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Treatment of milking parlor wastewater containing tetracycline by magnetic activated sludge and contact oxidation process

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Abstract

Milking parlor wastewater contains not only high concentrations of organic compounds, but often animal antibiotics. To discharge the antibiotics to public water area cause problem of antibiotics resistant bacteria. Magnetic separation was applied into improvement of milking parlor wastewater treatment process. A new process, composed of a magnetic activated sludge (MAS) process and a contact oxidation (CO) process, was proposed in this study. This process was evaluated by the simulated milking parlor wastewater (4500 mg/L COD_{Cr} and 10 mg/L tetracycline) using a bench scale experimental setup. As a result, the process was able to removed 97% COD_{Cr} as well as 94% tetracycline. The MLVSS (mixed liquor volatile suspended solids) concentration of MAS was maintained at 12000 mg/L without excess sludge drawing. This process was considered to be useful as treatment process for milking parlor wastewater in which waste-milk including antibiotics is often discharged.

Keywords: magnetic separation, dairy farm wastewater, antibiotics, magnetic activated sludge, contact oxidation

1. INTRODUCTION

Application of magnetic separation into biological wastewater treatment process has possibility to bring innovative progress to wastewater treatment. The activated sludge (AS) process which is aerobic biological water treatment process is basic water purification process widely used for sewage treatment and organic wastewater treatment. Recently, various attempts have been made to introduce magnetic separation into the AS processes [1-4]. Generally, the AS process is tended to be unstable sedimentation of microorganisms in the final stage of water purification, so it has become a problem in the process of operation. The process, that is called magnetic activated sludge (MAS) process, introducing magnetic separation has the potential to fundamentally solve this problem. If the MAS process could be put into practical use, it has the potential to develop large application fields of the superconducting magnet [5]. Similar approaches by magnetic separation using superconductive or permanent magnet have been tried in physicochemical treatment field for wastewater treatment [6-10].

The dairy industry discharges large volumes of organic waste and wastewater, and pollution from farm wastes has become a serious problem in rural areas [11]. The waste-milk from dairy farmyards that is not properly treated or managed can be a major point source of pollution in rural area [12], so that is one of the issues for dairy farm management [3, 4]. The colostrum, the milk for about a week after calving, and the milk from mastitis infection cows treated with antibiotics are prohibited from using as food material [13]. Therefore, the waste-milk generation cannot be avoided in dairy farming. These waste-milk are characterized by high concentration organic matter and nutrients, and are composed mainly of carbohydrates, proteins and fats and residual antibiotic. Serious problems can happen when waste-milk is handled incorrectly and discharges to the nearby public water area [14]. One is water pollution by high concentration organic compounds, the other is a risk of generating new resistant strains against antibiotics discharged [15]. Therefore waste-milk should be treated properly before discharge.

In Japan, many dairy farms have a plant for wastewater treatment according to "the act on the appropriate treatment and promotion of utilization of livestock manure (2003)". In general, AS processes are adopted in the plants. However, the AS process cannot treat successfully the waste-milk because of the very high organic compounds. Because the COD_{Cr} concentration of waste-milk is more than 200,000 mg/L which is roughly 100 times higher than that of usual milking parlor wastewater, wide fluctuation of the organic loading by mixing waste-milk might cause trouble of sludge bulking by deterioration of settleability and serious sludge leakage as a result. Additionally, the AS process cannot decompose sufficiently the antibiotics which are low biodegradable materials [16].

Though the AS process is a widely used biological wastewater treatment process, it is said to be difficult to operate successfully. The reason is mainly difficulty of

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maintenance of sludge settleability. The AS can immediately adsorb magnetite powder by only mixing [17, 18]. The AS adsorbing magnetite powder shows magnetic attractive property, so that become magnetically separable. Owing to adsorption equilibrium, the magnetite is shared dynamically by all microbes which can adsorb magnetite powder. These microbes which have ability of magnetite adsorption grow dominantly in the aeration tank by recovered magnetically. Therefore, the sludge-liquid separation of MAS process is able to be made stable against hard condition [19]. Magnetic separation is free from the problem of sludge settleability deterioration or membrane fouling. As a result, a good management of the water treatment become to easy. Because many farmers don't have enough skill of water treatment, the character of easy operation is effective for reduction of water treatment management loading.

