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LABORATORY INVESTIGATION ON THE PURIFICATION OF FOOD WASTEWATER BY FREEZE CONCENTRATION

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Abstract

This study was carried out to determine the feasibility of applying a freeze concentration technique to rarefy milking wastewater using either a stationary wastewater vessel (the first series of tests) or a rotary ice–making machine (the second series of tests). In this study, we investigated the impact of freezing temperature, initial milking wastewater concentration and vessel depth upon the removal rate of chemical oxygen demand (COD). Results show that when the freezing temperature was decreased (from –3°C to –15°C), the freezing rate increased. The freezing rate was not significantly affected for the different concentrations of the wastewater solution. The COD removal rates at 0–25 mm of ice layer for the COD concentrations of 500 mg/L, 1000 mg/L and 2000 mg/L were 94.56%, 92.78% and 91.25% respectively at the freezing temperature of –3°C in the first test. In the second test, the milking wastewater (500 mg/L) was frozen using a rotary ice-making machine. The COD removal rates at –6°C and – 15°C in the round ice (99.12% and 95.24%) and the surrounding ice (98.37% and 90.28%) were higher than the removal rate in the revolving ice (91.47% and 85.68%). Therefore, the freeze concentration method can become a powerful, simple and low–cost treatment method for purifying milking wastewater in the environment.

Key words: freeze concentration, COD, ice crystal, removal rate, wastewater

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1. Introduction

The freeze concentration treatment method is a concentration technology that is widely used, especially in the food industry (Deshpande et al., 1984; Miyawaki et al., 2005; Ramos et al., 2005; Thijssen, 1974). It is used to obtain concentrated juice by freezing the water content in juice squeezed from fruits and then separating the frozen water (ice) from the solution. This method utilizes the principle whereby the water molecules in the solution turn into the form of ice crystals by freezing; however, impurities are excluded from the ice crystals. Freezing leads to retention of impurities in the mother solution and to that solution (in an unfrozen liquid phase) being concentrated (Akyurt et al., 2002). Since this method can concentrate liquid while maintaining the volatile aromatic components as well as those (such as lychee juice components) that are sensitive to heat, it is often used for the concentration and separation of juice, liquors, drugs, and so forth (Feng et al., 2005; Milind and Siddharth 2005; Sun et al., 2007). Various devices for the freeze concentration treatment method have been developed to remove impurities from ice crystals effectively (Yu et al., 2007). Meanwhile, the development of technology to remove pollutants from wastewater in the environment is an extremely important matter with respect to environmental

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remediation. Various methods have been developed to eliminate pollutants from environmental water depending on the type or the concentration of the pollutants (Grcic et al., 2017; Latifoglu and Gurol, 2003; Li and Ernest, 2009). While the hydroxide precipitation method (Zhou et al., 1999) and chelating resin method (Jachula et al., 2018; Rivas et al., 2000) are used to remove heavy metal ions, activated carbon and various other adsorbents are used to remove organic pollutants (Covaliu et al., 2016; Dai et al., 2010a; Qin and Ma, 2007). Although these methods have high removal efficiencies, they all need prior addition of reagents or adsorbents to the wastewater. This implies the necessity to separate the reagent components or adsorbents from the solution after adsorbing pollutants.

On the other hand, the freeze –concentration method has several advantages in treating wastewater, such as freezing wastewater without special requirements, having no new pollutants, and simplicity and convenience of separating ice from the wastewater solution. The freeze –concentration method can also solve problems of wastewater treatment such as the inefficiency of sewage treatment by microbial activity in cold areas where activity is low. For freeze –concentration wastewater treatment, the layer crystallization method (Flesland 1995; Muller and Sekoulov, 1992) and the suspension crystallization method (Rousseau and Sharpe, 1980) of ice crystals can be applied. The freezing of the layer crystallization method has a high effective separation because it yields a larger size of ice unit. However, the freezing of the traditional suspension crystallization method produces small ice crystals in the mother solution, and the amount of ice produced is small so it is difficult to separate the ice from the wastewater solution.

