

Evaluation on the Biodegradability of the MBT Wastewater

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MBT 폐수의 생분해성 평가

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Abstract The possibility of the biological treatment of MBT wastewater generated from the vulcanization accelerator manufacturing process was investigated. MBT wastewater is not biodegradable because it hinders the activity of microorganisms, and approximately 10% of the total COD can be removed after a 7 day acclimation period. The optimal conditions of the MBT wastewater for the chemical pre-treatment was pH of 3.5 and the Fenton oxidation with the addition of Fe³⁺ to the wastewater after agitation for 2 hours. The Fenton-treated MBT wastewater showed approximately 20% removal of COD when treated with the activated sludge process for the mixed paper wastewater and Fenton treated wastewater.

요약 본 연구는 가황촉진제 제조공정에서 발생하는 MBT 폐수의 생물학적 처리가능성을 평가하였다. MBT 폐수는 미생물 활동을 저하시키기 때문에 생물학적으로 처리가 불가능하였지만, 7일의 순응기간을 거쳐 약 10%의 COD가 제거되었다. MBT 폐수의 화학적 전처리를 위한 최적조건은 pH 3.5, 2시간동안 교반 후 Fe³⁺를 주입하여 펜톤산화를 한 경우였다. 또한, 펜톤처리 된 MBT 폐수를 제지폐수와 혼합하여 활성슬러지공정에서 처리했을 경우 MBT 폐수의 COD가 약 20% 제거되었다.

Keywords : Vulcanization accelerators, Mercaptobenzo thiazole(MBT), Biodegradability, Fenton oxidation, Activated sludge

1. Introduction

Vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials via the addition of sulfur or other equivalent curatives or accelerators. These additives modify the polymer by forming cross-links between individual polymer chains. Vulcanized materials are less sticky and have superior mechanical properties. Effects of vulcanization accelerators are shortening of vulcanization time, lowering of vulcanization temperature, improvement

of quality, reduction of used vulcanizing chemical, etc. Thiazole is the most common chemical among kinds of vulcanization accelerators such as aldehyde ammonia, aldehyde amine, guanidine, thiourea, thiazole, thiuram, dithio carbamate, xanthate, sulfenamide etc[1-2].

The main components of wastewater produced in the manufacture of thiazole type accelerator are inorganic substances such as sodium sulfate, soda ash, hydrogen peroxide, sodium hydrosulfide, resin, etc., among them sodium sulfate(Na₂SO₄), is the largest. And the organic components are sodium-2-mercaptobenzothiazole(NaMBT),

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2-mercapto benzo thiazole(MBT), and dibenzothiazyl disulfide(or 2,2-dithiobisbenzothiazole) (MBTs) etc., which are used by the sources of chemical oxygen demand(COD) in the wastewater. NaMBT($C_7H_4NS_2Na$) is the crude material of thiazole accelerator, meanwhile MBT($C_{14}H_8N_2S_4$) and MBTs are formed in the washing process of the products. Crude MBTs contain some amounts of impurities of aniline derivatives which can lead to COD. That is, wastewater includes NaMBT, MBT, and MBTs etc., and they are insoluble except NaMBT[2].

MBT is characterized by low biological degradability, high photolysis low volatility[3]. And since it is known to exert antimicrobial effects that several proposals for biological purification of MBT manufacturing process waters include a dilution step or a preliminary elimination of certain compounds before entering the activated sludge process[4-10].

In this study the respiration rate and BOD_U were measured to examine the possibility of biological treatment of MBT wastewater, followed by activated sludge experiment, after that experiments of activated sludge in the continuous process were performed by the chemically treated water using iron chelates complex and Fenton's reagent. MBT wastewater followed by proper pre-treatment was designed to combine with the wastewater of adjacent paper manufactory operating on the activated sludge process. Therefore the possibility of cooperative treatment of MBT wastewater was examined by the comparison of results of treated water(22,000 m^3/day) from paper manufactory in this study.

2. Experimental methods

2.1 Biodegradability

Respiration rate($mg\ O_2/g\ MLSS-hr$), i.e. oxygen uptake rate(OUR) demonstrates the consumption rate of oxygen which is used by the organic matters when the microorganisms decompose the organic matters in the

wastewater. Respiration rate represents the short-term effect of influences on the microorganisms with a short experiment time. On the other hand, BOD_U involves in some sort of long-term effect. Therefore the experiments of BOD_U and activated sludge in batch type were performed in this study.

2.2 Pre-treatment by iron chelates complex and Fenton's reagent

Sulfur compound which consists of macromolecule such as MBT may bind metals and forms an insoluble complex, in which the sulfur acts as the electron donor. After having found an optimal pH to make an insoluble complex formation with iron and MBT wastewater in terms of adjusting the pH of sample wastewater in the range of 1~10, the removal rates of COD were measured by the variation of Fe(II) and Fe(III) in the inflows. After that, the treated wastewater was performed by Fenton treatment.

