks and also influenced by residues of human activities, such as coal-fired power plants, industrial effluent and wastewater treatment plants [5]. Based on the above-mentioned reasoning, it is important to remove bromide from raw water to minimize the content of bromide after the ozonation process. Bromide removal is also urgent, considering it is potential to form brominated disinfection by-products (DBPs), a naturally carcinogenic compound in drinking water [6,7]. Bromate formation in water processing is based on the reaction:

\[ 2\text{Br}^- + 7\text{H}_2\text{O} \rightarrow \text{Br}_2 + 14\text{H}^+ + 10\text{e}^- \]

WHO also mentioned that brominated DBPs is much more dangerous than chlorinated DBPs [8,9].

To date, the bromide removal method was reported scarcely in literature. Several methods like, for instance, adsorption using silver-doped activated carbon aerogels [10], coagulation using Al [11,12], and ion exchange [13] are commonly used for the removal. However, in those methods, Br⁻ removal is in competition with Cl⁻ removal. Other methods such as thermal distillation, reversed osmosis, nanofiltration, electrodialysis, and deionization [14,15] need high energy consumption [16]; they estimated minimum energy consumption of 11.412.214 kJ/g Br. Electrolysis-based direct oxidation of bromide into bromine has been studied for drinking water treatment [17–19] and bromine production from brine [15,20]. A substantially low energy profile was observed from this method, at a range of 1.3–4 kJ/g Br [16]. However, this configuration produced approximately only 60% efficiency and relatively ineffective for the low content of bromide. Moreover, an additional media of compressed air from the base of the reactor is needed to remove bromine.

This article examines and reports the performance of bromide removal unit in an adapted cell configuration for industrial application, called horizontal rotating drum electrocatalytic (HRDE) reactor. It was assembled and tested on one of the drinking water industry on specific variables, such as flow rate (4.8, 7.8, and 10 L/min), potential (5, 7, 7.5, and 8 V), rotor speed (30 and 120 rpm), and type of anode (MPL carbon cloth and Pt-carbon cloth).

2. Material and methods

2.1. Experimental methodology

HRDE reactor was constructed using microporous layer (MPL) carbon cloth (CeTech carbon cloth with MPL-W1S1009; 100 cm × 40 cm), Pt/C 40% (Cloth GDE -0.3 mg/cm³ Pt/C 40%, 100 cm × 40 cm), stainless steel roll, copper plate, food-grade stainless steel chamber box, electromotor (Tyrone-0.37 kW–1,450 rpm), variable speed drive (Schneider Electric) and PEM (proton exchange membrane, based on chemically stabilized perfluorosulfonic acid, 30 cm × 30 cm).

The reactor was supported by a power supply (rectifier 12 V, 100 A, PT. Rekayasa Plating), feeding tank, pump, reservoir tank, and circulation system. Raw water was taken from PT. Indotirta Jaya Abadi, Central Java, Indonesia. Other reagents, that is, kalium bromide (Merck Pro-analysis, 1.04905.0500), phenol red (Merck Pro-analysis, salt indicator 1.11748.0005), chloramine-T (Merck Pro-analysis, 1.02426.1000), and Natrium thiosulfate pentahydrate (Merck Pro-analysis) were used for bromide analysis.

The reactor was installed and then operated by feeding raw water at 4, 8 L/min, while DC current and electromotor were connected. The potential was set from the lowest, that is, 5 V, while the speed of the rotor at 30 rpm. The experiment was evaluated based on several variables, such as flow rate (4.8, 7.8, and 10 L/min), potential (5, 7, 7.5, and 8 V), rotor speed (30 and 120 rpm), and type of anode (MPL carbon cloth and Pt-carbon cloth).

2.2. Analytical methods

This study examines the above-mentioned variables by measuring the content of bromide based on an International Standard (SM: 4500-Br-B). Bromide measurement was performed by adding 2 mL acetate buffer solution, 2 mL phenol red solution and 0.5 mL of chloramine-T solution into 50 mL of samples or standards. After 20 min, the solution was dechlorinated using 0.5 mL Na₂S₂O₃ solution and then read in UV-Vis Spectrophotometer at 590 nm. The standard curve for bromide analysis is depicted in Fig. 2, which was obtained by using a spectrophotometer (Shimadzu A.1163580548).

The curve fit the six-point calibration well with the coefficient of correlation (R²) 0.99574 and can be used in bromide concentration measurement.

Bromate concentration was determined using the ion chromatography method. Potassium bromate, KBrO₃ (Merck) was used in spiked samples to ensure the accuracy of sample analysis. Distilled water was used for the preparation and dilution of the bromate stock solution. As the preparation of spiked samples, aliquots of the intermediate stock solution were accurately weighed and diluted.