We choose the layer crystallization method because of its simplicity in the separation of the solid ice layer from the liquid phase. Some researchers have studied the methods of wastewater treatment using freeze–concentration. Halde (1980) had used the freezing treatment method for the concentration of slurries or sludge and the purification of water. Lorain et al. (2001) had purified synthetic wastewater and industrial wastewater using the freezing–concentration process and obtained satisfying results. Gay et al. (2003) had attained good purification ratios by applying outdoor coldness, radial freezing and stirring to purify the wastewater (Gay et al., 2003). In a past investigation, pathogens in sewage sludge were found to be reduced using the natural freeze/thaw method (Sanin et al., 1994). Results of this study indicated that the freeze/thaw conditioning coupled with sludge digestion can significantly improve the overall pathogenic microorganism reduction rate achieved in a wastewater treatment plant. Gao et al. (2006) had studied the inactivation capacity of E. coli (strain ATCC 15597) in water by natural freezing via two freezing methods: spray freezing and freezing in a freezer. Jiang et al. (2011) had studied the effects of the removal of inorganic ions and organic pollutants under artificial frozen conditions. The results indicated that the removal rate of the practical wastewater mixed with inorganic–ions and organic pollutants was about 70–80%, so it is better to couple this method with other technologies to improve the treatment efficiency. The experiment of freezing separation on wastewater was carried out under natural conditions to study the effect of freezing purification on Total Nitrogen (TN), Total Phosphate (TP) and Chemical Oxygen Demand (COD). The results showed that more than 80% of TN, TP and COD in the original water could be removed through single stage freezing (Yu, 2012). Furthermore, wastewater treatment using the freeze –concentration method has not been preferred widely due to the high cost of freeze –concentration facilities. Therefore, if the freeze –concentration method was made possible using a simple facility, the process would become a powerful treatment method for wastewater while suppressing the operation cost. These findings may be effective and useful in developing wastewater treatment systems on an industrial scale.

The objective of this research was to investigate the feasibility of two different methods with a stationary wastewater vessel or a rotary ice-making machine to purify the milking wastewater. However, we did not compare advantages in the two different methods, then the experiments (a stationary wastewater vessel or a rotary ice-making machine) were carried out with different conditions, such as freezing temperature and initial wastewater concentration in this study. This study was carried out to purify milking wastewater using the freeze –concentrating technique using a refrigerator. This study consisted of two series of tests: the first series of tests applied the freeze –concentrating technique to rarefy the milking wastewater using stationary vessels (hereafter first series of tests) contained in a refrigerator. We examined the influence of freezing temperature, initial wastewater concentration, the freezing rates and the vessel depth upon removal rate of COD. The second series of tests applied the technique using a rotary ice–making machine (hereafter second series of tests). We examined the influence on the COD removal rates in the round ice, the surrounding ice and the revolving ice. We focused on the COD removal rates in this study.

2. Material and methods

2.1. Materials

During the first series of tests, the freeze –concentrating technique using stationary vessels was used to purify diluted milking wastewater. During the second tests, a rotary ice–making machine was used to apply the freeze –concentrating technique to diluted milking wastewater. The milking wastewater was filtered and diluted to COD concentrations of about 500 mg/L, 1000 mg/L, 2000 mg/L and 8000 mg/L. The milking wastewater was stored at 0 ± 0.5°C.

2.2. Experimental apparatus and procedure

2.2.1. Freeze –concentration using a stationary vessel

In the first series of tests, the milking wastewater was frozen in stationary vessels (acrylic resin, radius 50 mm, depth 100 mm) located in a refrigerator. The sides and bottom of the vessels were insulated by a polyurethane sheet (thickness, 20 mm), so the milking wastewater would freeze from the upper side only. The temperature of the refrigerator was set at –3°C, –6°C, –9°C, –12°C, and –15°C. When all or most of the milking wastewater from the top was frozen, the ice was cut and picked out using a saw at about every 25 mm from the top. The COD's concentration in the sample solutions and the melted ice layer formed in the sample solutions were measured using a COD meter (HC–407, Central Kagaku Corp., Japan). The experiment was repeated three times for each condition, and the results were presented as the average values. The relative standard deviation from three measurements was approximately 5%.

2.2.2. Freeze concentration using a rotary ice–making machine

A rotary ice–making machine is normally used to make ice flakes for storing fish and vegetables. The ice–making part of the machine consists of rotary evaporator columns made of stainless steel (diameter 120 mm, width 120 mm), a knife–edge to shave the ice from the evaporator, nozzles, a pump, a lower tank and an upper tank as shown in Fig. 1. The columns fall into a refrigerant (ethylene glycol solution) at a constant rate (45 mm/h) with ultrasonic irradiation. The evaporator rotated at 1/3 rpm during the tests. When the machine was used for its original purpose, fresh water was stored in the upper tank, such that one third of the evaporator was immersed in the water.