2.3 Continuous activated sludge process

An experimental apparatus for activated sludge process is a CSTR consisting of an aeration tank of 5.5 liter and a settling tank of 2.7 liter. The aeration tank is the water bath with heater, which is maintained with a temperature of $34\pm 3\ ^\circ C$ during the experimental periods.

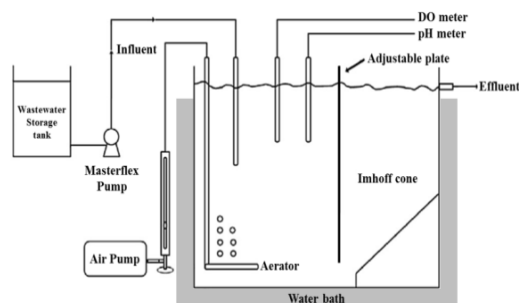


Fig. 1. Experimental apparatus for activated sludge process

3. Results and discussion

3.1 Biodegradability

Fig. 2 shows the results of respiration rate on the mixed wastewater of MBT and paper manufactory in which the MLSS concentration of the activated sludge is 2,160 mg/L. OUR has increased as paper wastewater increased, however OUR decreased rapidly. It seemed that the MBT wastewater inhibited the activity of microorganisms.

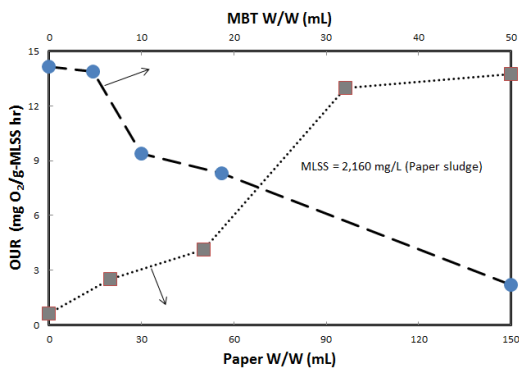


Fig. 2. Comparison of OUR on the MBT and Paper wastewaters

The toxicity of MBT to bacteria and other organisms is probably due to its metal-chelating properties, general interference with membrane-linked processes, and reactions with functional groups present in proteins[4].

Fig. 3 shows the BOD_U results of the MBT and paper wastewaters. The ratio of BOD to COD on the paper wastewater was 0.38, then its wastewater seemed to be biodegradable, on the contrary, the ratio on the MBT wastewater was almost zero, therefore it was noted that there are rarely biodegradable organic matters in the MBT wastewater.

However, it was observed that the MBT wastewater began to decompose the organic matters by the microorganisms after one week. The MBT wastewater could be decomposed by the long-term acclimation of microorganisms in a small amount, and it demonstrated

that the MBT wastewater revealed the microorganism decomposition as much as 10% among total COD under the environment of acclimated microorganisms.

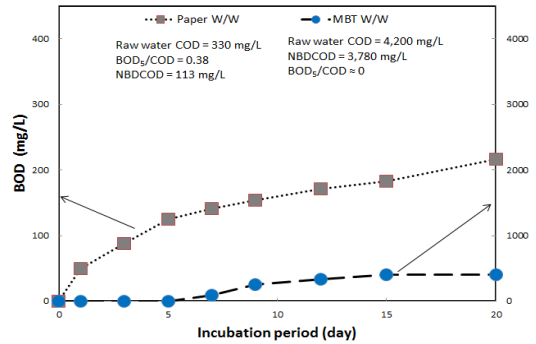


Fig. 3. Comparison of BOD_U on the MBT and Paper wastewaters

Fig. 4 shows the results of batch type experiments of mixed wastewater which consists of the paper wastewater and the MBT wastewater as much as 2.3 volume % of the paper wastewater using the experimental apparatus shown in Fig. 1.

The difference in the initial COD concentrations between the paper and the MBT mixed wastewaters was measured as 60 mg/L, and the change of COD concentrations was likely to decrease in a same trend as operation time went on. Accordingly, the MBT did not seem to play a role causing COD removal.

