

# CHANGE OF TEMPERATURE AND DISSOLVED OXYGEN CONTENTS IN THE PRODUCTION OF SLURRY ICE COMBINED WITH NITROGEN NANO

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## ABSTRACT

The combination research of slurry ice technology and Nitrogen Nanotechnology was implemented in order to create a new slurry ice solution of temperature from  $-1\text{ }^{\circ}\text{C}$  to  $-2\text{ }^{\circ}\text{C}$  and dissolved oxygen content of under  $1.0\text{ mg/L}$ . There were four experiment, including: (1) Turning on the Nitrogen Nano machine to reduce the DO content in the water to less than  $1.0\text{ mg/L}$  and then stopping it before turning on the slurry ice machine (CDH1); (2) Two machines operate simultaneously (CDH2); (3) Two machines start simultaneously and when the temperature of the water reaches to  $0\text{ }^{\circ}\text{C}$ , stop Nitrogen Nano machine priorly (CDH3); and (4) The slurry ice machine works until temperature of the solution reaches  $0\text{ }^{\circ}\text{C}$ , Nitrogen Nano machine starts running (CDH4) and one control experiment (NoNano). The results indicated that setting up for the Nitrogen Nano and slurry ice machines operates simultaneously (CDH2) or Nitrogen Nano machine is timed for running when the temperature of the mixture reached  $0\text{ }^{\circ}\text{C}$  (CDH4), that attained both DO content and temperature at the end of the process was less than  $1.0\text{ mg/L}$  and  $-1.5\text{ }^{\circ}\text{C}$  respectively. In concern about both economy and technology aspects, recommending while slurry ice working, Nitrogen Nano machine is timed for running when the mixture reaches temperature of  $0^{\circ}\text{C}$  then both machines operate to end of process.

*Keywords:* DO content, nitrogen nanotechnology, slurry ice, subzero temperature, technologies combination.

## 1. INTRODUCTION

Slurry ice (*iceflow, nanoice*) is a homogeneous mixture of micrometer ice crystals and liquid. The solution for making slurry ice has freezing point that is lower than which of fresh water. The solutions of Natri clorua, Ethanol, Ethylene glycol, and Propylene glycol are used normally for slurry ice-making in the industry field. In the field of seafood preservation, natural seawater solution is normally used to create slurry ice [1]. There are some advantages of slurry ice as liquid form, fast and uniform cooling, temperature from  $-1\text{ }^{\circ}\text{C}$  to  $-2\text{ }^{\circ}\text{C}$ , non-crystallization in hard mass, and non-refreezing [2]. It has been widely used for post-harvest product preservation on fishing vessels in many countries around the world. In Vietnam, the slurry ice technology has been studied and applied to tuna handliners, and tuna gill-netters. However, the ice has been not disinfected and removed impurity.

The Ultra Fine Bubble technology is a technique of creating air bubbles with micrometer size. These bubbles are invisible to the naked eye, it does not rise to the surface of the water and can remain in the water for a long time. The microscopic air bubbles carry a negative charge, so they cannot combine with each other to form larger air bubbles for rising to water's

surface like regular air bubbles. They can attract other organic substances with a positive charge, which means, they can purify water well. With the absorption effect of the Nano nitrogen bubbles, it will discharge dissolved oxygen from the water and, as a result, inhibit the growth and activity of aerobic bacteria. In addition, the Nano Nitrogen bubbles are effective in preventing the oxidation of fat from the outer surface to the inside of the fish's body. Thus, it effectively prevents rancidity, degeneration, and commercial value reduction of fish meat [3].