And also, MAS process is operated without excess sludge withdrawal under condition of low organic loading rate par weight of microorganisms by high concentration sludge [19]. The sludge concentration is kept constant automatically by balance of cell growth and decay. Additionally, the microbes are well acclimated to the organic materials in influent because of long sludge retention time. It was reported that some hardly decomposed materials, bis-phenol A [21], poly vinyl alcohol [22], dye [23], etc. were degraded by MAS process. Antibiotics may be biodegraded by acclimated MAS process. Therefore, the MAS process is considered to be useful for milking parlor wastewater treatment.

In order to make wastewater treatment technology by magnetic separation developed, the application of MAS process for milking parlor wastewater is proposed for simultaneous removal of high concentration organic compound and antibiotics in this paper. The performance of the proposed process was evaluated by a bench scale experiment with simulated waste-milk including tetracycline, an animal antibiotic.

2. EXPERIMENTAL

2.1. Waste-milk and tetracycline

Simulated milking parlor wastewater (4500 mg-COD_{Cr}/L) that was diluted milk with tap water was used for the wastewater treatment experiment. Milking parlor wastewater is generally main organic wastewater in dairy farm wastewater. For antibiotics biodegradation test, 10 mg/L tetracycline was added to the simulated milking parlor wastewater from 53 d (d is unit of day) to the end of the experiment.

2.2. Magnetic activated sludge (MAS) and contact oxidation (CO) process

The treatment process consisted of two steps process: (i) MAS process as first step (ii) CO process as second step (Fig. 1). The MAS process is major process for organic compounds removal. The CO process removes suspended solids and residual organic compounds. The MAS was prepared by adding magnetite powder (Fe_3O_4, Iron oxide, Kanto Chemical) to the conventional AS at the ratio of MLVSS (mixed liquor volatile suspended solids): magnetite by 1:1. The 5.0 L-aeration tank was used for the MAS process and the hydraulic retention time (HRT) was adjust to 5 d. The COD_{Cr}-volumetric loading rate was 0.9 kg/(m^3・d). Magnetic separator was used a rotating magnetic drum (10 cm diameter, 10 cm length), which has surface maximum magnetic flux of 0.08 T and magnetized pattern of striped magnetic pole interval of 6 mm. The volume capacity of the magnetic separator is approximately 0.1 L. The MAS suspension in aeration tank was flowed into the magnetic separator and separated to the treated water and the thickened MAS. The MAS attached on the drum surface was scraped off and was returned to the aeration tank. For the experimental period, the MAS process was operated without excess sludge withdrawal. The experiment was carried out at temperature 25℃±2℃. The total volume capacity of CO reactor is 2.5 L. Small cubic sponges (1 cm×1 cm×1 cm) about 1.5 L bulk volume were used as microbe support media. The CO reactor was mixed by circulation flow using air lift system. Dissolved oxygen concentration of CO reactor was maintain more than 5 mg/L. The HRT of CO process was 2.5 d.

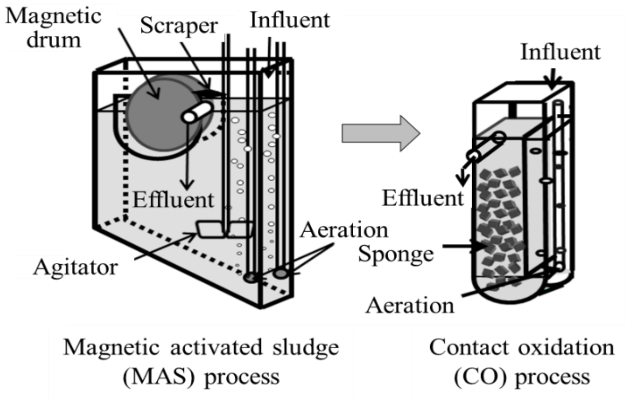

Fig. 1. A schematic diagram of the laboratory-scale MAS and CO process. All effluent from the 5 L-MAS process feed to the 2.5 L-CO process as influent.