Fresh water was also sprayed onto the revolving evaporator at the same time. The water in the upper tank and the sprayed water were frozen on the evaporator surface and the knife–edge shaved the frozen ice. In the second series of tests, diluted milking wastewater was stored in the lower tank and it was sprayed onto the evaporator to make ice flakes. The rotary ice–making machine worked at evaporator temperatures of –6°C and –15°C. The temperature in the sample was measured at two points using thermocouples.

Three kinds of ice were made by the machine as follows: (1) revolving ice – when the wastewater was sprayed onto the revolving evaporator, the wastewater was frozen on the evaporator surface and the knife–edge shaved the ice. In this paper, we refer to ice formed in this manner as "revolving ice". (2) Round ice – in some of the tests, wastewater was sprayed onto the evaporator when it was not revolving, and it froze on the surface. The ice that formed at a small round spot on the evaporator surface where the sprayed water hit directly is called "round ice" in this paper. (3) Surrounding ice – when wastewater was sprayed on the non–rotating evaporator, some of it froze immediately in the small round spot described above. The rest of the wastewater flowed away from the round ice spot and also froze on the evaporator in an area surrounding the round spot. Ice formed in this manner is called "surrounding ice" in this paper. Ice samples were taken from three sites in each of the round ice, revolving ice and surrounding ice using a pickax. After melting all the ice samples, the COD concentration in the solutions were analyzed using a COD meter. The experiment was repeated three times for each condition and the average of the three trials was determined. The relative standard deviation from three measurements was approximately 5%.

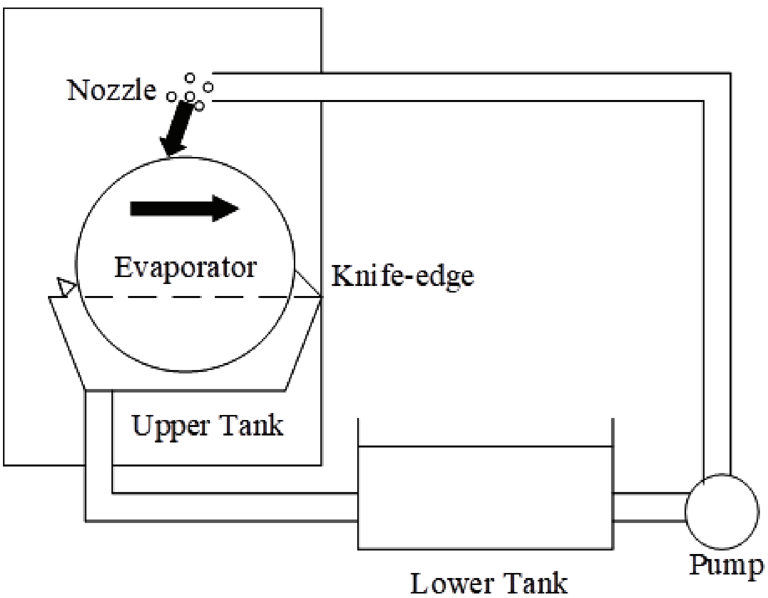


Fig. 1. Schematic of ice–making machine

3. Results

3.1. Freeze–concentration using a stationary vessel

3.1.1. Effect of freezing rate with different temperatures and concentrations

Comparison of ice thickness at different freezing temperatures (from –3°C to –15°C) at the COD concentration (1000 mg/L) of the milking wastewater in the ice layer using a 100 mm–deep vessel is shown in Fig. 2. The temperatures were one of the most important parameters affecting the freezing rate, as can be observed from Fig. 2. All of the milking wastewater was frozen in stationary vessels (785mL volume with radius 50 mm, depth 100 mm) at –3°C, –6°C, –9°C, –12°C and –15°C, the freezing times were about 105h, 81h, 68h, 51h, 38h, respectively. When the freezing temperatures (from –3°C to –15°C) were decreased, the freezing rate increased (see Fig. 3). The freezing rate (vessel volume (785mL)/ freezing time) at the freezing temperature of –3°C was 7.48 mL/h, however, that of –15°C was 20.66 mL/h. The relationship between ice thickness and freezing time under different concentrations (from 500 mg/L to 2000 mg/L) of the milking wastewater and temperatures (from –3°C to –15°C) in the ice layer using a 100 mm–deep vessel is shown in Fig. 4. The freezing rate (8.01 mL/h) of the milking wastewater for 500 mg/L was slightly greater than that (7.14 mL/h) of 2000 mg/L at the freezing temperature of –3°C (Fig. 4a). However, results show that the thickness of ice mass produced over a given time was almost the same for milking wastewater solutions with different concentrations (from 500 mg/L to 2000 mg/L) under the freezing temperatures of –9°C and –15°C (Fig. 4b and Fig. 4c). Therefore, the freezing rates were not significantly affected by the different concentrations of the wastewater solution (Beier et al., 2007).

