

TREATABILITY OF HIGH STRENGTH BREWERY WASTEWATER WITH STABILIZED REFUSE

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ABSTRACT

A column with a surface area of 790 cm² and effective height of 105 cm was used for the study. The column was filled with stabilized refuse (which had been studied for two consecutive years regarding leachate recycling) compacted to an average density of 500 kg/m³. High strength brewery wastewater, with a COD of 6000 mg/l, was homogeneously trickled over the top of the refuse at daily flow rates of 8, 16, 24, and 36 liters/day. Each flow rate was maintained for more than three weeks to achieve steady performance. After six months of intensive study, it was demonstrated that the stabilized refuse had a very good ability to treat the brewery wastewater. The COD was reduced to as low as 60 mg/l, which was equivalent to a removal efficiency of 99%, after the wastewater had trickled through the 90 cm refuse layer. The COD reduction achieved in the stabilized refuse layer perfectly fitted the following equation:

$$Se/S_o = \exp(-1.3835DQ^{-0.5873})$$

The variations of major parameters such as pH, alkalinity, and volatile fatty acids, strongly indicated that acidogenesis occurred quickly in the first 15 cm. As the flow rate increased, acidogenesis occurred deeper in the column and its recovery became slower. The oxidation reduction potential (ORP) dropped to as low as -290 mV in the refuse column, indicating the anaerobic conditions of the system.

KEYWORDS

Brewery wastewater; treatability; stabilized refuse; treatability factor; Schulze equation.

INTRODUCTION

The strength of leachate from landfilled municipal solid waste (MSW) is related to the maturity of the waste. When leachate strength is plotted against time, an 'S-shaped' curve is produced. Although leachate strength varies depending on such factors as precipitation, nature of the MSW, age of the landfill, type of landfill, etc., it takes many years for the leachate to stabilize (Hanashima *et al.*, 1983; Wanielista and Taylor, 1979). The major parameters of BOD/COD, COD/TOC, VFA/TOC, and VS/FS are used to monitor leachate stability (Chian and DeWalle, 1977). Leachate is usually considered as stabilized when its BOD/COD is less than 0.1. The study by Hanashima *et al.* (1983) indicated that leachate BOD may decrease to as little as 10 mg/l, but the COD of the stabilized leachate was still around 500 mg/l.

When landfills have stabilized, the sites are often used as recreation areas. However, at this stage, the configuration of the landfill is similar to that of a trickling filter. Both consist of media (i.e., refuse or filter media) covered by a microbial layer which is able to utilize the percolating organic substances. The main difference between these two systems is that trickling filters are aerobic and landfills are anaerobic. Although anaerobic processes have slower reaction rates, landfill refuse systems have higher microbial populations and longer hydraulic retention times than trickling filters, therefore it was thought that stabilized MSW landfills would be able to treat organic wastewaters more economically and effectively than trickling filters. Thus, a study of the treatability of brewery wastewater using stabilized refuse was proposed. There were two specific objectives:

1. Determination of the feasibility of using the stabilized refuse layer as an alternative for wastewater treatment.
2. Development of kinetic models of removal of organic substances.

The operation of conventional wastewater treatment processes such as trickling filters or activated sludge systems requires skilled operators and has high costs, and these processes have limitations if high strength wastewater is treated. This study on the use of refuse should suggest a new direction in wastewater treatment.

EXPERIMENTAL FACILITIES AND METHODS

Experiments were conducted with a laboratory-scale reactor. Stabilized municipal solid waste (MSW) was compacted in the reactor to an average density of 500 kg/m³, which is close to the actual density of landfilled MSW. Diluted brewery wastewater from a nearby winery was pumped to the reactor at four flow rates. Samples of leachate were collected from different depths of the reactor and analysed for COD, BOD, pH, oxidation reduction potential (ORP), total Kjeldahl nitrogen (TKN), ammoniacal nitrogen (NH₃-N), alkalinity, total phosphorus (TP), and volatile fatty acids (VFAs) using standard methods (Greenburg, 1985).

