Journal of Environmental Sciences Vol.16, No.2, pp.230—233, 2004

ISSN 1001—0742
CN11—2629/X

Article ID: 1001-0742(2004)02-0230-04 **CLC number**: X703 **Document code**: A

Effect of preozonation on improvement of settleability of solid in highly concentrated organic wastewater of Japanese wheat and sweet potato spirit-distillery

Masafumi Tateda[1,*], Masanori Fujita[2], Michihiko Ike[2], QUI Yen-feng[3], Satoru Kokubo[4]

(1. College of Environmental Technology, Toyama Prefectural University, Japan. E-mail: tateda@pu-toyama.ac.jp; 2. Department of Environmental Engineering, Graduate School of Engineering, Osaka University, Japan; 3. Espec Co., Ltd., Japan; 4. JC Engineering Co., Ltd., Japan)

Abstract: Solid-liquid separation of the wastewater is very difficult because of high viscosity and high SS concentration. In this study, the effectiveness of preozonation on improving the settleability of the solids in wheat and sweet potato wastewaters was investigated using a bench-scale system and pilot treatment system respectively. Results showed that solid-liquid separation in the wheat wastewater was greatly improved by the decanter in the system(SS reduction from 24100 mg/L to 100 mg/L). However, preozonation practice did not show a significant effect on solid-liquid separation of the sweet potato wastewater. Effect of preozonation on solid-liquid separation between wheat and sweet potato wastewater showed different.

Keywords: Japanese spirit-distillery wastewater; wheat wastewater; sweet potato wastewater; London dumping convention; ozonation; settleability; solid-liquid separation

Introduction

Japanese spirits or Shochu is one of the most popular alcoholic beverages in Japan. The singularly distilled spirits is one type of Shochu and is mainly produced by midsized companies. The total production of singularly distilled spirits was 310000 kl in the fiscal year of 1994 in Japan, and approximately 84 percent of it or 263000 kl was produced in the south of the Kyushu Island, the southernmost island among the four main islands. Raw materials of Shochu are rice, sweet potatoes, wheat, and buckweeds, but wheat has been used primarily. The amount of wastewater is the same as that of products in case of rice spirits, but wastewater doubles or triples for wheat and sweet potato spirits. The total generation of wastewater was 390000 kl in southern Kyushu, which was one and a half times more than the total amount of spirit production.

The practice of dumping wastewater into sea becomes difficult following the exaction of London dumping convention from January 1st, 2001. The wastewater is still on the list of the exempted wastes from obligation of the convention, however, the world consensus will terminate the exemption status for the wastes. The wastewater contains high concentration of suspended solids(SS) and it difficult to be treated difficulty. Solid-liquid separation is necessary as a pretreatment of the wastewater for the process, however, the separation is very difficult because of the characteristics of the wastewater, high viscosity and high SS concentration. Ozonation has been employed as a pretreatment followed by a coagulation-flocculation process in wastewater treatment to improve the efficiency of wastewater treatment (Farvardin, 1989). Improvement of the settleability of SS in wastewater is attributed partly to change of surface condition of the SS in wastewater; electric balance among SS particles is lost by ozonation, and the particles easily coagulate with each other (Tanaka, 1998; Yeh, 1987; Beltran, 1999). Consequently, a total treatment system with preozonation process for the Japanese spirit-distillery wastewater was proposed (Fig. 1). The wastewater was treated by preozonation first and separated into solid and liquid by a decanter, then treated in a highly concentrated activated sludge, and finally treated in an aerobic submerged filter process.

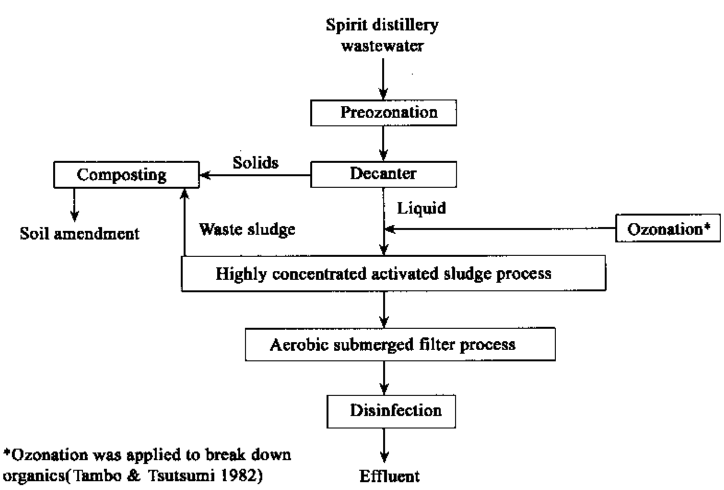

Fig. 1 The proposed combined system of ozonation and biological process for treatment of Japanese spirit-distillery wastewater. Ozonation was applied to break down organics(Tambo, 1982)

* Corresponding author

The purpose of this study was to investigate effectiveness of preozonation to improve solid-liquid separation of the Japanese wheat and sweet potato spirit-distillery wastewaters in the proposed system. Basic information of ozonation of the wastewaters are obtained from a bench scale experiment and the pilot scale system was operated to confirm the effectiveness of preozonation for treatment of the wastewaters.

