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A Newly Developed Wastewater Treatment by Using Solidification Reaction of Milk Fats and Proteins through Ozonation

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Environmental regulations for dairy farms and milk-plants tend to be tightened in Asian countries, particularly in Japan, because the milk-including wastewater discharged from them causes serious regional environmental problems. For small and medium-sized dairy farms and milk plants, we propose a novel process of using ozone which has very strong oxidative power. This proposed process is different from conventional treatment processes with ozonation, and rapidly reduces BOD, TOC, total nitrogen (T-N) and chromaticity of the wastewater containing milk. This new ozonation process imposed partial polymerization of the unsaturated fatty acids including carbon-double bonds as well as simple decomposition of the above acids into low molecules. Whitish solid-like products formed from the polymerized fatty acids (i.e. ozonide) and the insoluble proteins were adsorbed to the ozone bubbles. The solidification and purification efficiency of this process depended on the initial condition of the milk-containing wastewater. Thus, we propose a two-stage process against this wastewater treatment method. Under an acid initial condition, the ozonation increases yield on the solid-like products which are compounded from the polymerized fatty acids and the insoluble proteins. When these solid-like products were removed from the wastewater, the pollutants (i.e. BOD, TOC, T-N and chromaticity) in the wastewater were decreased almost simultaneously. Accordingly the water quality was improved in a short time. The ozonation under an alkaline initial condition with a low temperature also improved the water quality, despite the fact that the yield of the solid-like products was small. In this condition, the solubility of the ozone was higher than that under the high temperature condition, hence the OH-radicals generated from the ozone were enhanced in the alkaline condition and decomposed the pollutants powerfully. These two reaction pathways depending on the pH and temperature were strongly related to the decomposition of the pollutants by ozone. Thus, the ozonation under an acid condition is more useful for small and medium-sized dairy farms and milk plants, because they do not need the control of the wastewater temperature under an acid condition.

1. Introduction

Wastewater from dairy farms or milk plants includes some milk and is very difficult to treat by means of conventional wastewater treatment methods, due to the included milk fats and proteins. This type of wastewater has been usually discharged into a river directly particularly in many Asian countries due to their undeveloped environmental legal system and poor wastewater treatment facilities. Rapid increase (e.g. in India and China) in milk production has caused more serious local environmental impacts. In Japan, environmental problems of different types such as stench, chromaticity and antibiotics, are very serious in suburban areas, by which milk farmers are forced to close their milk production. A pollutant level of this wastewater is very high in relations to the small amount of the milk (Omil et al., 2003). Hence, worldwide, environmental regulations in agricultural industries regarding to dairy farms and milk plants are trending to be stricter (e.g. EPA, 2011; EC government, 2011). For treating the wastewater including milk (WIM), traditional microbial oxidation and anaerobic bio-decomposition are often used (Demirel et al., 2005). Recently, an artificial wetland system is sometimes used for wastewater treatment (Vymazal, 2009). These conventional

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treatment methods need additional processes (e.g. enzymatic hydrolysis of fatty acids (Jung et al., 2002) in order to completely decompose fats, proteins and antibiotics. As a result, the treatment of the WIM by the conventional treatment methods requires a large-scale system, longer treatment time and larger energy (which increase treatment costs and becomes in a great trouble).

Hence, small-size milk factories and milk farmers have been yearning for a newly economical and maintenance-free wastewater treatment process replacing the conventional ones as reliable treatment. The most hopeful option is an ozonation treatment that is already applied in the field of urban drink water treatment. The ozonation process was applied to treatment of olive-mill wastewater, because it was highly effective in saturated fatty acids (Lafi et al., 2009). Since the ozonation process is very useful for decolorization against colored products, it has been applied to bleaching pulp in a paper industry (Prat et al., 1990) and to decolorizing azo dyes of textile wastewater (Tokumura et al., 2009). However, white turbidity (chromaticity) of milk is different from the above substances, from total reflection of visible light of casein micelles and milk fat globules. On the basis of our experimental results, the expected decolorization by the ozonation against milk was considered to be of destruction effects on hydrophobic structure of the casein micelles and milk fat globules which were immediately pollutants. Consequently, the ozonation was considered to effectively bleach and purify WIM at one treatment action. It is useful and attractive for simultaneously treating the chromaticity and pollutant of WIM for the small and medium-size farms and milk plants.