Apparatus

A laboratory-scale reactor was used for the investigation. This consisted of 9 cells including a distribution unit, as shown in Fig. 1. Plastic boxes (29 x 26.5 x 17 cm) were used as the cells and were filled with the MSW. A 2 cm layer of gravel was laid on the bottom of each cell for water distribution, thus the MSW column had a total depth of 105 cm. The cells were filled with a total of 40.35 kg of compacted stabilized MSW, with an average density of 500 kg/m³. Sampling ports were drilled to collect samples of leachate trickling from the cells above. Gaps between the cells were sealed with silicon glue to prevent air invasion. Diluted brewery wastewater was pumped to the reactor semi-continuously. The wastewater supply system was composed of an interval timer and a Masterflex pump. The former controlled the power supply interval and the latter pumped the wastewater from a reservoir to the reactor at a preset flow rate. Thus, the daily flow rate could be fixed by setting the time interval. The pumping frequency was deliberately kept as high as possible to simulate continuous flow. The flow rates selected for the study were 8, 16, 24, and 36 l/d, which were equivalent to 0.104, 0.208, 0.312, and 0.468 m³/m²/d. The whole experimental apparatus including the reactor and the wastewater supply system was housed in a constant temperature room which was controlled at 28.5 ± 0.5°C.

Materials

The stabilized MSW used in the experiments had been studied for two years in a previous project on leachate recycling (Fan, 1989). The original MSW had been transported from a sanitary landfill in Kaohsiung. Table 1 shows the physical compositions of the original MSW and the stabilized MSW. Noncombustibles had increased from 15.9% by weight in the original MSW to 40% in the stabilized waste. Combustibles, on the other hand, had decreased from 84.1% to 60%, respectively. Plastics had become the dominant component, amounting to 41.2% after the refuse

had been digested for two years. The disappearance of easily biodegradable materials such as food wastes and paper indicates the maturity of the refuse. In addition, the COD of the leachate from the stabilized refuse had decreased to less than 40 mg/l by the end of the leachate recycling project. Brewery wastewater from Taichung Winery (which mainly produces rice wines) was used in the treatability study. The COD of the raw brewery wastewater was around 24 000 mg/l. The COD/BOD ratio was as low as 1.2. This indicates the biodegradability of the wastewater. In order to maintain a steady influent strength, the raw brewery wastewater was diluted to a COD of 6000 mg/l with distilled water before pumping to the reactor. The pH was also adjusted by adding Na_2CO_3 solution.

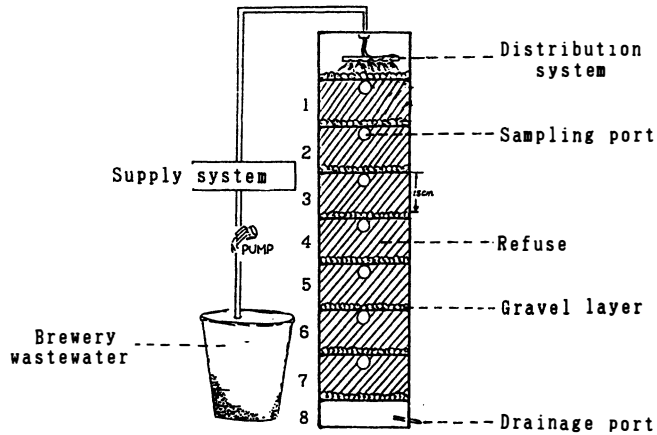


Fig. 1. Schematic diagram of the treatment system

TABLE 1 Physical Characteristics of the Municipal Solid Waste

Item	Municipal solid waste	
	Raw	Stabilized
A. Combustibles		
1. Paper	14.5	0.2
2. Fiber and cloth	4.6	2.6
3. Wood, bamboo, leaves, and grass	8.3	14.1
4. Food wastes	26.1	0
5. Plastics	16.8	41.2
6. Leather and rubber	1.4	0
7. Others	12.4	1.9
SUBTOTAL	84.1	60.0
B. Noncombustibles		
1. Metals	1.6	3.8
2. Glass and ceramics	8.2	10.5
3. Gravel and others	6.1	25.7
SUBTOTAL	15.9	40