![Fig. 1. Bromate formation from bromide in the water processing industry.](image-url)
to obtain the final bromate concentration which was set as the reference value to calculate the analytical recovery. All samples were filtered through a 0.45 µm membrane filter.

Anode stability is also another interesting aspect that needs to be further evaluated. Physical alteration of carbon surface and its decomposition will be characterized in detail. Surface image and composing element of anode were observed using scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM-EDX) (Phenom Desktop ProXL).

3. Result and discussion

3.1. Br removal

HRDE reactor, as depicted in Fig. 3, was operated based on electrochemical reaction as it was evident from physical and current response observed. Physical phenomena were observed as gas bubbles in the cathode chamber, especially at the PEM. Gas is generally produced as water is reduced into hydrogen (H₂) and hydroxide (OH⁻).

\[ \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  \hspace{1cm} (5)

It is noteworthy to say that the gas produced was hydrogen because water treated in this cell was raw water with minimum level of impurities or contaminants.

Current response is another indicator of electrochemical reaction, which represents chemical reaction occurred in cell. Current is highly influenced by potential, salt concentration (electrolyte) and anode surface area which is submerged in liquid. During experiment, current response was recorded at 0.7, 2.1, 2.5, and 3 Å while potential was 5, 7, 7.5, and 8 V, respectively. It is clear that the current response increased as the potential applied increased, which is in accordance with Faraday’s law.

The aforementioned parameters, that is, gas bubbles and positive current response, are indicating that...
electrochemical reaction has occurred in the HRDE reactor, even in a separated chamber (anode and cathode chambers). PEM membrane plays an important role as it facilitates ion transfer in the liquid phase and controls the balance of electron transfer in the external circuit. Furthermore, the rotating anode design used in this reactor did not inhibit electron transfer, which is obviously indicated by the high conductivity recorded in this setting.

Bromide removal in the HRDE reactor was influenced by potential, flow rate, rotor speed, and salt concentration, as described in Table 1.

At 0.35 mg/L bromide concentration, 8.7 L/min flow rate, and 50 mg/L salt concentration, oxidation of bromide into bromine (gas) was significantly enhanced (16%, 30%, and 51%) as potential increased, (5 V, 7 V, and 7.5 V, respectively). These results were based on a linear relationship between potential and electrochemical reaction. However, this phenomenon did not occur for the whole treatment process, as bromide removal was observed to decrease to 24% at 8 V potential. This trend was possibly occurred due to a competition with the oxidation of water into oxygen (O₂) and hydrogen (H⁺):

\[
2H_2O^- \rightleftharpoons O_2 + 4H^+ + 4e^- \quad E^* = 1.229 \text{V (SHE)}
\]

Even though the potential of water oxidation (1.2 V) is higher than bromide (1 V), water is quantitatively dominant in the cell thus increasing the possibility of a reaction. This phenomenon was commonly known as oxygen evolution which is a major obstacle to the electrochemical process in the liquid phase.

It was observed that flow rate is the second parameter influencing the removal of bromide, as implicated by the results, that is, 26%, 61%, and 10% at 4.8, 8.7, and 10 L/min, respectively. It was possibly due to the physical factor in which a higher flow rate might create agitation and thus enhanced bromide transfer to the anode surface. Yet, on the contrary, the opposite trend was observed at the highest flow rate (10 L/min) when low bromide removal was achieved instead (10%). It is possibly due to the short retention time (10 min) resulting in a limited bromide diffusion from the liquid phase to the surface anode and thus decreased the removal process.

Reactor performance is also defined by another parameter, that is, the rotation speed of the anode. The result indicates that high rotation speed resulted in a higher bromide removal, 30% and 21% at 120 rpm and 30 rpm, respectively. Rotation speed may enhance diffusion and mass transfer from liquid to the gas phase, in which higher rotation would lead to an enhanced diffusion of bromide to anode surface and an immediate transfer of bromine to the gas phase.

Salt concentration is another important variable in bromide removal. Salt plays the role of electrolyte and helps ion transfer in the liquid phase. Even high potential, without ion transfer in the liquid phase, will not induce electrochemical reaction. As summarized in Table 2, bromide removal was 30% and 24% at 8 V potential and 100 and 50 mg/L salt concentration, respectively. On the contrary, bromide removal was 31% and 51% at 7.5 V potential and 100 and 50 mg/L salt concentration, respectively.

### 3.2. Effects of an anode on bromide removal efficiency

Table 3 summarizes bromide removal efficiency achieved using two different anodes, that is, microporous layer carbon (MPL) and platinum-doped carbon (Pt-carbon).