3.1.2. Effect of freezing temperature and depth of ice layer

The relationship between freezing temperature, depth of ice layer and COD concentration in the ice layer using a 100 mm–deep vessel is shown in Fig. 5. The initial COD of the milking wastewater was 1000 mg/L in this run. After freezing most of the milking wastewater solution at –3°C, –9°C, and –15°C, the ice was divided at every 25 mm from the top.

Fig. 5 shows the COD concentration in each part of the ice. The COD concentrations in the surface ice (0–25 mm) at –3°C, –9°C, and –15°C were 72.21 mg/L, 90.62 mg/L and 99.31 mg/L, respectively. However, the COD concentrations of that part of the ice at lower depth (51–76 mm) were 259.41 mg/L, 312.72 mg/L and 329.11 mg/L, respectively. Results show that as the freezing temperatures (from –3°C to –15°C) decreased, the COD at the same depth within the ice layer increased. Also, as the ice layer grew in thickness, the COD concentration of the newest ice also increased. As a result, the COD concentration varied with the location within the ice layer, such that the concentration was lowest at the ice surface and increased with increasing ice depth.

The fact that the COD in the upper ice layer was lower than the COD in the deeper ice layer shows that it was easier for the pollutants to escape from the upper thin layer of ice than the deeper layer. Under a low freezing temperature (such as –15°C), the solution requires a large area to release latent heat. Ice crystals branched out and produced more advance branches at the trunk; at all levels to the end of the branches, pollutants were easily captured in the ice (Khusnatidinov and Petrenko, 1996; Martel, 2000).

