

The decrease of high chlorine on seaweed industry wastewater

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Abstract. In the seaweed processing industry to obtain quality products that are free of microorganisms, high concentrations of chlorine are used in the cooking process. Thus the wastewater from the cooking process still contains high concentrations of residual chlorine, where the wastewater when disposed of into the aquatic environment can cause pollution and damage of environmental. The aim of the research is the reduction of high concentrations of residual chlorine in seaweed wastewater using a combination process of aeration, heating and addition of Hypochlorous acid (HCl). The experiment was conducted by adding wastewater from the seaweed cooking process with HCl (1; 2; 3; and 4% v/v), aeration flowrate (1; 1.5; 2; and 2.5 L/minute) and heating temperature (35; 40; 45; and 50°C). Residual chlorine concentration was measured using the iodometric method. The experimental results showed that the maximum reduction of residual chlorine by 96.3% was obtained by adding HCl by 3%, aeration flowrate of 2.5 L/minute and heating temperature of 45°C.

1. Introduction

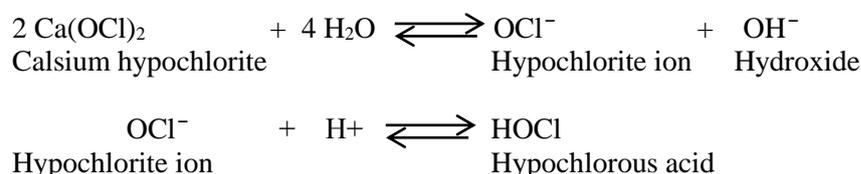
The seaweed processing industry using the Semi - Refined Carrageenan (SRC) process is a strategic industry as a provider of added value of carrageenan - producing seaweed (*Eucheuma cottonii*). To produce carrageenan products, seaweed obtained from seaweed cultivation in the sea is processed with the following process steps: washing, cooking, re-washing, drying and cutting. The process of washing aims to remove dirt and oil on the surface of seaweed, while the cooking process aims to provide a better color and form soft conditions on seaweed so that it is easy to process[1–4]. In the washing process generally uses water while the cooking process uses an potassium hydroxide (KOH) solution of 7 - 8% with a water use ratio of 1:21. For that the wastewater output from the SRC industry is very large in volume, blackish brown with a very high pH of 12-13 and potassium concentrations of 1 - 7%. The characteristics of wastewater produced by SRC seaweed are as follows: Potassium (0.87 - 2.88%); Chloride (1.37 - 2.41%); Nitrogen as N-total (0.03%), Phosphorus as P₂O₅ (3.2 - 20.72%), and pH (9.92 - 11.76) [3].

Seaweed treatment wastewater when discharged directly into the aquatic environment can cause environmental pollution. For this reason, seaweed treatment wastewater from the washing and cooking process with KOH is generally treated using a chemical - biological process (neutralization - coagulation, flocculation and activated sludge). However, in certain conditions, especially according to the order of buyers who seaweed is free of microorganisms, so the cooking process uses an calcium hypochlorite (Ca(OCl)₂) solution of high concentrations (chlorine concentration: 200 - 400 ppm) [5,6].

Chlorine in calcium hypochlorite is an effective disinfectant for inactivating pathogenic bacteria, more stable, more soluble in water and relatively cheaper. The use of excess chlorine can cause the



formation of residual chlorine in the form of Trihalomethan (THMs), where THMs are toxic and mutagenic [7]. Thus the wastewater output from the cooking and washing processes that use high concentrations of chlorine cannot be treated using a biological process. This is due to calcium hypochlorite in wastewater reacting as follows.



Hypochlorous acid and hypochlorite ion are both disinfection agents. These forms can exist together, but their concentration depends on the pH of the solution. $\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$ at 25° C and a pH of 7.5 (7 is average for water or neutral) half of the chlorine present in a solution of OCl^- and half is HOCl. At higher pH values, the quantity of OCl^- increases at the expense of HOCl and at lower pH values, the shift is toward conversion of OCl^- to HOCl. At a pH of about 5, nearly all the chlorine is present as HOCl, and at pH 8.5, nearly all the chlorine is present as OCl^- . In water, hypochlorous acid (HOCl) is 80-100 times more effective as hypochlorite ion (OCl^-). Chlorine gas lowers the pH of the solution, thus more HOCl is present and many times more effective. At pH 7 (neutral), 76% of the chlorine is in solution as HOCl [8].