1 Materials and methods

1.1 Wastewater

Wheat and sweet potato spirit-distillery wastewaters (wheat and sweet potato wastewaters) were used in experiments, and main compositions are shown in Table 1. Major compositions of SS are amino acid, saccharide, protein, and citric acid (Konno, 2002). These wastewaters were sampled from a Japanese spirit production factory in Kagoshima Prefecture, Kyushu Island, and sent to the Water Science and Environmental Biotechnology Laboratory at Osaka University, Osaka, Japan, being stored at 4℃ for a bench scale experiment.

Table 1 General characteristics of wheat and sweet potato spirit wastewater

Paramaters	Wheat	Sweet potato
CODt, mg/L	28000—35000	22000—49000
Suspended solid, mg/L	14000—31000	14000—37000
pH	3.6—4.2	4.0—4.3
ORP, mV	173—220	72—151

1.2 Analyses

Soluble COD (CODs) and CODt were measured by an HC-507 type COD meter (Central Kagaku Corp. Japan) and a K-7 type COD meter (Kasahara Rika Kogyo, Japan) for a bench and a pilot scale experiments, respectively. A 50 ml aliquot of raw sample (CODt) and supernatant of the samples (CODs) was collected into a 200 ml beaker for the measurement. CODs were measured only for pilot scale experiment. Measurement of MLSS and SS concentration was followed by Japanese Standard Methods for Sewage Examination (Japan Sewage Works Association, 1997). The pH of the sample was measured by a TPX-90i type pH meter (Toko Chemical Laboratories Co., Ltd., Japan) and an FD-70P(M) Series (Fuji Kagaku Keisoku, Japan) for the bench and the pilot scale experiments, respectively. ORP (Oxidation-Reduction Potential) was measured by a TPX-90i type pH meter (Toko Chemical Laboratories Co., Ltd., Japan) and an OM-14-L1 type ORP meter (Horiba, Ltd., Japan) for the former and the latter experiments, respectively.

1.3 Scanning electron microscope (SEM)

SEM observation was done by a JEOL 5410LV (JEOL, Ltd.) and followed the gold-ionizing coating process described by the instruction of the SEM. The SS of the wheat wastewater was freeze-dried after ozonation, treated by gold-ionizing coating, and examined by SEM.

1.4 Ozonation

A bench scale ozonation process is illustrated in Fig.2. The process consisted of Ozonizer POX-20 type (Mitsubishi Electric, Co., Ltd.), an ozonation reactor, a circulation pump, an ozone monitor, a reactor of waste ozone adsorption by KI solution, and a reactor of waste ozone treatment by activated carbon. Pure oxygen gas was used as source of oxygen. The ozonation reactor was made of glass, and its volume was 1.5 liter. The circulation pump was used for mixing in the reactor. Ozone generation was allowed for 5 to 15 min. Generated ozone was absorbed by 300 ml of KI solution (3%), and its generation was measured by nitrating with 0.01 mol/L sodium thiosulfate, resulted in a standard curve. For ozonation practice of wheat and sweet potato wastewaters, the reactor was filled with 1.2 liter of the wastewaters. A flow rate of ozone was 0.6 L/min. Generation of waste ozone was simultaneously measured by the same method as measurement of ozone generation.

A pilot scale ozonation process, consisting of an ozonizer, an ozonation unit, and a decanter, was set on the site of the Japanese spirit production factory in Kagoshima Prefecture. The ozonizer was IOH 750AC-25 type (Japan Ozone), and the ozonation unit was a gas and liquid mixed by counter-flow system. Ozonation of the wastewaters was performed under high pressure ($1.0—3.0\ kg/cm^2$) in order to accelerate ozonation. The BDN-006 (P-660BD) decanter (Tomoe Engineering Co., Ltd.) was used for solid-liquid separation after ozonation. 100 L of the wastewaters was diluted to approximately a half in concentration, and ozonation practice was performed.