Storage of fish at temperatures between 0 °C and -4 °C is called super-chilling or partial freezing. The shelf life predicted by the square root model at -1 °C, -2 °C and -3 °C for a product that keeps 14 days in ice is 17, 22 and 29 days, respectively [4]. So, if fish is preserved in a solution with temperature of around -1,5 °C, shelf life stays about 20 days which is suitable with current cruises of fishermen. Some spoilage bacteria and lipid oxidation require oxygen - thus, reducing the oxygen around the fish will increase storage and shelf life [5]. It is important to note that oxygen is almost totally expelled from ice crystals as they are formed [6]. So, combining slurry ice and Nitrogen Nano technologies create a storage environment with the preservation temperature at -1 °C to -2 °C and dissolved oxygen (DO) concentration in the ice mixture is lower than 2 mg/Liter, the mixture inhibits the growth of aerobic microorganisms effectively.

The article shows results of Nitrogen Nano and slurry ice machines running in combination to create a preserved mixture of Nitrogen Nano - slurry ice with temperatures from -1 °C to -2 °C, and dissolved oxygen content under 1 mg/Liter. The data source is from the project of pilot production "Completing preservation technology of oceanic tuna and mackerel onboard by slurry ice combining with Nitrogen Nano".

## **2. MATERIAL AND METHODS**

### **2.1. Experimental place**

The study was researched at the laboratory of The South Research Sub-Institute for Marine Fisheries, belonging to Research Institute for Marine Fisheries (RIMF).

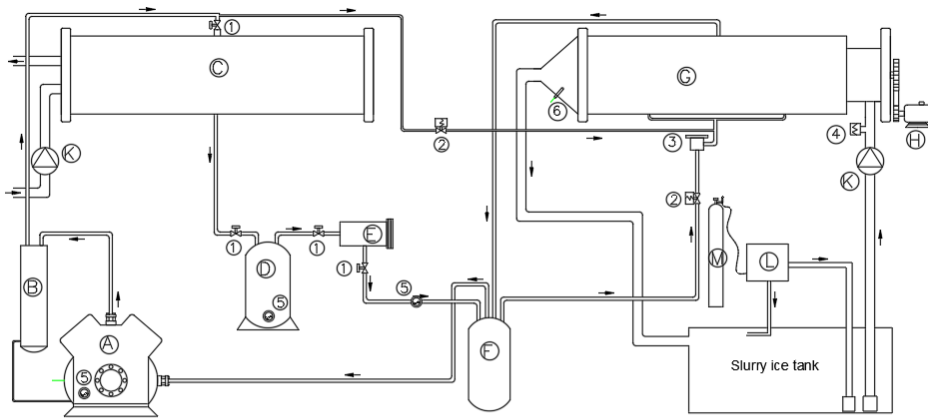
### **2.2. Experimental equipment**

The devices used in this study include:

- A slurry ice machine, ice capacity of 3 tons per 24 hours, power consumption of 10 kW, 03 phases, 380 ÷ 400 V, 50 - 60 Hz.
- An insulated tank: volume 300 liters.
- A Nitrogen Nanomachine: capacity 1 m<sup>3</sup>/h, DO < 1 mg/L.
- Temperature measure: HANNA - HI93501 (Range -10 to + 80) and I-wire Button chips (-20 °C to + 50 °C, step 0,05 °C).
- DO measure: HANNA HI 98193.
- Salt measure: Hydrometer.
- Time counter: Smartphone.

### **2.3. Experimental period**

The study was conducted from June to July 2022.



- Notes:
- |                                      |                          |                    |                     |                        |
|--------------------------------------|--------------------------|--------------------|---------------------|------------------------|
| A - Compressor                       | D - high pressure bottle | H - Motor          | 1 - Valves          | 5 - Gas window         |
| B - Oil separator                    | E - Filter               | K - Pumps          | 2 - Electric valves | 6 - Temperature sensor |
| C - Condenser                        | F - Liquid separator     | L - Nitrogen mixer | 3 - Throttle valve  |                        |
| G - Evaporator (slurry ice operator) | M - Nitrogen bottle      | 4 - Current sensor |                     |                        |

Figure 1. The figure of working principle of slurry ice and Nitrogen Nano Technologies combination