2. Experiments

2.1 Experimental setup and ozonation procedure

The experimental setup used in the present investigation is outlined in Figure 1. The setup consists of a cylindrical plastic reactor vessel (a) of 550 mm in diameter and 900 mm in depth, a vortex pump (j) (Nikuni, 20NPD), and an ozone generator (d) (Hamanetsu, OG-R6: a type of silent electric discharge, it's provided with discharge tube (e) and gas flow meter (f)). O_2 gas is supplied to the ozone generator from O_2 gas cylinder (g). A inner cylinder for fixing the pipe (b) of 250mm in diameter set in the reactor vessel. The reactor vessel was filled with simulated wastewater of 0.1 m^3 (a mixture of 1 kg/m^3 raw milk and 999 kg/m^3 tap water). The properties of the initial simulated wastewater are listed in Table 1. The temperature of the wastewater was adjusted to the initial targeted temperature through iced water or heated water, and kept at the initial temperature ±5°C during the experiments. By using a pH meter (h) (DKK-TOA, IM-32P: a type of glass electrode), the initial pH of this wastewater was adjusted by addition of HCl in the case of an acid condition and was done by addition of KOH in the case of an alkaline condition. By using an electrical conductivity meter (i) (DKK-TOA, CM-31P: a type of alternating double electrodes), the electrical conductivity was adjusted in 0.5 dS/m by addition of KCl. The simulated wastewater was circulated through the vortex pump at a flow rate of 0.02 m^3/minute adjusted by a Karman's vortex flow meter (k). The ozone gas from the ozone generator was injected into the simulated wastewater through an injector (c) (Mazzei, Model 648) inserted in a downcomer set in the vessel. The ozone generator stably generated O_3 gas of 0.135 mol/h from O_2 gas of 23.7 mol/h. The ozone concentration of injected mixture gas was 0.24 mol/m^3 (in mass).

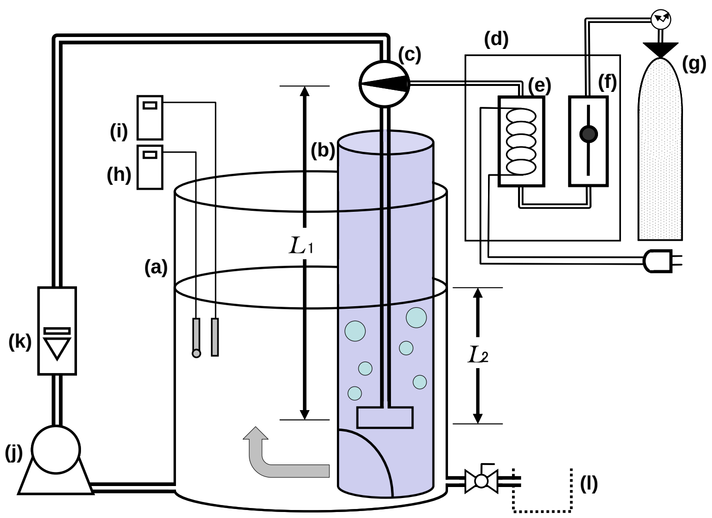

Figure 1: Diagram of the experimental setup. Pipe length of ejector to discharge position (L_1) = 105 cm, Water depth of discharge position(L_2) = 38 cm

Table 1: Properties of the simulated wastewater

Chromaticity	COD_{Mn}	BOD_5	TOC	Total Nitrogen
549±131	349±26 mg /L	1,110±177 mg/L	453±105 mg/L	35.9±6.9 mg/L

2.2 Capture and separation of the solid-like products from the ozonized wastewater

The drain outlet of the reactor was equipped with a solid-like products catcher (nylon 40 mesh) (Figure1 (l)). After 3 hours ozonation, the ozonized wastewater (including foam) in the reactor was discharged through drain outlet. During this step, the solid-like products in the ozonized wastewater were separated and captured on the mesh. The recovered solid-like products were inserted more than 12 hours into a circulation dryer (60°C). The weight of well dried solid-like products was measured by an analytical balance.