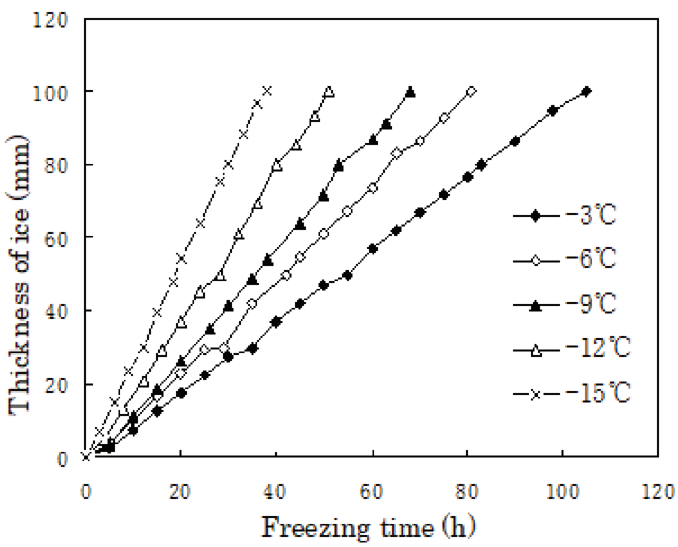


Fig. 2. Comparison of ice thickness at different freezing temperatures

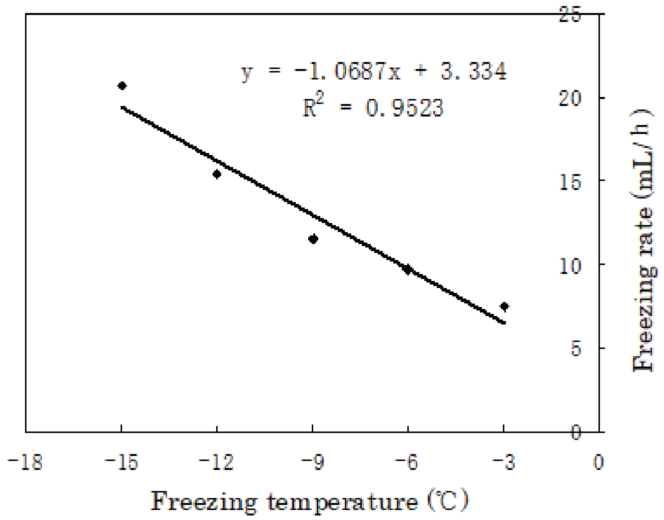
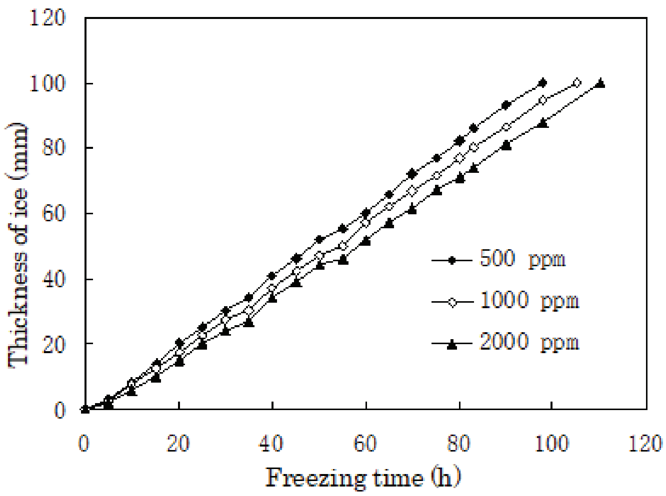
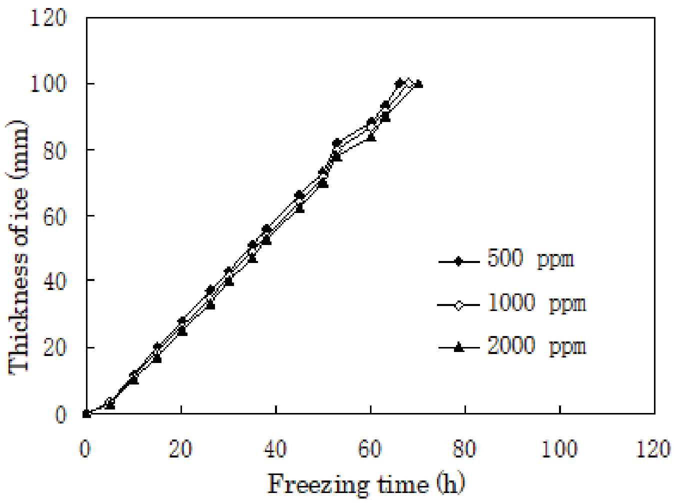


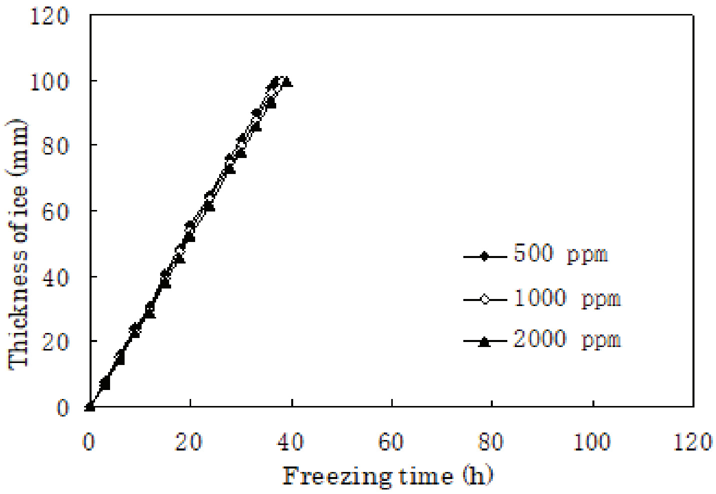
Fig. 3. Relationship between freezing rate and freezing temperature



(a)



(b)



(c)

Fig. 4. Relationship between ice thickness and freezing time under different concentrations (a, at –3°C; b, at –9°C; c, at –15°C)

The parameters in Eq. (1), which were determined from the freezing experiment, are summarized in Fig. 6.

$$R = \frac{C_0 - C}{C_0} \times 100\% \tag{1}$$

Here, R is the COD removal rate (%); C_0, the initial COD concentration of the milking wastewater (mg/ L); C, the COD concentration in the ice (mg/L).

Fig. 6 shows the removal rates of COD in the ice layer with different freezing temperatures (from –3°C to –15°C) at COD concentration (1000 mg/L) of the milking wastewater. Fig. 6 shows that the COD removal rates in the 0–25 mm ice layer were 90.07%–92.78%, but the removal rates in the 51–75 mm layer were 67.09%–74.06%. Under the conditions of rapid freezing (such as –15°C), ice crystals appear with tree branches and needle–like crystals at the solid–liquid interface. Much more pollutants (the milk) was retained caged in the ice crystals, the removal rate of milking wastewater solution was decreasing because the speed of freezing for water molecules was faster than that of exclusion of the pollutant (the milk) from the wastewater solution.