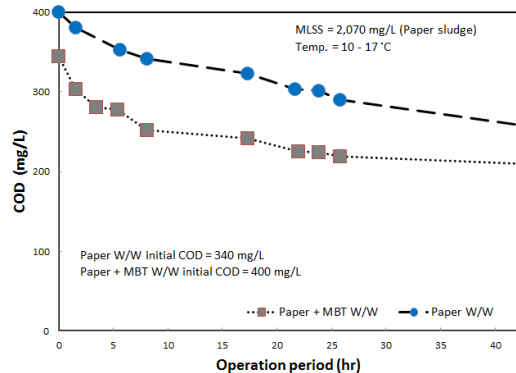


Fig. 4. Change of COD concentration on the Paper and MBT+Paper wastewaters

3.2 Pre-treatment by iron chelates complex and Fenton's reagent

After adjusting the MBT wastewater pH of 1 and 10 using concentration. H_2SO_4 , the wastewater kept Fe^{3+} concentration in 213 mg/L with $Fe_2(SO_4)_3$. An experimental reactor was operated with 200 rpm for 30 minutes, having continued to mix the wastewater with 20~40 rpm for 10 minutes, and making it precipitation. After that, the COD analysis was performed in the supernatant, and the results are displayed in Fig. 5. It was observed that the lower pH of the wastewater, the higher removal efficiency of COD. However, it needed more alkali chemical which was used by the neutralization reaction in the wastewater treatment process when the pH was too low. It was accomplished that the pH of 3.5 was optimal for the MBT wastewater treatment, which was based on the experiment that acid-base neutralization reaction was performed in order to find the optimal quantities of H_2SO_4 for pH adjustment and NaOH for the neutralization reaction[Fig. 6].

Making the MBT wastewater(COD 4,500 mg/L) in pH of 3.5 and adding Fe^{2+} and Fe^{3+} in 852 mg/L, then COD of the supernatant was examined after 30 minutes. The removal rates of COD between the MBT wastewater and Fe^{3+} dosed wastewater were 24% and 27% respectively, and the supernatant color is much transparent in the case of Fe^{3+} dose. Also, making the MBT wastewater in pH of 3.5 and it was done by two cases of experiments whether adding Fe^{3+} immediately to the wastewater and agitating or agitating it for about 2 hours and adding Fe^{3+} .

As shown in Fig. 7, it was known that COD removal was efficiently effected by the sequence of agitating first and adding Fe^{3+} . Meanwhile, COD concentrations were examined by the two cases; one thing of doing Fenton oxidation directly with the MBT wastewater(COD 2,300 mg/L), the other thing of doing Fenton oxidation with the dosed Fe^{3+} MBT wastewater. There was no difference between two cases in the COD concentration of 1,700 mg/L. However, the color

and sludge precipitability have been good for the Fe^{3+} plus Fenton oxidation. It was found that the use of hydrogen peroxide(35%) was 360 ton/yr for the Fenton oxidation operation, and 145 ton/yr for the Fe^{3+} plus Fenton oxidation operation.

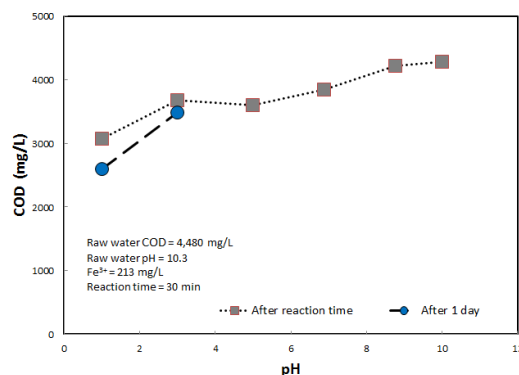


Fig. 5. Effects of initial pH on the COD concentration

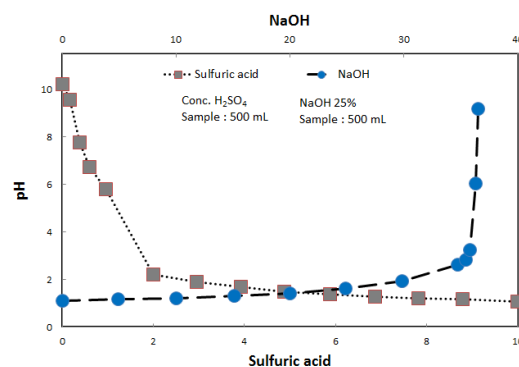


Fig. 6. Experimental results of acid-base neutralization on the MBT wastewater

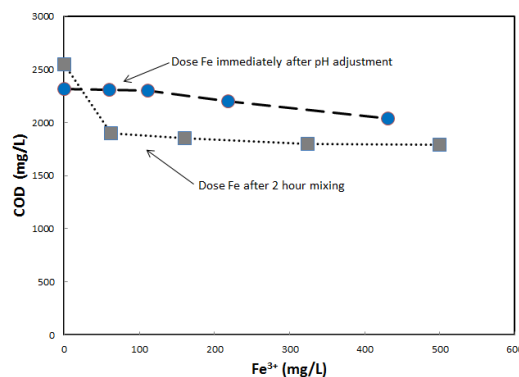


Fig. 7. Change of COD concentration against Fe^{3+} dose on the MBT wastewater

Consequently, the wastewater treatment cost could be saved as much as about 2.5 times by the latter case.