2.3 Analysis of the pollutant levels

The Biological oxygen demand (BOD) was measured by determining oxygen consumption (measurement of a concentration of residual dissolved oxygen via Winkler's method), during 5 days in incubation at 20 °C with microorganisms obtained from a liquid compost of a dairy farm. The Chemical oxygen demand (COD) was measured from a consumption of residual potassium permanganate titrated by sodium oxalate after 5 min oxidation at 105 °C. These two methods (BOD, COD) conformed to ISO 5815 and ISO 6060. Total organic carbon (TOC) was measured using TOC analyzer (Shimadzu, TOC-5000). Total nitrogen was measured through a steam distillation method of thermally decomposed organic nitrogen in sulphuric acid according to ISO 8425. The chromaticity was measured through a chromaticity sensor (Kasahara-Rika, TCE-5Z).

3. Results

3.1 Solid-like products by the ozonation, and the floatation process

Small flocculated particles were generated in the simulated wastewater after injection of the ozone-including bubbles. Most of the small flocculated particles were gradually adsorbed on these bubble surfaces, and the rest was settled on the bottom of the vessel. Most part of the contaminated bubbles ascended to the wastewater surface, and some of them circulated in the wastewater. Thus the bubbles reaching the wastewater surface grew into break-resistant and flexible foam gradually (Figure 2). At the end of the ozonation, the solid-like products existed on the degassed foam or in the aqueous solution. The solid-like products caught on the mesh looks like whitish clay (Figure 3). This solid-like products contain 60 ~ 70 % water.

Figure 2: Foam at the upper part of reactor

Figure 3: Features of collected solid-like products

3.2 Yields of the solid-like products under the conditions of pH and temperature

Yields of the solid-like products changed with a pH level of the wastewater; pH level of 5.5 was a border value against the yields (Figure 4). In an acid condition under pH 5.5, the yield of solid-like products increased rapidly with decrease in the pH level. The yield of the solid-like products was less than 10 g under a natural-alkaline condition. These phenomena suggested that the yield of the solid-like products depended on the pH level of the wastewater. On the other hand, the temperature of the wastewater did not influence the yield of the solid-like products under any pH conditions. In addition, the yield of solid-like products varied widely even under the acid condition. This was considered to arise from variation of the used raw milk; i.e. the initial pollutant levels ranged from 800 mg/L to 1,450 mg/L (BOD). Figure 5 shows the close correlation between the yield of the solid-like products and the initial pollutant level (BOD).

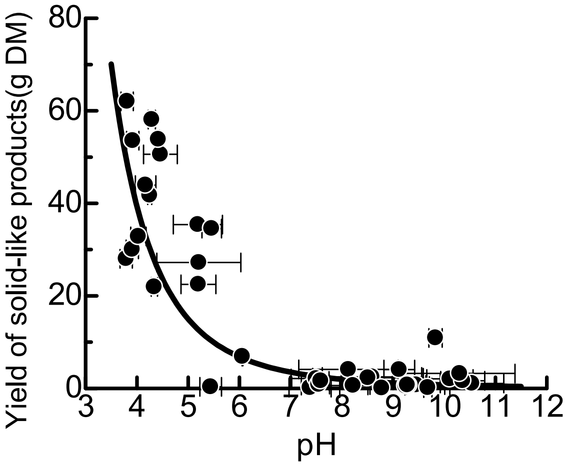

Figure 4: Effects of pH against yield of solid-like products

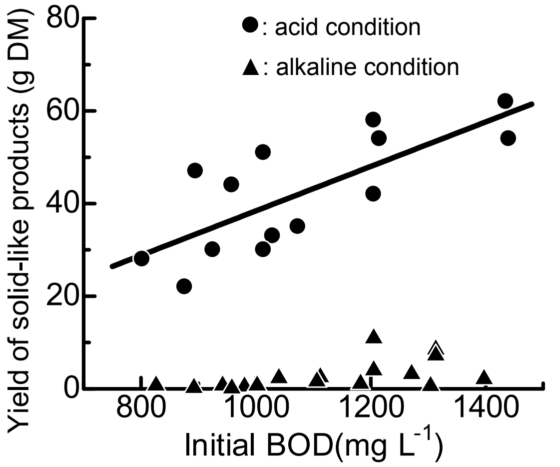

Figure 5: Effects of initial BOD against yield of solid-like products in acid or alkaline conditions

3.3 The relations of water quality and ozone consumptions under tested conditions of pH and temperature

The water quality depended on the initial pH level and temperature of the wastewater. For the chromaticity, the higher color removal ratio (CRR) of 0.88 ~ 0.99 was obtained under the acid condition at any temperature conditions. Under an alkaline condition, the CRR took 4/5 levels of that under the acid condition, only at below 10 °C. However, the CRR rapidly dropped with the temperature increase. Over 25 °C, the chromaticity became higher than the initial level (Figure 6).