In the other hand, the added chlorine dose can influence the formation of chlorine residuals and free residuals as is known in the breakpoint curve. Recognition of these two forms of residual chlorine is of the greatest importance since the chemical, bactericidal and virucidal properties of free chlorine are vastly superior to those of combined chlorine. For maximum safety in the production of germ-free water, it is essential to chlorinate to the point of establishing free residual of chlorine [9,10].

For this reason, in the SRC industry, the addition of chlorine dosage, contact time and method to reduce residual chlorine concentrations are the main focus in handling wastewater treatment. Some factors that influence reducing residual of chlorine include: pH, temperature, dose, turbidity, contact time, mixing, and control of the system [6,10,11].

The purpose of this research was to determine the effect of temperature, HCl addition and aeration flowrate on decreasing the concentration of residual chlorine in seaweed industry wastewater that using high doses of chlorine.

2. Materials and methods

Materials used in the experiment included: seaweed wastewater from the process of cooking and washing, The HCl solution of 27%, the solution of sodium thiosulfate, starch indicator. While the equipments used include: aeration kits, hot plates, burettes, erlenmeyer. While the experimental variables are heating temperatures (35; 40; 45; and 50°C); air aeration flowrate (0; 1; 1.5; 2; 2.5 L/minute); and adding HCl solution (0; 1; 2; 3; and 4% (v/v)). Hydrochloric acid (HCl) is used to reduce the pH of the solution.

The experiment was carried out by decant of wastewater (effluent) from the washing process and cooking as much as 5 L into a tank in the aeration kits. Wastewater from the washing and cooking process contains active chlorine of 200 ppm. The aeration kits is connected to the heating system and aeration system. The tank containing wastewater is given treatment is adding HCl solution and given an air supply and heating at a temperature in accordance with the experimental variable. Before and after treatment, the amount of residual chlorine was measured using the Iodometry method [12].



Figure 1. The equipment of experiment.

3. Result and discussion

Each glass beaker containing 2 L of wastewater that has been heated at 45°C then added HCl solution of 0%, 1%, 2%, 3% and 4% (v/v) respectively and aerated at a flowrate of 0, 1, 1.5, 2, and 2.5 L/minute respectively and then is measured the amount of residual chlorine in wastewater is as follows.

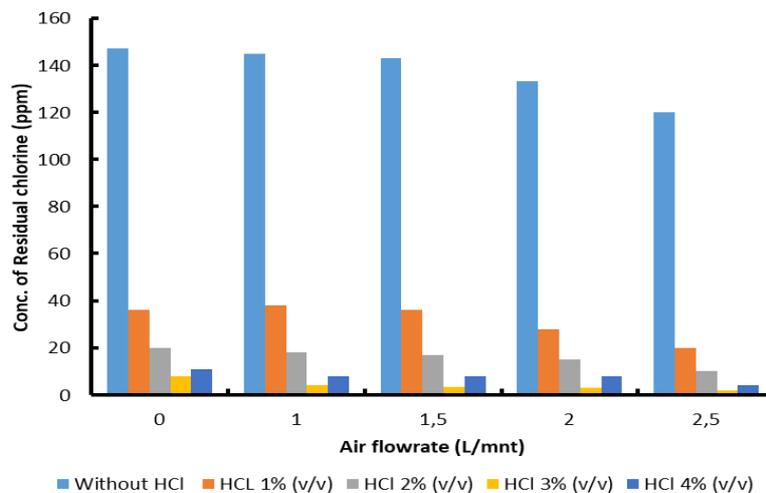


Figure 2. Residual chlorine concentration in various additions of HCl and air flowrate.