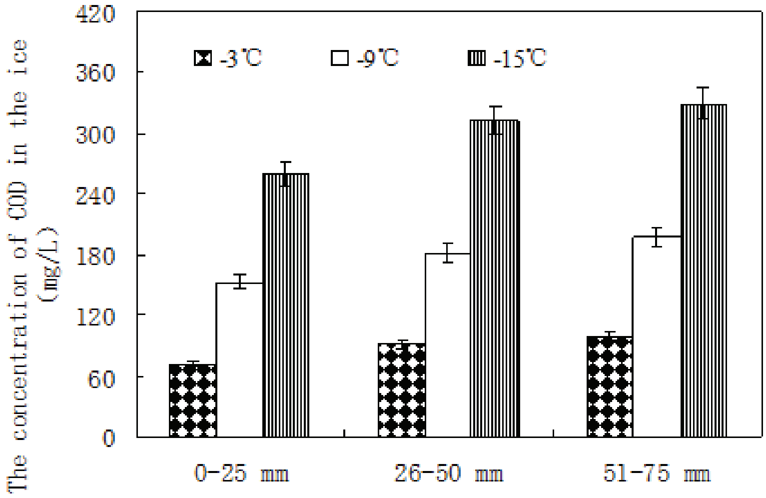


Fig. 5. The concentration of the COD in the ice layer from different freezing temperatures at COD concentration (1000 mg/L) of the milking wastewater

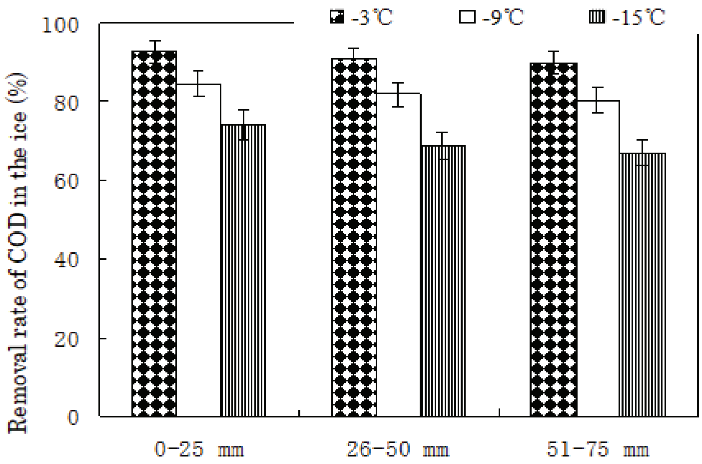


Fig. 6. Removal rates of COD in the ice layer from different freezing temperatures at COD concentration (1000 mg/L) of the milking wastewater

3.1.3. Effect of COD concentration of wastewater

The milking wastewater (500 mg/L, 1000 mg/L and 2000 mg/L) was frozen using a 100 mm–deep vessel at the freezing temperature of –3°C. The COD removal rates in the 0–25 mm ice layer is shown in Fig. 7. The COD removal rates at this ice depth (in the 0–25 mm) for the COD concentrations of 500 mg/L, 1000 mg/L and 2000 mg/L were 94.56%, 92.78% and 91.25%, respectively. Results (Fig. 7) show that the COD removal rates in the 0–25 mm ice layer were not significantly affected by the different concentrations (500 mg/L, 1000 mg/L and 2000 mg/L) of the milking wastewater.

3.2. Freeze–concentration using a rotary ice–making machine

3.2.1. Effect of the evaporator revolution

The influence upon COD removal rate of the freezing methods on the evaporator is shown in Fig. 8. The initial COD of the milking wastewater was 500 mg/L in this run. In the tests of revolving ice at different evaporator temperatures (–6°C and –15°C), the COD removal rates at an evaporator temperature of –6°C were higher than the removal rates when the evaporator temperature was –15°C.

These results were dued to the fact that when the freezing temperature was lower, at –15°C, the freezing speed increased and pollutant (the milk) was trapped during the ice crystallization process, because the ice did not have time to exclude the pollutant (the milk) from newly formed ice crystals. Fig. 8 shows that the COD removal rates of –6°C and –15°C in the round ice (99.12% and 95.24%) and the surrounding ice (98.37% and 90.28%) were higher than the removal rate of the revolving ice (91.47% and 85.68%).