2.3. Analysis

The samples obtained from MAS and CO effluents were analyzed for the following parameters: Chemical oxygen demand (COD_{Cr}) was measured by Spectrophotometer (DR2800, HACH). Turbidity were measured by turbidity meter (Turbidimeter 2100P, HACH). Tetracycline was measured by UV spectrophotometric analysis (spectrophotomater, V-630, JASCO) and LC-MS system which was composed a UHPLC system (Nexera X2, Shimadzu) and a triple linear ion trap instrumental (QTRAP 5500, AB Sciex). The concentrations of MLSS (mixed liquor suspended solids) and MLVSS were measured by JIS standard methods.

2.4. Measurement of tetracycline acclimation of MAS

In this experiment, the plate culture method by Nutrient Agar was used for the test of effect of AS and MAS by tetracycline. 1 mL of Homogenized AS or MAS was inoculated to the Nutrient Agar medium (15 ml) and incubated at 35℃ for 36 hours.

3. RESULTS AND DISCUSSION

3.1. Treatment of the simulated wastewater and antibiotics

The COD_{Cr} concentration changes of each effluent from the MAS and CO processes are shown in Fig. 2. In the MAS process, it was found that the COD_{Cr} concentration decreased gradually until the 52 d by acclimation to the organic compounds in the simulated wastewater. After adding 10 mg/L tetracycline into the simulated wastewater from 53 d, the effluent COD_{Cr} concentration increased temporarily, but that recovered gradually by the 130 d. This recovery is considered to be acclimation of the MAS to antibiotics. On the other hand, turbidities of MAS effluent increased after around 90 d and reached constant around 25 NTU as shown in Fig. 3. This increase of turbidity was considered low biodegradable organic suspended solids which cannot adsorb magnetite particles was generated by microorganisms cell decay in MAS reactor. It is known that MAS process generally leaks a few percent of influent organic compounds as low biodegradable organic compounds in the effluent [1, 2]. After the 140 d, the COD_{Cr} concentration was increased up to about 140 mg/L due to increase of organic suspended solids in effluent. The MAS process was able to biodegrade to less than 140 mg/L from 4500 mg/L COD_{Cr} of simulated wastewater including 10 mg/L tetracycline as antibiotics during all experimental periods. This result suggests the MAS process can remove 97% organic compounds from milking parlor wastewater including tetracycline. The purification level can be expected to achieve the Japanese effluent standard, 120 mg-BOD/L in daily average.

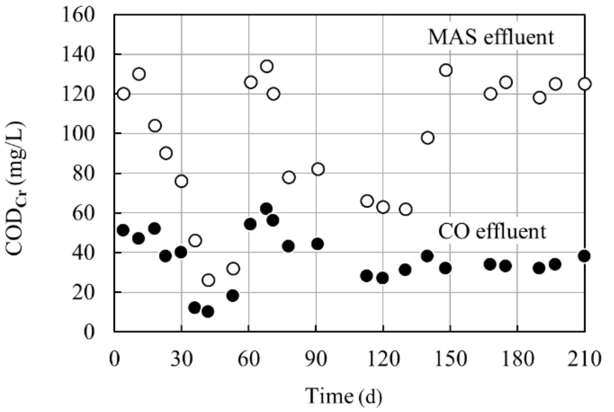

Fig. 2. COD_{Cr} concentration changes in effluent of the MAS and CO process.

Moreover, by adding CO process after the MAS process, COD_{Cr} concentration (CO effluent in Fig. 2) decreased in half or less from the effluent of MAS process. This purification level might achieve advanced effluent standard in Japan. The influence of tetracycline to the COD_{Cr} removal activity was not observed after 100 d. It was considered the result clearly showed that a stable treatment could be attained in combination of the MAS and CO process.

The MLSS and MLVSS concentration changes in the MAS process are shown in Fig. 4. Initially, the MLVSS was increased about 1% per day due to without excess sludge withdrawal. By increasing MLVSS concentration, the organic loading rate par weight of microorganisms, which was defined here treated COD_{Cr} (kg-COD_{Cr}) per day / total weight of volatile suspended solids in the reactor, decreased from 0.14 kg-COD_{Cr}/(kg-VSS･d) at 10 d to 0.10 kg-COD_{Cr}/(kg-VSS･d) at 60 d. At the 150 d, the MLVSS concentration reached to a constant value, about 12000 mg/L. At that time, the organic loading rate par weight of microorganisms was about 0.075 kg-COD_{Cr}/(kg-MLVSS･d). In order to adjust of the magnetite/MLVSS ratio into 1/1, magnetite was added into aeration tank of MAS process at the 42 d so that MLSS was increased to 15000 mg/L. After that, it was unnecessary to add of magnetite into MAS aeration tank.