## 2.4. Experimental design

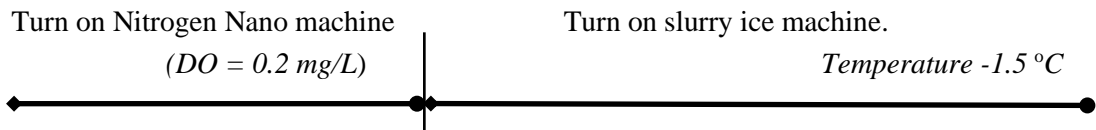
### 2.4.1. Preparing solution

Pure seawater of 200 liters (salt density at 30‰), mixed with fresh water 100 liters to create a mixture of 300 liters at a density of 25‰ (the density at 25‰ was proved efficiently for seafood preservation by slurry ice).

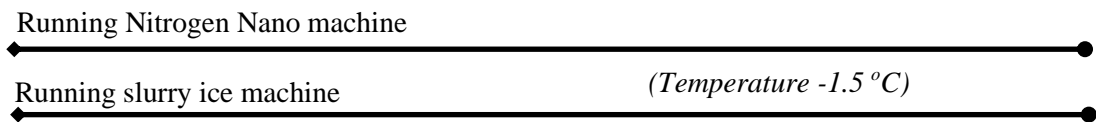
### 2.4.2. Experimental design

This study was conducted with four experiments and one control experiment, each one with 3 repeats:

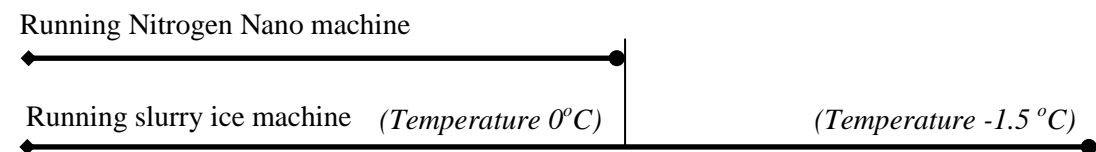
+ CDH1: Turning on the Nitrogen Nano machine to reduce the DO content in the water to 0,2 mg/L and then stop it before turning on slurry ice machine.



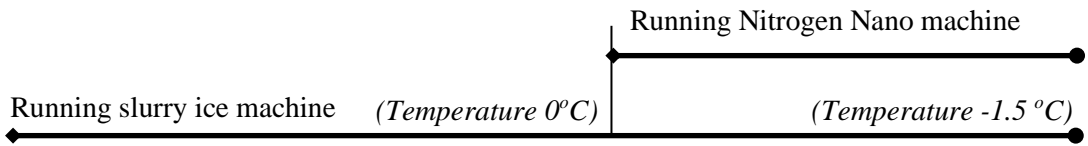
+ CDH2: Two machines operate simultaneously.



+ CDH3: Two machines start simultaneously and when the temperature of the water reaches 0°C, then stop the Nitrogen Nano machine priorly.



+ CDH4: The slurry ice machine works until temperature of the solution reaches 0°C, then Nitrogen Nano machine starts running.



+ NoNano (controlled test without Nitrogen Nano): Running only slurry ice machine.



Experimental conditions are assumed that ambient indicators such as temperature, humidity, and wind do not significantly affect the test results.

Each mixture of 5 experiments is sampled at the end process.

#### *2.4.3. Data collection*

The temperature value was automatically recorded by I-wire button chips and manually measured by the Hanna HI-93501. The temperature was recorded at a frequency of 4 sets per hour.

DO value was measured by HANNA HI 98139 device with the frequency of 4 sets per hour and repeating three times for each value to get the average of the measurements.

Salinity content in seawater was measured by hydrometer in three times for each value to get the average of the measurements.

#### **2.5. Data analysis**

The data were analyzed by Excel software.