3.2.2. Effect of the COD concentration of wastewater

The milking wastewater (500 mg/L, 2000 mg/L and 8000 mg/L) was frozen using a rotary ice–making machine at the freezing temperature of –15°C. As the COD concentration in the wastewater decreased, the COD removal rates in all kinds of ice (the round ice, the surrounding ice and the revolving ice) increased (see Fig. 9). The COD removal rates in the round ice, the surrounding ice and the revolving ice for the initial COD concentration (500 mg/L) were 95.18%, 91.21% and 63.36%, respectively. However, the COD removal rates in the round ice, the surrounding ice and the revolving ice for the initial COD concentration (8000 mg/L) were 85.24%, 74.31% and 46.18%, respectively. This was due to the fact that as the COD in the wastewater increased, it was harder for the COD to escape, as described for the COD removal rate in the first series of tests in the stationary vessel.

When the pollutant's concentration in the wastewater solution was increased, the particles of newly produced ice crystals were smaller, and the surface area of ice crystals was much larger. So, much more pollutant was caged into the ice crystals. As the removal rates of wastewater increased, the pollution (the milk) concentration of the wastewater solution decreased. For this reason, as the stability of the solid–liquid contact surface was lowered, there would be a lot of ice crystals like dendritic branching and the viscosity of the wastewater solution was increased, with the increased concentration of the pollution in wastewater solution (Yu et al., 2007).

4. Discussions

The ice–forming process normally tends to exclude every substance other than the water molecules from ice crystal (Dai et al., 2011). Therefore, most solutes are moved into the liquid phase from ice crystals during the ice–forming process and are concentrated there. When the solute between the ice crystals is further concentrated, the freezing point of the solution decreases (Kobayashi et al., 1996). This prevents the solution from freezing until at a lower temperature. Meanwhile, ice crystals grow slowly to a larger size when the temperature is closer to the freezing point (Dai et al., 2010b).

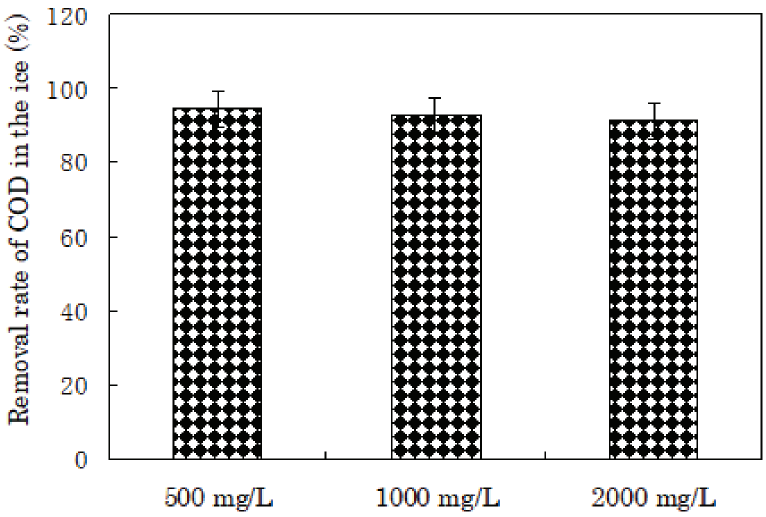


Fig. 7. Removal rates of COD in the 0–25 mm ice layer from different initial concentrations of the milking wastewater in 100 mm vessel at the freezing temperature of –3 °C

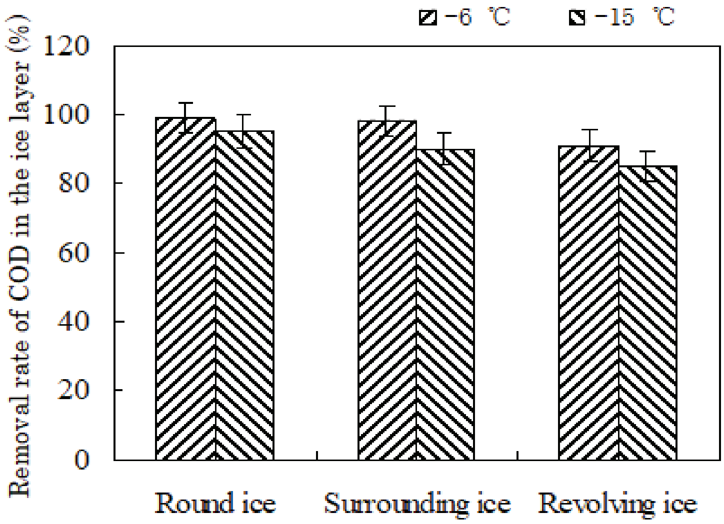


Fig. 8. Removal rates of COD in the flake ice from different freezing temperatures at COD concentration (500 mg/L) of the milking wastewater.