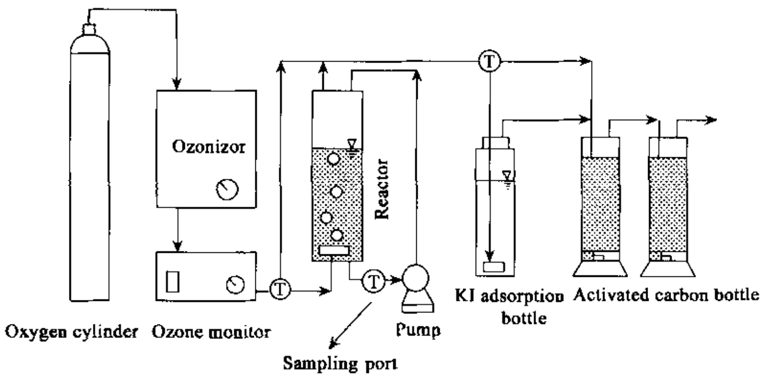

Fig.2 Bench scale ozonation equipment

2 Results and discussion

2.1 Bench scale experiment

To confirm the optimal condition for settleability of the SS in wheat and sweet potato wastewaters, change of SV60 was observed as a function of values of the ozone dose-reaction time (DT). SV60 indicated the volume of sludge in a 1000 ml measuring cylinder after 60 minutes, and ozone reaction time was set 20 to 100 min. The result is shown in Fig.3. Values of SV60 decreased as DT values increased and the decrease stopped at DT values of 576 mg/(L·min) and 864 mg/(L·min) for wheat and sweet potato wastewaters, respectively. When the DT values increased further, the SV60 values showed a slight increase, which confirmed the observation that there is the optimal preozonation dose for treatment of wastewater (Farvardin, 1989). Percentages of SV60 at the optimal DT values were 52% and 73% for wheat and sweet potato wastewaters, respectively, and comparing to the control values (SV values when DT value was zero), approximately 30% and 20% respectively were reduced. The reason for a slight increase on SV60 values after DT values reached optimal could be that the SS of the wastewaters was broken into smaller particles by ozonation, and that coagulation of the SS was more difficult (Tanaka, 1998). A change of ORP values as a function of DT values is shown in Fig.4. The ORP values both of the wastewaters increased greatly until DT achieved approximately 500 mg/(L·min) and, after that, the increase became slight. The ORP values of the wheat wastewater increased greater than those of the sweet potato wastewater, and it indicated that the wheat wastewater was in a more oxidized state than the sweet potato wastewater. The CODt values after ozonation were observed as a function of DT values and showed quite different patterns (Fig.5). The CODt value of the wheat wastewater reached the minimum at the DT value of 576 mg/(L·min), whereas, that of the sweet potato wastewater reached the maximum at that DT value. It could be possible that, at low DT values, smaller SS which is produced as a result of degradation of large SS by ozonation consumed more $KMnO_4$ and contributed to an increase in values of CODt. As DT values became large, smaller SS may have been degraded completely into inorganics, therefore, CODt values decreased. The pH values of the both wastewaters were not changed by DT values in a range from 0 to 1500 mg/(L·min) and stayed at approximately 3.8 for the wheat wastewater and 4.2 for the sweet potato wastewater (data not shown). According to the results of SV60, ORP, and CODt, the optimal DT values for the wheat wastewater was 576 mg/(L·min) and may be as high as 864 mg/(L·min) for the sweet potato wastewater.

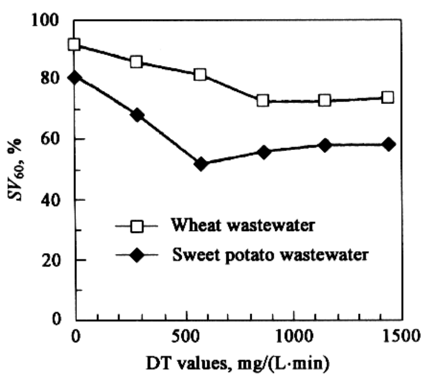

Fig.3 Change of SV60 as a function of DT values

It was found that SV60 decreased as pH of the wheat wastewater increased (data not shown). Moreover, ozonation exhibited the optimum when pH of the wastewater was 7 in terms of CODt. These results implies that more effective preozonation will be expected when pH of the raw wastewaters is adjusted to 7.

SEM observation was performed to observe the physical effects of ozonation on the surface condition of the SS in the wheat wastewater after 40 min of ozonation. The results are shown in Fig. 6. Many tubercle-like forms were on the surface of SS before ozonation (Fig. 6a). They disappeared after the ozonation, and formation of many pores were observed instead (Fig.6b).