The leak of suspended solids or magnetite from the MAS and CO process was hardly observed for the experimental period. The turbidities of effluent of the MAS and CO process were 4 NTU at average (10 NTU at maximum). This result suggests this process was clear the advanced effluent standard in Japan.

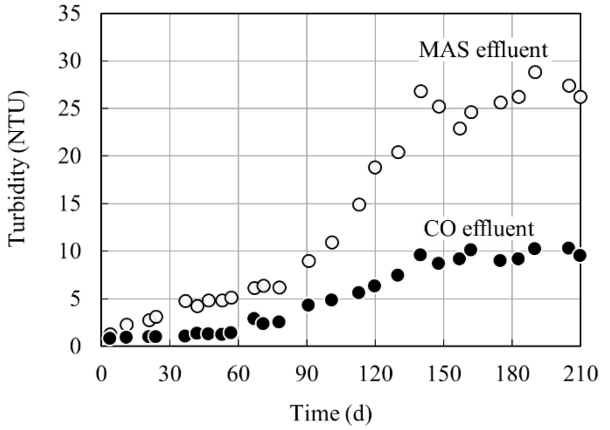

Fig. 3. Turbidity changes in effluent of the MAS and CO process

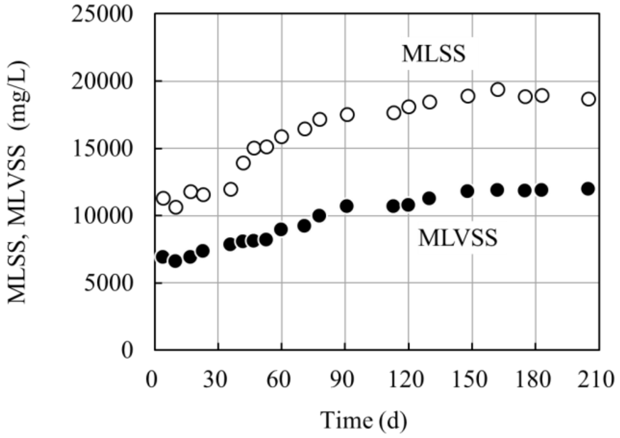

Fig. 4. The MLSS and MLVSS concentration changes in the aeration tank of the MAS process.

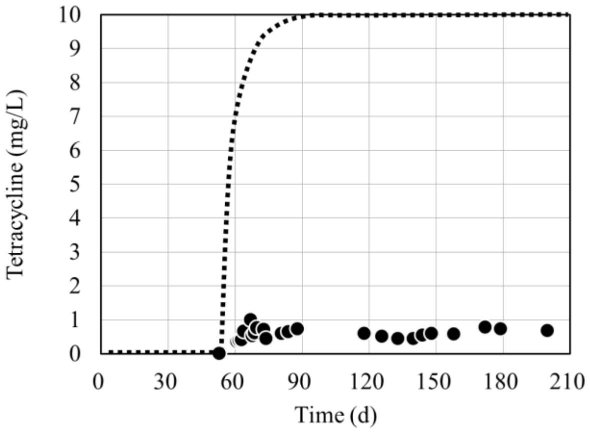

Fig. 5. Tetracycline concentration change in MAS effluent. The dotted line shows dosage concentration curve of tetracycline in the aeration tank of MAS process.