Table 1

<table>
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<th>No.</th>
<th>Salt concentration (mg/L)</th>
<th>Flowrate (L/min)</th>
<th>Rotor speed (rpm)</th>
<th>Potential (V)</th>
<th>Current (A)</th>
<th>Concentration (mg/L)</th>
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</table>
It can be concluded that the performance of MPL carbon was superior to that of Pt-carbon. Bromide removal efficiency at 8.7 L/min flow rate, 50 mg/L salt concentration and 7 V potential was 51% and 22% using MPL carbon and Pt-carbon, respectively. Platina-doping showed no effect on bromide oxidation, and possibly only affected the oxygen evolution reaction.

3.3. Effect of bromide initial concentration on bromide and bromate removal efficiency

Table 4 shows data related to the reaction between bromide and ozone into bromate. At high concentration of bromide (0.3858 mg/L), high concentration of bromate was detected (0.3 mg/L), and vice versa (0.002 mg/L of bromate at 0.0147 mg/L of bromide). A linear relationship (80%) was found between bromate formation and bromide reduction ([C]_{initial} 0.3858 mg/L) and ([C]_{final} 0.0147 mg/L). This result supported the theory of BrO\(_3\)\(^-\) formation from bromide ozonation, as described below:

\[ \text{Br}^- + O_3 \rightarrow \text{BrO}_3^- \quad (7) \]

Table 4 also demonstrates superior performance of the HRDE reactor in bromate removal.

3.4. Anode stability

The stability of electrode materials, specifically anode, is another important aspect investigated in this study.
Figs. 4 and 5 present SEM examinations of carbon surface used as the anode.

Both MPL carbon and Pt-carbon showed changes in their surface textures. They both exhibited cracked surfaces while a peeling phenomenon was observed on Pt-carbon after the experiment. It was possibly due to the friction between water and electrodes and also the impact of rotation on the surface of the anode. The effect of a chemical reaction (electrolysis) via oxidation was also possible, which was observed in our experiment during reactor optimization at 8 V potential. This phenomenon was also in agreement with the EDX result, which showed the presence of Fe, Cr, and reduction of carbon.

3.5. Energy consumption

Reactor performance was also evaluated based on its energy consumption, as it is the main consideration for further application on an industrial scale. Major electrical energy consumption of HRDE reactor is associated with power supply, water pump, and electromotor. In order to achieve bromide removal of 0.3858 mg/L at 7 V potential, 2.7 A current, 8.7 L/min flow rate, one water pump (30 W) and electromotor of 0.5 hp (420 W) were employed. Electrical consumption for each component was 0.33, 1.09, and 6.75 kJ/g Br for power supply, water pump, and electromotor, respectively. So it can be concluded that the total energy consumption for the HRDE reactor is about 8.17 kJ/g Br. This value is lower than thermal distillation, nanofiltration, reversed osmosis, and electrodialysis, with an energy consumption of 11,412,214 kJ/g Br.

Energy consumption of HRDE is notably higher than direct oxidation, as reported by Gregory (2011) at, that is, 1.3 kJ/g Br. It is possibly due to the different components contributing to the estimation. The energy consumption in direct oxidation process is calculated only based on the energy of potentiostat, whereas, the energy consumption in the HRDE reactor is mainly associated with the electromotor (82% of total consumption energy or 6.75 kJ/g Br). However, on the other hand, energy consumption for the oxidation process in HRDE is only 0.33 kJ/g Br, which is lower than the direct oxidation process.

Based on the calculation, energy consumption for drinking water production will cost about Rp 1.2/L or 0.083 × 10⁻³ USD/L or 0.067 EUR/L, with the industrial electrical rate of Rp 1,400/kWh or 0.097 USD/kWh or 0.081 EUR/L, volumetric shrinkage and operator wage not included. Volumetric shrinkage is highly likely to occur in the anode, and it is the most expensive part of the reactor.

4. Conclusion

HRDE reactor has effectively removed bromide in the raw water of drinking water industry. Potential, flowrate, anode rotation speed, and salt concentration were factors influencing reactor performance. MPL carbon and copper, as
paired electrodes, showed higher performance than Pt-carbon and copper. Bromide removal was achieved about 93% at 0.3858 mg/L bromide initial concentration, 8.7 L/min flow rate, 7 V potential, 2.3 A current, and 100 mg/L salt concentration, and final bromate concentration achieved was about 0.002 mg/L. Energy consumption for HRDE reactor was about 8.17 kJ/g Br or equivalent to Rp 1.2/L of raw water.

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References