The BOD removal ratio (BODRR) took higher levels of 0.65 ~ 0.83 in an acid condition. However, the BODRR slightly decreased with the temperature increase. In an alkaline condition, the BODRR remarkably decreased with the temperature increase. At 35 °C, the BODRR took 1/4 levels of that at 10 °C as shown in Figure 7. In addition, the TOC removal ratio (TOCRR) indicated a similar tendency to the BODRR in the alkaline condition. While, the TOCRR increased with increase in the temperature, in the acid condition (Figure 8). In addition, a similar tendency is observed at the T-N removal ratio. The COD removal ratio (CODRR) took below 0.3 in any conditions. It was lower levels than the CRR, BODRR and TOCRR, as shown in Figure 9.

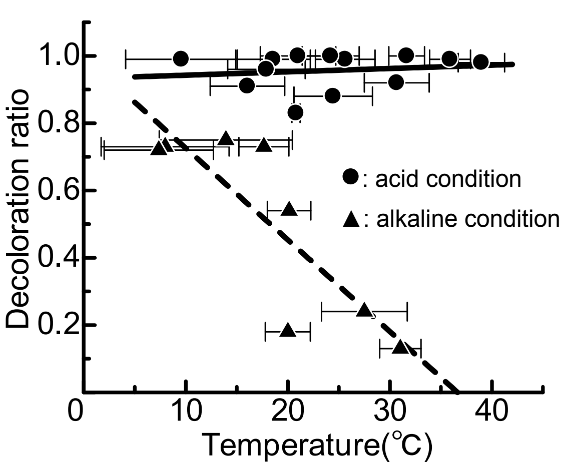

Figure 6: Decoloration ratio by ozonation in temperature and acid or alkaline conditions

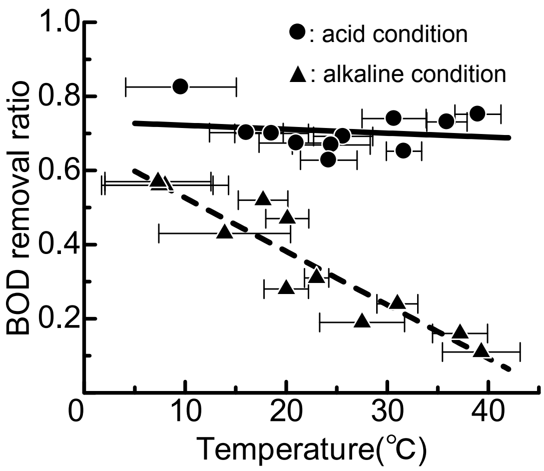

Figure 7: BOD removal ratio by ozonation in temperature and acid or alkaline conditions

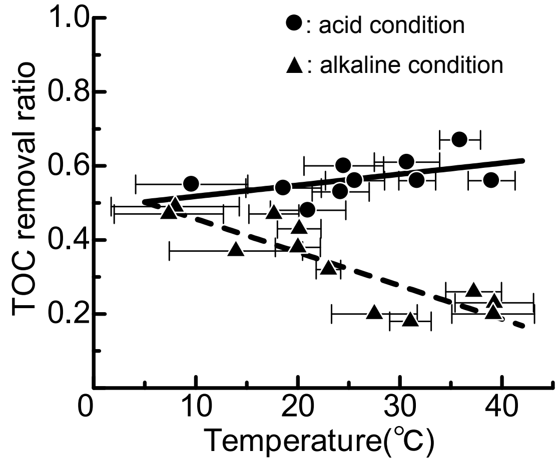

Figure 8: TOC removal ratio by ozonation in temperature and acid or alkaline conditions

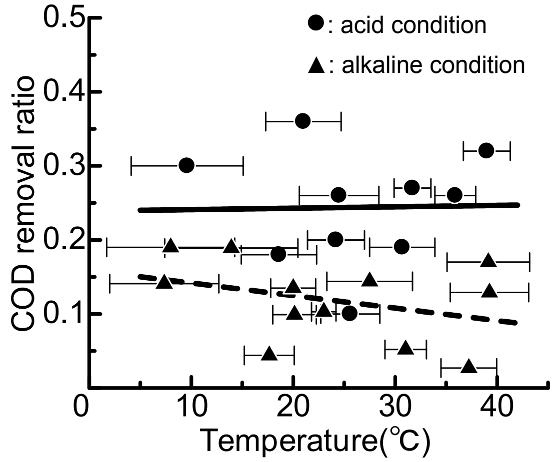

Figure 9: COD removal ratio by ozonation in temperature and acid or alkaline conditions

4. Discussion

The treatment process discussed in the present study is different from conventional ones which use oxidative decomposition effects of ozone. The effects of the pollutant decomposition by ozone are very low in the conventional treatment processes; hence they need larger energy consumption to treat wastewater including milk (WIM). The conventional treatment processes using oxidative decomposition are impractical for wastewater treatment including high concentration pollutant such as WIM.