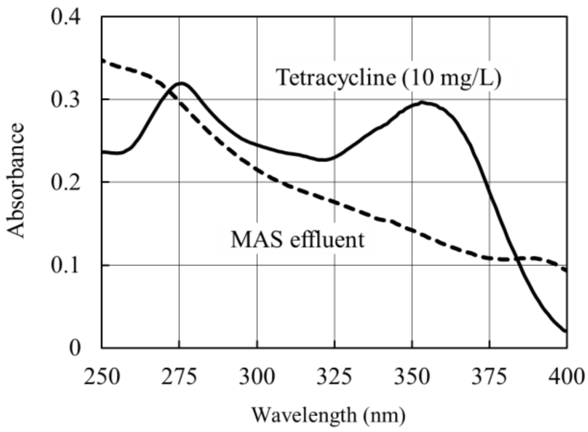

Fig. 6. UV spectra of the 10 mg/L tetracycline and MAS effluent at 191 d

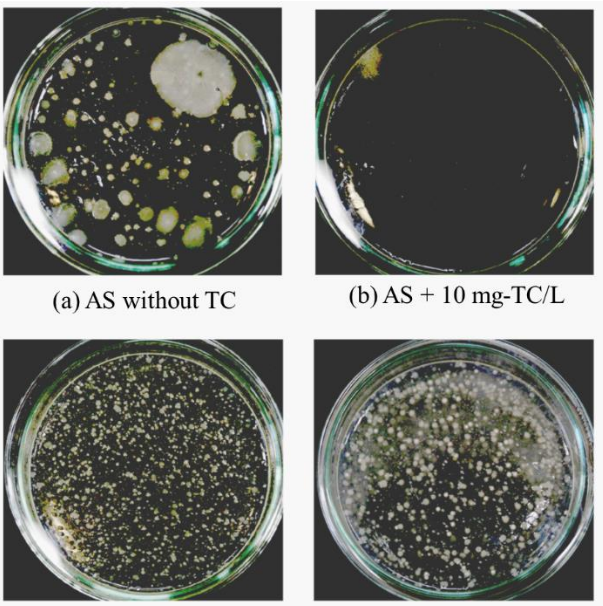
(a) AS without TC
(b) AS + 10 mg-TC/L
(c) MAS without TC
(d) MAS + 10 mg-TC/L

Fig. 7. Photographs of AS and MAS culture plates after 36 h incubation at 35°C. TC : tetracycline.

3.2. Biodegradation of tetracycline by the MAS process.

The change of tetracycline concentration by measured using LC-MS with time was shown in Fig. 5. The simulated increasing curves of tetracycline was shown in Fig. 5 by dotted line. Because the HRT of MAS reactor is 5 d, tetracycline concentration increase gradually. Average tetracycline concentration in the MAS effluent from 60 d to 200 d was 0.6 mg/L. About 94% of tetracycline was removed successfully. From temporal increase of COD_{Cr} concentration from 32 mg/L at 53 d to 126 mg/L at 61 d (Fig. 2), it was considered that microbes was affected to biodegradation activity. In spite of some deterioration of COD_{Cr} removal, Tetracycline removal rate was more than 90% in the experimental period.

The UV spectra of tetracycline solution and filtrate of MAS effluent at 191 d was shown in Fig. 6. By the absorption peaks characteristic of polycyclic compounds has disappeared, the polycyclic structure of tetracycline could be estimated to be degraded by the MAS process.

It is calculated that theoretical COD_{Cr} of tetracycline is about 19 mg/L. Because a very few tetracycline is only included as organic compounds compared to other organic nutrients (4500 mg-COD_{Cr}/L) in the influent, it is considered that the growth rate of tetracycline acclimated microbes would be very slow compared other microbes. In conventional AS process, 10% to 20% of sludge is drawn from reactor as excess sludge, generally. The microbes must grow at faster rate than the sludge withdrawal rate in order to survive in the reactor. It was considered that the MAS process operated without excess sludge drawing had been effective for tetracycline acclimated microbes to grow in the reactor.

The acclimation activity was examined by plate culture method. The photographs of culture medium after incubation were shown in Fig. 7. Various types of colonies were observed at AS culture plate without tetracycline (Fig. 7 (a)). On the other hand, few colonies were observed at AS culture plate with 10 mg/L tetracycline (Fig. 7 (b)). However, many small colonies were observes at both MAS culture plates without and with tetracycline (Fig. 7 (c) and (d)). These photographs indicated that tetracycline acclimated microbes lives in the MAS process. The MAS process can be expected to be widely useful to remove low concentration antibiotics in high concentration organic wastewater.

4. CONCLUSION

The MAS and CO process proposed for wastewater treatment of milking parlor wastewater including tetracycline as antibiotics was able to purify the simulated wastewater to around advanced effluent standard level during 210 d without excess sludge discharge. By magnetic separation, the MAS process has potential of reduction of operation and maintenance work of water treatment process. By the acclimation to antibiotics, MAS was able to grow in 10 mg/L tetracycline and decompose by 90% or more. It is expected that this process is useful for wastewater treatment with the milking parlor wastewater including antibiotics.

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