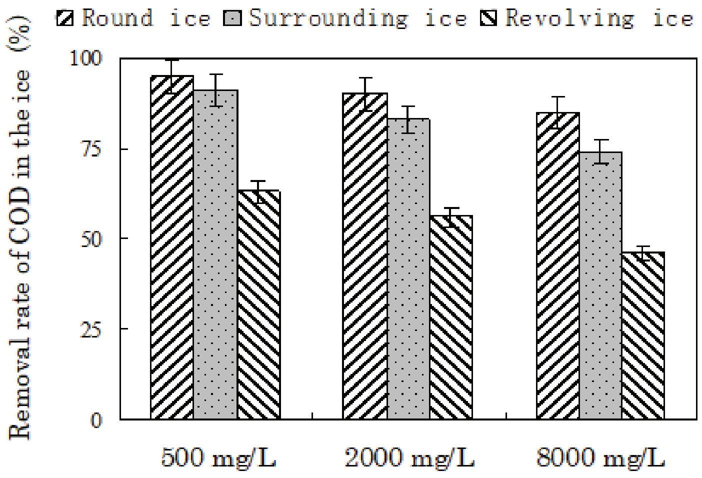


Fig. 9. Removal rates of COD in the flake ice from different initial concentrations of the milking wastewater at the freezing temperature of –15 °C

However, when the temperature is much lower than the freezing point, the rate of ice growth becomes faster than the rate of exclusion of the solute, and crystal nucleation occurrs in the whole solution (Wakisaka et al., 2001). Consequently, a greater amount of the solute (pollutant) is incorporated among the ice crystals. When the temperature of the solution drops to below the freezing point, the ice crystal nuclei are produced. At this point, there exist two kinds of diffusion of the solute and solvent (water molecule) in the system of solution. As a result of the driving force of diffusion due to the concentration difference of wastewater solution, water molecules separate out wastewater solution by the intention of hydrogen bonds and become ice crystals covering the surface of the ice in the vicinity of the solid–liquid interface. At the same time, the pollutant molecules are still retained in the mother solution of wastewater and become concentrated.

Diffusion of water molecules in the liquid phase is carried out at the solid–liquid interface, pollutant molecules at the solid–liquid interface are diffused to the solution of wastewater (Gao et al., 2000, 2004). When the wastewater first hit the evaporator, the velocity of the flowing wastewater at the round ice spot was fast enough to wash out the pollutants that escaped the ice crystallization process, resulting in the lower COD concentrations in the round ice. The velocity of the wastewater decreased as it flowed into the surrounding area, and as a result the COD concentration of the surrounding ice was higher than that in the round ice, as reported (Dai et al., 2010a). Nevertheless, the COD concentrations in the surrounding ice were lower than that in the revolving ice. The reason for the lower removal rate of the revolving ice is as follows: when the evaporator was revolving and wastewater was sprayed on its surface, the point where new wastewater was sprayed moved along with the revolution of the evaporator. So, the pollutant (the milk) that escaped from the crystallization process was not washed away by the new wastewater, but instead froze on the ice surface (Miyawaki, 1995).

The round ice and the surrounding ice were created when the evaporator was not revolving, so the new wastewater was continuously sprayed on the same spot and this continuous flow was able to wash away the pollutant (the milk) that was excluded from the ice crystallization process.

5. Conclusions

This study was carried out to determine the feasibility of applying a freeze–concentrating technique to rarefy the milking wastewater using either a stationary wastewater vessel (the first series of tests) or a rotary ice–making machine (the second series of tests). In the first test, when the freezing temperatures were decreased, the freezing rate increased. As the freezing temperature decreased, the COD concentration varied with the location within the ice layer, such that the COD concentration was lowest at the ice surface and increased with ice depth. In the second test, the COD removal rates in the round ice and the surrounding ice were higher than the removal rate of the revolving ice. As the COD concentrations in the wastewater increased, the COD removal rates in all kinds of ice decreased.

Our results shown in this study could lead to the conclusion that the freeze–concentration treatment method can become a powerful treatment method for milking wastewater.

Acknowledgments

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