We have developed a new wastewater-treatment technique by a different approach from the conventional ozonation processes. We utilized ozone in order to solidify pollutants of the WIM and removed the pollutants as solid-like products from the WIM. In this technique, the ozone-containing bubbles were injected in the WIM and the solid-like products were adsorbed on the bubble surfaces and captured/separated from the WIM. For practical use of this technique, we have to investigate the most suitable conditions to increase a removal efficiency of the pollutants.

The most important factor is the dissolution rate of ozone into the WIM, which depends on the WIM temperature. The dissolution rate of ozone is decreased with increase in the temperature; for instance the Henry's constant increases from 5.10 $H_0/kPam^3mol^{-1}$(at 5 °C) to 9.19 $H_0/kPam^3mol^{-1}$(at 20 °C) (Rischbieter et al., 2000). However, the present results showed that the WIM temperature had no influence on the yield of the solid-like products. The WIM pH level influenced the yield of solid-like products more remarkably than the temperature. The yield of solid-like products increased in an acid condition under pH 5.5, rapidly.

We considered that three factors affected the increase in the yield of the solid-like products in the acid conditions. The first factor was that the milk protein (mainly casein) depressed its own solubility due to higher-order structural change by ozone attacking. The second factor was that the casein was considered to be coagulated as "curd" in an acid condition, because isoelectric point of casein was pH 4.6 (Schmidt and Poll, 1986). Third, considering that this reaction was of oxidation by direct reaction of ozone and unsaturated fatty acids (Criegee,1975), in the acid conditions, the yield of the ozonide which was formed or polymerized by the reaction of unsaturated fatty acid and ozone must have increased. The direct oxidation of ozone and unsaturated fatty acid was active only in an acid condition which decreased the self-decomposition of ozone.

These reactions which made distinctive structures produced by ozonation occurred in short time. Actually, the pollutant level (namely chromaticity, BOD, TOC and T-N) of the WIM rapidly decreased with generation of the solid-like products. As a result, this fact suggested the purification through this technique was more effective than the complete decomposition, because this technique consumed less energy than that of other techniques.

In this study, interestingly the purification through ozonation in the alkaline conditions was effective. The alkaline conditions were considered to enhance the self-decomposition of ozone and generate many OH radicals (Ku et al., 1996). Immediately the OH radicals attacked the pollutants, the pollutants were degraded to the low-molecular compounds. In the alkaline conditions, the purification ratio was depressed rapidly with increase in the wastewater temperature. This fact suggested that the wastewater temperature constituted a limiting factor of the purification under an alkaline condition; similarly it was a limiting factor of purification in conventional techniques by ozonation process. This fact means that it is disadvantageous for dairy farms, because the farmers discharge heated water from washing a milking machine or storage tank. On the other hand, the reaction under an acid condition that possessed solidification process is more advantageous for dairy farm, because the wastewater temperature had no influence against the purification through the solidification process.

Thus, the pH level significantly influenced the reaction producing the solid-like products (including ozonide) and the performance of removing the pollutants in the WIM. Especially, pH 4.6 (isoelectric point of casein) and pH 5.0 (inflection point of the self-decomposition speed of ozone) were boundary of the two type of the purification reactions, namely the solidification and the decomposition. The solidification was polymerization and coagulation. Our study is considered to be an innovative technique in the way of using solidification by ozonation.

5. Conclusion

In acid conditions below pH 5.5, the pollutants in wastewater containing milk were solidified into pure ozonide (that was formed by reacting unsaturated fatty acid and ozone) and the proteins coagulate as "curd" due to decreased solubility attacked by ozone. In this ozonation technique, the pollutants are removed as the solid-like products immediately and it improved the water qualities in short time and with low input of energy. These properties of the new technique are suitable for small and medium dairy farmers.

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