### **3. RESULTS AND DISCUSSIONS**

#### **3.1. The change of DO content in the mixture during making slurry ice combined with Nitrogen Nano**

Fatty fish are, of course, particularly susceptible to lipid degradation which can create severe quality problems even on storage at subzero temperatures.

The result showed that oxygen content in the mixture of slurry ice and nitrogen Nano significantly changed during making the ice. CDH2 experiment indicated the best result, it means starting and finishing the operation of both slurry ice and Nitrogen Nano machines at the same time, then oxygen content reached approximately 0,2 mg/L with standard deviations at 0,1 at the end of process.

DO content in the ice affects lipid oxidation in fish. Fat levels in fish can be categorized in four basic groups: lean (<2% fat), low-fat (2-4% fat), medium-fat (4-8% fat), and high-fat (>8% fat) [9]. In the mixture of low oxygen content about 0,2 mg/L, as a result lipid oxidation will be restricted.

According to the CDH1 experiment, DO content in the mixture increased remarkably compared with the original water. The DO content in the mixture was up from 5.5 mg/L to 8.0 mg/L after finishing the process. The reason for this consequence was the mixture was disordered strongly during operating of the slurry ice machine but without dissolved oxygen is discharged at the same time by Nitrogen Nano machine, consequently, oxygen from the air will replace nitrogen.

For CDH3, the Nitrogen Nano machine was stopped when the temperature of the mixture reached 0 °C. The results showed that DO content increased significantly with 5.5 mg/L at the

end process. In the first 15 minutes, the DO content dropped down quickly from 5,5 mg/L to under 1,0 mg/L before keeping contain value merely 0,2 mg/L for next 45 minutes. After 75 minutes of operation, there is a dramatic increase from around 0,2 mg/L to over 5,0 mg/L because the Nitrogen Nano machine was stopped when temperature of solution reached 0 °C at that time.

For CDH4, from the first 60 minutes, because of without Nitrogen Nano machine operation, the oxygen content in the mixture increased significantly from 5.5 mg/L to around 7.8 mg/L in the solution. Next 15 minutes, although the Nitrogen Nano machine running, DO content increased slightly to 8.0 mg/L before falling rapidly to under 1.0 mg/L at 150 minutes. The DO content in the solution decreased rather quickly because the state of the solution started changing regularly from liquid to solid, so DO will be difficult to infiltrate into.

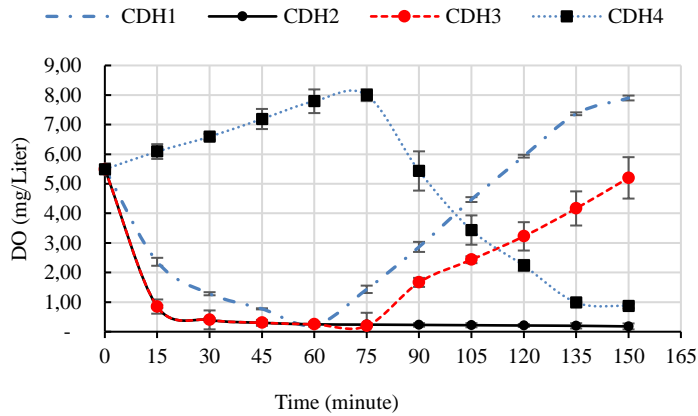


Figure 2. Fluctuation of dissolved oxygen content during the making slurry ice combining nitrogen Nano

According to 04 experiments, concerning about dissolved oxygen respect, both slurry ice and Nitrogen Nano machines operate simultaneously, or the Nitrogen Nano machine starts to run when the temperature of the mixture reached 0 °C, this creates the good ice with DO content of less than 1.0 mg/L.



Figure 3. The picture of bubbles with impurities on surface of the tank

According to Prescott L.M, et al (1996) [7] and Hogg Stuart (2005) [8], aerobic bacteria only live in the environment of oxygen content from 2.0 mg/L to 10,0 mg/L. Thus, with the mixture of slurry ice and nitrogen containing oxygen content of less than 1.0 mg/L, it can restrict completely the development of aerobic microorganisms and thermophilic microorganisms.