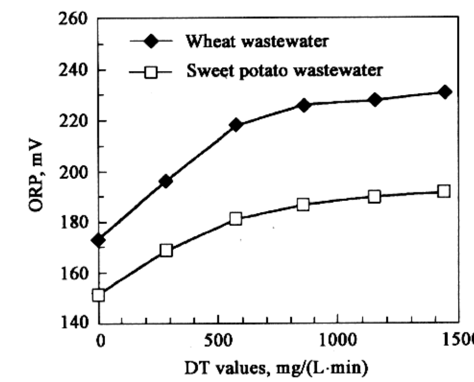

Fig.4 Change of ORP as function of DT values

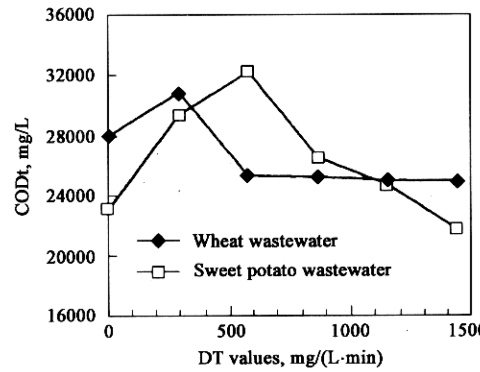

Fig.5 Change of CODt as a function of DT values

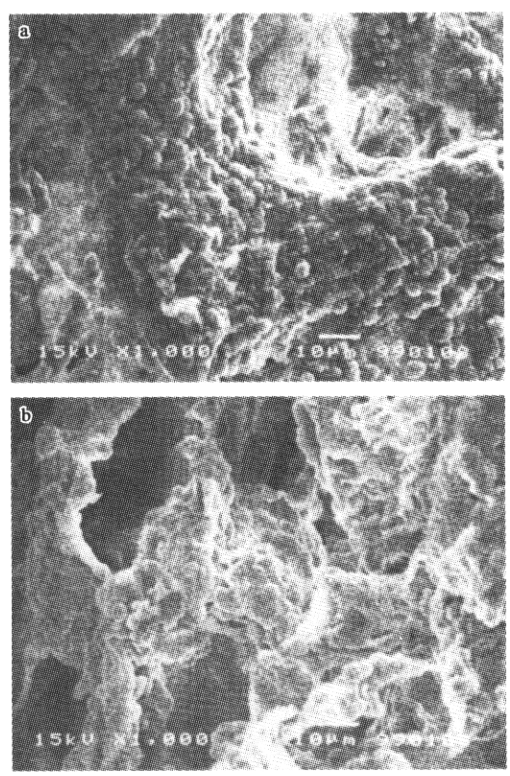

Fig.6 SEM observation of the wastewater (a) before and (b) after ozonation

2.2 Pilot scale experiment

Preozonation was practiced for 60 min, and changes of color, ORP, and pH were observed at 10 min intervals. Settleability of the SS in the wastewaters was also observed at

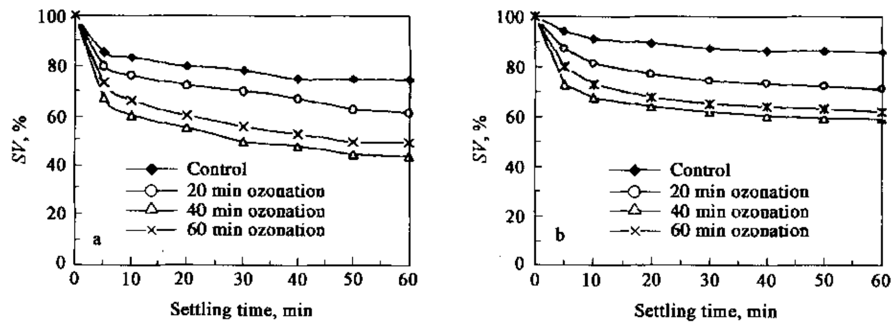

Fig.7 Settling characteristic after ozonation for wheat(a) and sweet potato(b) wastewater