All expressed as % dry basis

RESULTS AND DISCUSSION

The study was conducted over four periods. During each period, the wastewater flow rate was maintained at a steady level. Table 2 summarizes the operational conditions for each period. The influent COD concentration was around 6000 mg/l throughout the whole of the research. The uniformity of the initial COD concentrations indicates the stability of the brewery wastewater quality during the study, and problems due to wastewater variation were minimal. The daily organic loading increased from 0.596 to 2.704 kg COD per m^3 refuse. Each study period lasted for more than three weeks, to ensure steady performance of the reactor. The transition between periods was not less than a week, to allow for hydraulic

adaptation. The statistical analysis shows that, during each period, the standard deviations were mostly within 10% of the averages, as illustrated in Table 3. The small variation ensured that the conditions in each period were steady. Thus, the averages for each depth were used in the following plots as well as in the discussion. Figure 2 shows the average COD concentrations in the various refuse layers for each wastewater flow rate. It can be seen that the process had a very good performance regarding COD removal. During Period I (flow rate of 8 l/d), the COD was reduced from an initial concentration of 6011 mg/l to a final concentration of 60 mg/l after the wastewater had passed through a refuse layer of 90 cm. Each cell (15 cm in depth) had a COD removal efficiency of more than 50%. As the hydraulic load increased to 36 l/d, the final COD increased to 995 mg/l (after passing through the same depth), giving a removal efficiency of 83.4%. The COD removal efficiency for each cell had decreased, and remained steady at between 20 to 30%, which was about half that obtained during Period I. In other words, it would need about twice the depth to achieve the same removal for $Q = 36$ l/d as for $Q = 8$ l/d.

TABLE 2 Operational Conditions

Operating Period	Influent COD, mg/l	Hydraulic loading, l/d	Surface loading, $m^3/m^2/d$	Organic loading, kg COD/ m^3/d
I Nov. 24 - Dec. 17, 1988	6011	8	0.1041	0.596
II July 20 - Aug. 18, 1988	5818	16	0.2082	1.154
III Sept. 2 - Oct. 4, 1988	5843	24	0.3123	1.738
IV Oct. 10 - Nov. 3, 1988	6060	36	0.4684	2.704

TABLE 3 Statistical Analysis of COD Concentration for Each Period

Period	Influent	Depth, cm							
		15	30	45	60	75	90	105	
I	Average	6011	3081	1509	716	323	134	60	-
I	Standard deviation	271	134	116	51	32	13	13	-
I	Number of samples, n	9	9	9	9	9	9	9	-
II	Average	5818	3244	1885	1071	612	373	223	149
II	Standard deviation	414	291	225	128	116	52	45	33
II	Number of samples, n	11	11	11	11	11	11	11	11
III	Average	5843	3931	2669	1722	1129	796	498	255
III	Standard deviation	341	169	232	230	119	46	57	28
III	Number of samples, n	10	10	10	10	10	10	10	10
IV	Average	6060	4484	3337	2379	1580	1227	995	-
IV	Standard deviation	239	177	228	165	132	127	89	-
IV	Number of samples, n	10	10	10	10	10	10	10	-