Moreover, during the experiments, Nitrogen Nano machine discharged impurities out of the mixture, it is cleaner and has more effective about hygiene and food safety. The impurities should be collected immediately when it is concentrated and up well to the surface (Figure 3).

### 3.2. The change of temperature during the process of making slurry ice combined with Nitrogen Nano

The diagram showed that CDH1 was not effective because the temperature only reached 0 °C after finishing the operation time. In the first 60 minutes, the temperature of the solution increased remarkably from 28 °C to 33 °C before getting down sharply by the slurry ice machine acting. However, the solution only reached 0 °C at the end of the process. It means that needs more time to reach temperatures of lower 0 °C, as a result, CDH1 is not effective. The heat increases caused by molecules of water colliding with each other and with pump edges but temperature declining process by slurry ice machine have not worked yet. So, solution temperature increases from 28 °C to around 33 °C in the first 60 minutes of CDH1 before sharply getting down to 0 °C at the end of process.

In terms of CDH2 and CDH3 experiments, the result indicated that there was a quick regular decrease in temperature in the first 75 minutes before reaching minus temperature value of the ice-making process.

In order to obtain maximum shelf life from RSW-systems, temperature homogeneity in the region of -1 °C is very important. The necessary chilling rate was suggested to be: fish temperature must be below 3 °C within four hours and below 0°C after 16 hours, and the temperature should be kept between -1.5 °C and 0 °C until unloading [9]. The percentage of frozen water in super-chilled fish is highly temperature-dependent (-1 °C = 19%; -2 °C = 55%; -3 °C = 70%; -4 °C = 76%) [9]. Compared to ice storage, the refrigerated sea water systems chill fish more rapidly, reduce the exposure to oxygen, reduce the pressures that often occur when fish are iced and give significant labour-saving [10].

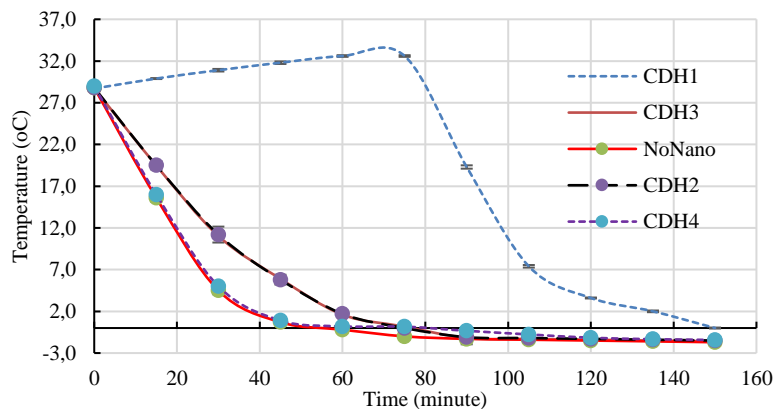


Figure 4. The fluctuation of temperature during making the ice

Temperature changes of the mixture after reaching 0 °C did not differ discernibly between experiments of CDH4, CDH3, CDH2 and the controlled test.

In the first 70 minutes of the ice-making, there was a big gap in the value of temperature between group 1 (CDH2, CDH3) and group 2 (CDH4, NoNano). This gap happened because of the effect of nitrogen Nano machine operation. There was the same trend of temperature decline in both the groups because the slurry ice machine worked during the process in all experiments of CDH2, CDH3, CDH4 and NoNano.

According to temperature terms, CDH2, CDH3 and CDH4 experiments all met the requirement of temperature value, that was -1 °C to -2 °C. According to Power et al. (1965) [11] as the temperature of fish muscle is lowered to -1° C and -2 °C, the presence of water frozen is 19 and 55 respectively. In the first major use of super-chilling, mechanical refrigeration was used to hold fish onboard at about -1.1 °C [12]. According to Louis, J.R et al., (1981) [13],

super-chilling is effective and practical, provided that the temperature does not fall below the point where freezing is discernible (about -2 °C).