Figure 2 shows that at a fixed aeration flowrate, the addition of HCl solution with a higher concentration causes the pH of the solution to decrease so the residual chlorine concentration decreases. The addition of HCl as much as 1% (v/v) gives a pH of 9, HCl of 2% (v/v) gives a pH of 8. While giving HCl of 3% (v/v) gives a pH of 7.5, and HCl of 4% (v/v) gives a pH of 7. This is due to the greater HCl added or the lower the pH of the solution, the lower the HOCl value, but at pH 7 an increase in residual chlorine concentration is caused by exceeding the pH equilibrium point where at pH 7 is the pH equilibrium point as the reaction $\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$.

Likewise with the addition of a fixed HCl, the greater the aeration flowrate, the lower the chlorine concentration in the wastewater except at a flowrate of 2.5 L/minute. This is due to the greater flowrate of the aeration flowrate, which causes the HOCl oxidation reaction by oxygen to be higher so the remaining residual chlorine concentration will decrease. Figure 2 shows that a maximum reduction in

residual chlorine concentration of 75% occurs in addition of HCl by 3% (v/v) and aeration flowrate of 2.5 L/minute.

Furthermore, the experiment was done at a fixed aeration flowrate of 2.5 L/minute and the addition HCl solution of 1% (v/v), 2% (v/v), 3% (v/v), and 4% (v/v) and heating temperatures of 35°C, 40°C, 45°C, and 50°C are obtained experimental data as shown in Figure 3.

Figure 3 shows the higher the heating temperature and the greater the addition of HCl solution, the lower the pH of the solution so that the residual chlorine concentration decreases. Except at a temperature of 45°C and the addition of HCl 3% (v/v), there is a maximum decrease in residual chlorine. This is due to the temperature of 45°C and the addition of HCl 3% (v/v), pH of solution 7 where at pH 7 occurs the reaction equilibrium so that the residual chlorine is at the lowest concentration [13–15].

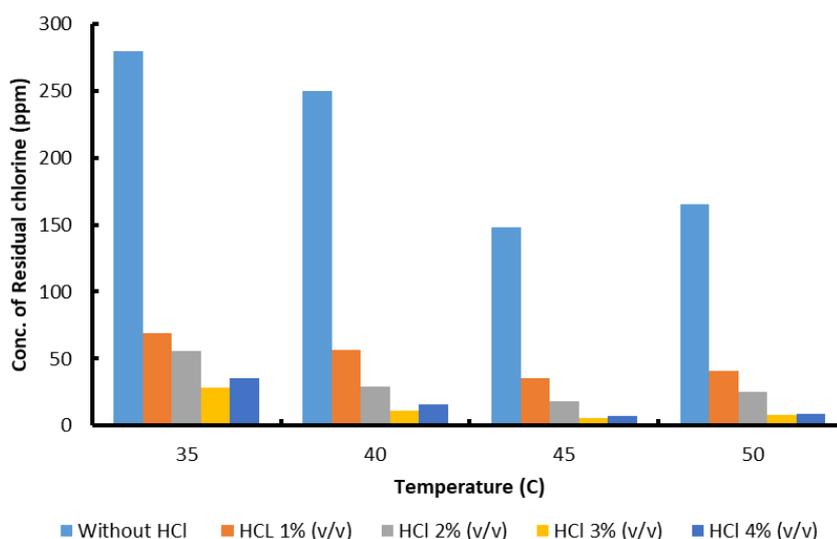


Figure 3. Residual chlorine concentration in various additions of HCl and heating temperature.

By using high heating, oxidation reaction occurs hypochlorine to chlorine and reserved so that at a temperature of 45 °C is the equilibrium reaction point between hypochlorine with chlorine.

Based on the results of this study, for the treatment of wastewater containing high doses of chlorine it is necessary to treat wastewater using a combination of heating processes, addition of HCl solution and enlarge aeration, which through the combination of these processes can reduce the residual chlorine content in wastewater.

4. Conclusion

The maximum reduction of residual chlorine of 96.3% was obtained by adding HCl solution of 3% (v/v), aeration flowrate of 2.5 L/minute and heating temperature of 45°C.

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