All units are mg COD/l except for number of samples

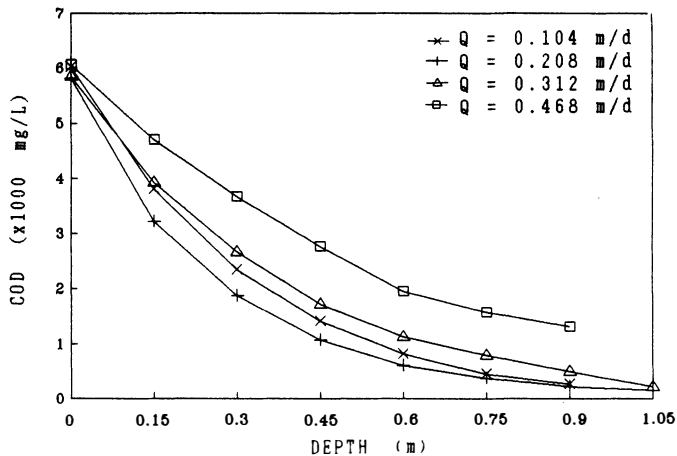


Fig. 2. Variation of COD with depth of refuse layer

The Schulze equation is widely employed in the simulation of removal of organic substances in trickling filters (Schulze, 1960). The refuse system has the same biofilm reactions as trickling filters, therefore the Schulze equation should also be applicable to this system, as long as the following three assumptions are correct: 1. the organics reduction is a first order reaction; 2. a constant microbial film uniformly covers the filter media; and, 3. plug flow occurs. The Schulze equation is expressed as:

$$Se/S_o = \exp(-K'DQ^{-n}) \tag{1}$$

where: S_o = influent COD, mg/l; S_e = COD at depth D , mg/l; K' = treatability factor, day^{-1} ; Q = hydraulic load, $\text{m}^3/\text{m}^2/\text{d}$; D = filter depth, m; n = constant characteristics of the media.

By taking logs of both sides, the equation yields:

$$\log(S_e/S_o) = (-K'DQ^{-n})/2.3 \tag{2}$$

If Se/S_o is expressed as a percentage, then the following equation is obtained:

$$\log(100 Se/S_o) = -(K'DQ^{-n})/2.3 + 2 \tag{3}$$

Equation (3) is a linear expression, therefore the slope, m , of the $\log(100 Se/S_o)$ versus depth plot can be determined. The slope, m , is:

$$m = -K'Q^{-n}/2.3 \tag{4}$$

Taking logs of both sides, the equation gives:

$$\log(-2.3 m) = -n \log Q + \log K' \tag{5}$$

Again, n and K' can be calculated by plotting $\log(2.3 m)$ versus $\log Q$. Figure 3 shows the plot of Equation (3) for each flow rate in which all the raw data, instead of averages, were used for the plot. The statistical results are also summarized in the figure. These results demonstrate the excellent fit of Equation (3), with correlation coefficients (r) above 0.97. Figure 4 shows the plot of $\log(2.3 m)$ versus $\log Q$. The result also shows good fit with Equation (5) with $r = 0.988$. n and K' were determined as 0.5873 and 1.3835 day^{-1} , respectively. Thus, the complete model for this process is expressed as:

$$Se/S_o = \exp(-1.3835DQ^{-0.5873}) \tag{6}$$

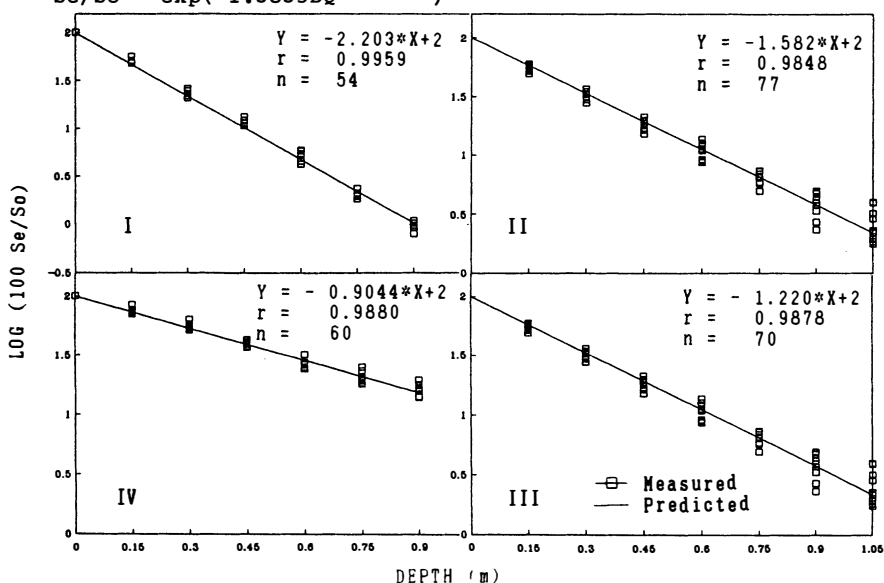


Fig. 3. $\log(S_e/S_o)$ versus depth

Finally, Figure 5 summarizes the measured and predicted Se for all flow rates and depths. The correlation follows the 45° line perfectly. This indicates that the Schulze model not only fits trickling filters but also the anaerobic process which occurs in the refuse system. For domestic sewage, typical values of n and K' of various trickling filter media are equivalent to 0.274 - 1.00 and 0.2619 - 1.099 day⁻¹, respectively, at 28.5°C while Q is expressed as m³/m²/d (Liptak, 1974). The higher K' value obtained in this study is thought to be caused by the highly biodegradable nature of the brewery wastewater. However, the n value of the refuse cells was close to that of regular filter media.

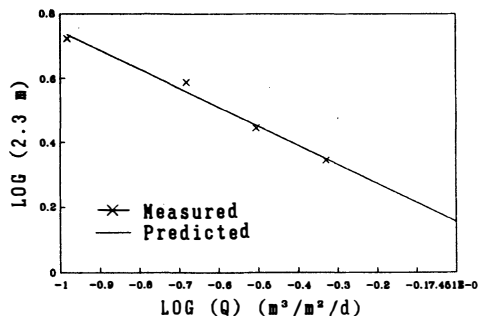


Fig. 4. Plot for determination of K' and n

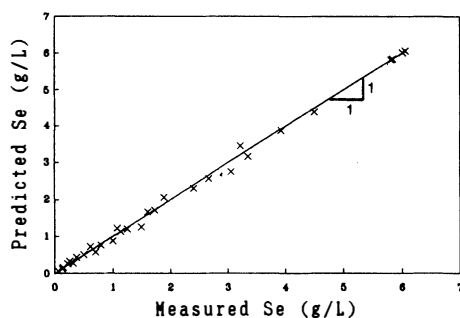


Fig. 5. Correlation between predicted and measured Se

The variation in the BOD was very similar to that of the COD. Both showed a smooth decrease. BOD/COD is a good indicator of biodegradability. The initial ratio was 0.89 for all flow rates. This indicates the high biodegradability of the wastewater. However, the ratio gradually decreased to around 0.33 for all the final discharges, although it varied with the flow rates at each depth. The accumulation of microbial metabolic products and nonbiodegradable materials decreased the BODs as well as the BOD/COD ratio. Figure 6 illustrates the variation of pH with depth. The pH dropped to as low as 5.7 at 15 cm below the surface for all operation periods. At this point, the volatile fatty acids (VFAs) reached a peak of 2228 mg/l as acetic acid, as shown in Fig. 7. It is believed that acidogenesis occurred quickly in the top 15 cm. Although the initial pH in Period I was higher than the others, it also decreased by 1 unit after the first layer. As the hydraulic loading increased, acidogenesis occurred deeper in the column. In Period IV ($Q = 36$ l/d), the pH did not return to 7.0 until a depth of 75 cm, while during Period II ($Q = 16$ l/d), a pH of 7.0 was reached in only 30 cm.