20 min intervals. The wheat wastewater was yellowish brown at the beginning and turned blackish red brown at the end along with the change of ORP from 220 mV to 320 mV. In case of the sweet potato wastewater, the color was light yellow at the beginning and turned to blackish red brown at the end along with the change of ORP from 72 mV to 217 mV. Because of no change of the pH values 3.7 and 4.1 for the wheat and sweet potato wastewaters, respectively, it might be assumed that no chemical changes of the wastewaters such as production of organic acids occurred but physical changes shown in Fig.6 occurred throughout the ozonation practice. The settling curves of 20, 40, and 60 min ozonation of the wastewaters are shown in Fig.7. Comparing each result with the control, all samples showed improvement of settleability, and the best result was obtained from the 40 min ozonation. A solid-liquid separation test was conducted by the decanter without using coagulants to minimize the volume of waste sludge(Tambo, 1982). After the 40 min ozonation, each wastewater was supplied into the decanter at either a 100 L/h or 300 L/h rate. In case of the wheat wastewater, the SS concentration of the liquid portion was, at 100 L/h, 1400 mg/L and 100 mg/L for the control and the ozonation sample, at 300 L/h, 13000 mg/L and 2400 mg/L respectively. Since the original concentration was 18300 mg/L and 24100 mg/L respectively, it can be concluded that ozonation improved the settleability of the wheat wastewater and aided solid-liquid separation. Separated liquid from the decanter was treated by the highly concentrated activated sludge process (MLSS: approximately 8000 mg/L, HRT: 10 d) and CODs of the effluent was 100 mg/L. The effluent was treated further by the aerobic submerged filter process, and CODs of the final effluent of the proposed system achieved less than 20 mg/L and could meet the criteria of discharge. Waste sludge from the decanter and from the activated sludge process was treated by composting and returned to soil as a soil amendment. In the case of the sweet potato wastewater, the SS concentration of the liquid portion was, at 100 L/h, 920 mg/L and 460 mg/L for the control and the ozonation sample, at 300 L/h, 6000 mg/L and 5100 mg/L respectively. Since the original concentration was 16700 mg/L and 14800 mg/L respectively, it can be concluded, unlike the result of the wheat wastewater, that ozonation did not improve the solid-liquid separation.

Preozonation after adjusting the initial pH value of the wastewaters was not practiced in the pilot scale this time, but adjustment of pH to the neutral value will allow the proposed system to achieve better efficiency because it is apparent that the original low pH values of the wastewaters(3.8 and 4.2) would cause a negative effect to the microorganisms in the activated sludge.

3 Conclusions

Effect of preozonation on solid-liquid separation of the wheat and sweet potato spirit-distillery wastewaters was investigated in a bench and a pilot scale experiment. Japanese spirit-distillery wastewater is very difficult to be treated by an activated process without pretreatment because of its extremely high CODt values and poor settleability. Solid-liquid separation is needed as a pretreatment for the process but is very difficult due to their characteristics, high viscosity and high SS concentration. Preozonation was employed and investigated for effectiveness of solid-liquid separation in the wastewaters, which is the first study and has not been reported yet. In the bench experiments, the optimal DT values were found for each wastewater in terms of SV60 or/and CODt. In the pilot scale experiments, preozonation showed a great improvement in solid-liquid separation of the wheat wastewater and the wastewater could be treated by the proposed system. On the other hand, preozonation did not show a significant effect on solid-liquid separation of the sweet potato wastewater although settleability of the SS was improved by ozonation. It is concluded that effect of preozonation on solid-liquid separation depended on types of the wastewater. Preozonation could be more effective when original pH of the wastewaters is adjusted to neutral values because settleability of the SS in wheat wastewater increased when pH was 7 in terms of the CODt value. Further study is needed to understand applicability of ozonation in terms of improvement of solid-liquid separation of Japanese spirit-distillery wastewater.

Acknowledgments: Authors expressed their great appreciation to the factory which provided the Japanese spirit-distillery wastewaters.

References:

Beltran F J, Gonzalez J F, Alvarez P *et al*., 1999. Improvement of domestic wastewater primary sedimentation through ozonation[J]. Ozone Science and Engineering, 21: 605—614.

Farvardin M R, Collins A G, 1989. Preozonation as aid in the coagulation of humic substances-optimum preozonation dose [J]. Water Research, 23: 307—316.

Japan Sewage Works Association, 1997. Japanese standard methods for sewage examination[M]. Japan Sewage Works Association. 116.

Konno T, Fujino K, 2002. Make a resource from the slurry generation at Shochu production by disrillation[J]. Kankyo Kenkyu, 127: 17—20.

Tambo N, Tsutsumi K, 1982. Oxidation of organics in water by ozonation and flocculating tendency[J]. Journal of Japan Sewage Works Association, 19: 24—32.

Tanaka M, Somiya I, 1998. Change of surface characteristics of suspended particles by ozonation [C]. The 7th annual Japan ozone association conference. 125—128.

Yeh H H, Chen J M, 1987. Effect of preozonation on organics coagulation removal from water[J]. Journal of Chinese Institute of Engineers, 10: 335—344.

(Received for review January 13, 2003. Accepted April 27, 2003)