### 3.3. The change of temperature and DO content in the mixture via time in producing process of slurry ice combining with Nitrogen Nano

There are two stages of change of temperature and DO content of CDH1. In detail, during the first 60 minutes (DO in the water reached under 1.0 mg/L), while temperature increased slightly from 28 °C to 33 °C. Otherwise, the trend reversed in a period of 70 minutes to 150 minutes of the process for both the indicators with DO content growth up to 8.0 mg/L approximately and the temperature got down to 0 °C at the end of the process. This showed that CDH1 did not match the fresh fish preservation requirement.

The CDH2 indicated a positive result for both temperature and DO content in the water after the process of combining two pieces of equipment in operation. According to the figure, the temperature and DO content of the water dropped significantly in the first stage. The trend continued a slight stable decrease from 60 minutes and reached a good value at 150 minutes of the process in DO of less 1.0 mg/L and temperature of -1.5 °C. The temperature and DO value from the CDH2 are suitable for the requirement of aquatic preservation onboard. According to Nguyen Lan Dung, 2015 [14], if the dissolved oxygen content is less than 2.0 mg/L, the development of all aerobic bacteria will be slow or decreased remarkably. In terms of temperature, temperature is reduced then the rate of protein denaturation is reduced [15]. It means, the temperature at -1.5 °C of the slurry ice nitrogen Nano mixture will reduce the protein denaturation rate more significantly compared to traditional ice with 0 °C.