3.3 Continuous activated sludge process

Fig. 8 shows the COD experimental results of continuous activated sludge process on the paper wastewater and paper plus Fenton treated MBT wastewater. The COD concentrations were investigated with the F/M ratio in the range of 0.2~0.35[Fig. 9], considering the operating temperature of 33.7°C and the F/M ratio of 3.3~3.4 on the activated sludge process in the paper plant.

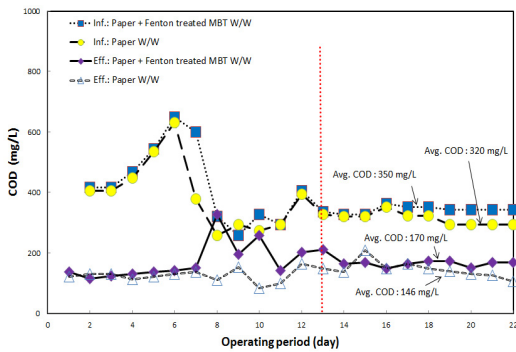


Fig. 8. Experimental results of continuous activated sludge process on the Paper and Paper+Fenton treated MBT wastewaters

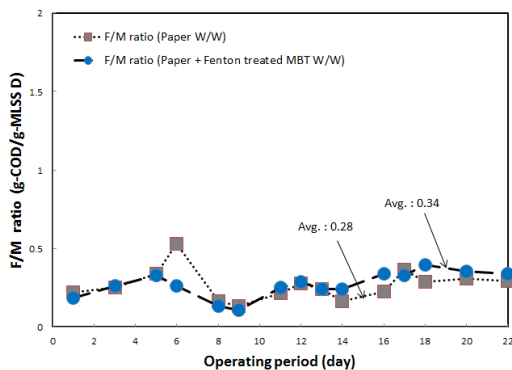


Fig. 9. Change of F/M ratio on the Paper and Paper+Fenton treated MBT wastewaters

Meanwhile the aeration tank kept the dissolved oxygen concentration under 6~7 mg/L and the pH under 7, but then the pH began to drop slightly to 6.5.

The pH change might resulted in the nitrification of sludge which had long sludge age because of the slight consumption of sludge for the MLSS growth in the aeration tank during the experiment. As shown in Fig. 8 and Fig. 9, the sudden increases of COD and F/M ratio in the early stages of experiment resulted in the suspended solids of the paper wastewater, which had highly contributed to the COD.

It seemed that the suspended solids should be removed before the inflow of activated sludge process because organic loading rate remained high if the wastewater was pumped into the experimental tank without removing the suspended solids. Therefore, the suspended solids of the raw wastewater were removed by the gravitational sedimentation methods in the middle of the experiment, and the supernatant was pumped to the aeration tank. The average COD concentration of the Fenton treated MBT wastewater was as much as 24 mg/L higher than that of the paper wastewater at 13 days after the operation, as shown in Fig. 8. It meant that the Fenton treated MBT wastewater was removed by about 20 % of COD.

MLSS concentration of the aeration tank increased gradually from 900 mg/L in the initial stage of experiment to 1,600~1,700 mg/L, and decreased a little in the late stage, as shown in Fig. 10. And MLVSS/MLSS ratio was maintained by the 0.7, which was lower than the ratio of activated sludge in the wastewater treatment plant, 0.85.

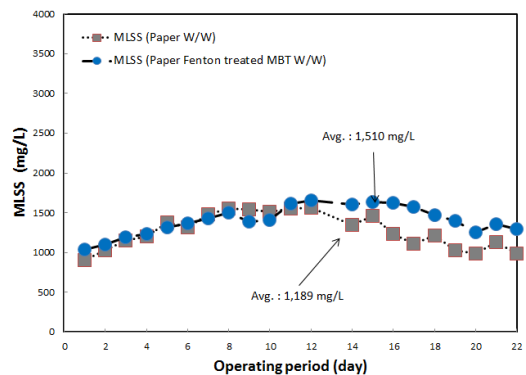


Fig. 10. Change of MLSS concentration on the Paper and Paper+Fenton treated MBT wastewaters

4. Conclusions

It was investigated that the MBT wastewater was not biodegradable because it hindered the activity of microorganisms, and about 10 % of total COD could be removed after 7 days as acclimation periods. The optimal conditions of the MBT wastewater for the chemical pretreatment was pH of 3.5 and the Fenton oxidation with adding the Fe^{3+} to the wastewater after agitation for 2 hours. The Fenton treated MBT wastewater was removed by about 20% of COD when it was treated by the activated sludge process for the mixed wastewater of the paper wastewater and the Fenton treated wastewater.

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