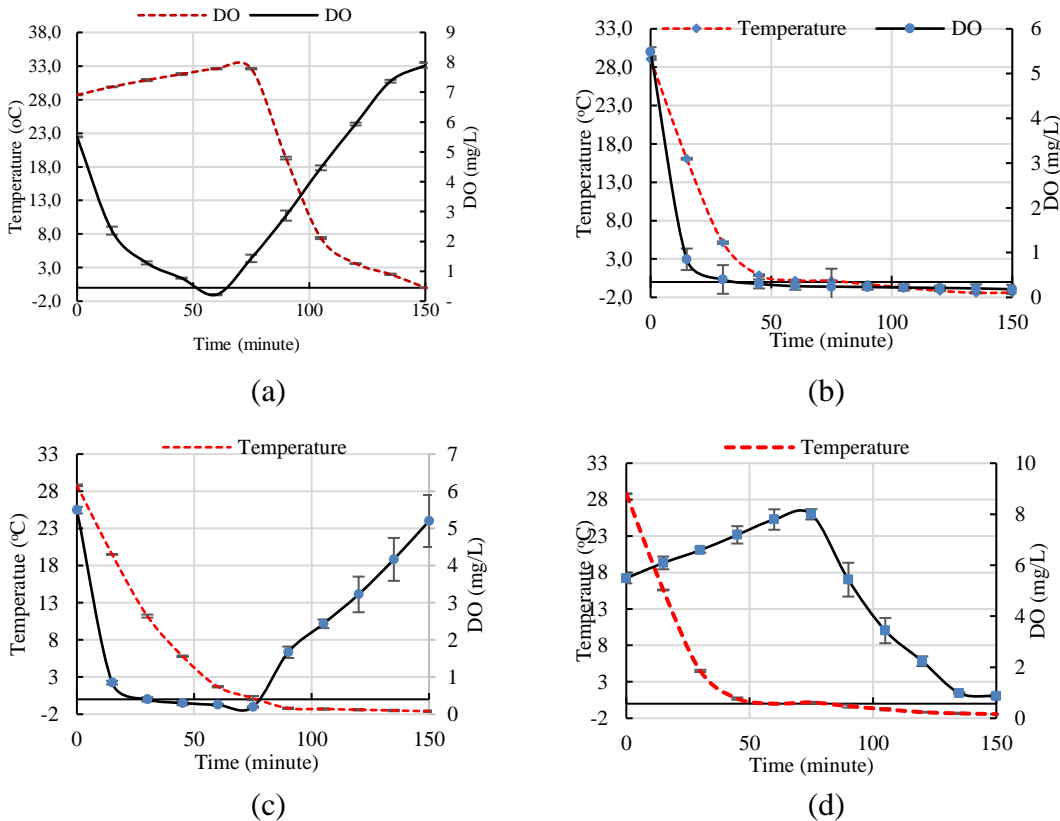


Figure 5. The fluctuation of both temperature and dissolved oxygen content in the mixture by experiment terms of CDH1 (a), CDH2 (b), CDH3 (c) and CDH4 (d).

CDH3 experiment showed the status of the slurry ice Nitrogen Nano mixture was almost the same as CDH1, except the temperature at the end of the CDH3 process reached a lower value of -1.5 °C. In detail, in the first 15 minutes of the operation, DO content was less than 1.0 mg/L and remained still for more next 45 minutes before increasing rapidly to around 5.3 mg/L, while temperature decreased steadily in terms of CDH2.

#### **4. CONCLUSIONS**

In the experiments, setting up for Nitrogen Nano and slurry ice machines operates simultaneously or the Nitrogen Nano machine is timed for running when the temperature of the mixture reached 0 °C, that attained both dissolved oxygen content and temperature in slurry ice solution at the end of the process was less than 1.0 mg/L and -1.5 °C respectively.

Concerning both economic and technique respects, in terms of combining two technologies, while slurry ice machine is running, the Nitrogen Nano machine should be timed to start when the temperature of the mixture attained 0 °C and then both machines operate to end of process.

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## **TÓM TẮT**

### **SỰ BIẾN ĐỔI CỦA NHIỆT ĐỘ VÀ HÀM LƯỢNG OXY HÒA TAN TRONG QUÁ TRÌNH SẢN XUẤT ĐÁ SỆT KẾT HỢP VỚI NI TƠ NANO**

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Nghiên cứu phối hợp vận hành giữa thiết bị đá sệt và Ni tơ Nano được triển khai để tạo ra đá sệt có hàm lượng DO thấp dưới ngưỡng phát triển của vi sinh vật hiếu khí và nhiệt độ cận đông. Nghiên cứu gồm có 04 nghiệm thức: (1) bật thiết bị tạo Nitơ Nano để giảm hàm lượng oxy trong nước xuống dưới 1,0 mg/L rồi dừng trước khi bật máy đá sệt (CDH1); (2) Khởi động hai thiết bị cùng lúc (CDH2); (3) Hai máy khởi động đồng thời và khi nhiệt độ về 0 °C thì tắt máy Nitrogen Nano (CDH3); (4) Khởi động thiết bị tạo Nitrogen Nano khi nhiệt độ nước đạt 0 °C (CDH4) và 01 đối chứng NoNano (không sục khí Nitơ Nano). Kết quả cho thấy, chế độ cho 02 thiết bị Nitrogen Nano và đá sệt hoạt động đồng thời (CDH2) hoặc máy Nitrogen Nano được hẹn giờ chạy khi nhiệt độ hỗn hợp đạt 0 °C (CDH4) đạt mục tiêu về hàm lượng oxy hòa tan và nhiệt độ ở cuối quá trình quá trình lần lượt nhỏ hơn 1,0 mg/L và -1,5 °C. Xét hai khía cạnh hiệu quả kinh tế và hiệu quả kỹ thuật, đề nghị chọn phương án máy đá sệt vận hành đến khi nhiệt độ hỗn hợp đạt 0 °C thì khởi động thiết bị Ni tơ Nano và cho hoạt động đến hết quá trình tạo đá.

*Từ khóa:* Đá sệt, Ni tơ Nano, nhiệt độ thấp, oxy hòa tan, sự kết hợp công nghệ.