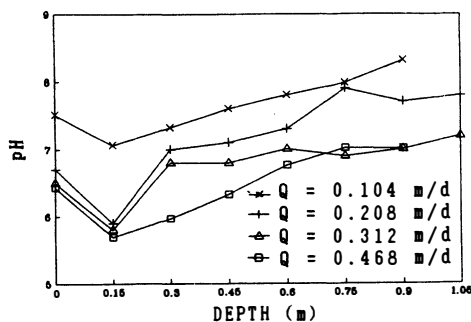


Fig. 6. Variation of pH with depth in the refuse layer

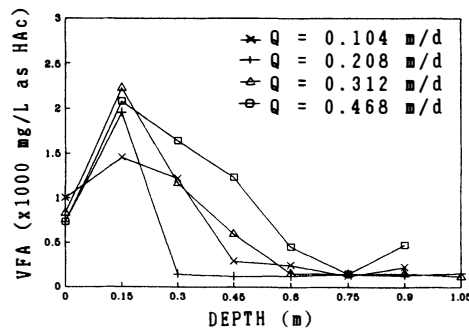


Fig. 7. Variation of VFAs with depth in the refuse layer

Figure 8 shows the variation of alkalinity with depth. Compared with the variation of pH, there is no doubt that the high alkalinity in Period I was caused by over-dosage of Na₂CO₃ during initial pH adjustment. In the other periods, the variation of alkalinity was similar to that of pH. It dropped to the lowest concentration at a depth of 15 cm, then gradually increased to around 2000

mg/l. The low pH and high VFAs neutralized part of the alkalinity. On the other hand, the formation of ammonium, carbonate, and the release of CO_2 , should increase alkalinity.

In general, the total Kjeldahl nitrogen (TKN) maintained a stable level throughout the refuse column, although it decreased slightly with depth. Ammoniacal nitrogen ($\text{NH}_3\text{-N}$) was also measured at each depth. The concentration of this parameter varied between 51.3 and 160.7 mg/l. The percentage of $\text{NH}_3\text{-N}$ in the TKN increased from 49% to 73% or even higher down the reactor. It is understood that anaerobic digestion breaks down organic nitrogen to form $\text{NH}_3\text{-N}$ but retards further oxidation. This is the reason for the increase in $\text{NH}_3\text{-N}$.

Oxidation reduction potential (ORP) is an excellent indicator for monitoring system stability. It is of particular value in aerobic and anaerobic processes. As biological oxidation progresses, the concentration of reductants decreases, and the concentration of oxidized materials increases. As a result, the ORP of the system increases. The opposite occurs with biological reduction. Figure 9 shows the variation of ORP with depth in the refuse layer. For all flow rates, the initial ORP was in the positive range, and between 105 and 140 mV. The existence of oxygen in the wastewater was one of the reasons for this. Then, the ORP dropped quickly to around -200 mV after the first cell. The rate of decrease was as high as 24.7 mV/cm depth. The ORP decreased further to between -260 and -290 mV before starting to increase. It is thought that methanogenesis was occurring at this depth. By the end of the reactor, the ORP had recovered back to between -100 and -200 mV. This increase in ORP indicates that the system conditions had become less reducing, due to microbial conversion. As the hydraulic load increased, the critical point generally occurred deeper in the reactor, and the rate of recovery was slower. There is no absolute ORP value which distinguishes either aerobic or anaerobic conditions, due to the variety of reductants and oxidants which may be present. However, systems with an ORP of -250 mV or lower are generally considered to be strictly anaerobic (Happer, 1986). This clearly indicates that anaerobic fermentation was taking place in the reactor, and air invasion had not occurred.

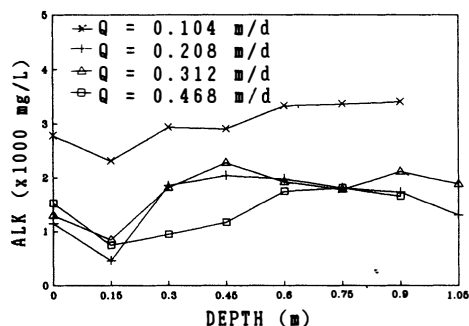


Fig. 8. Variation of alkalinity with depth in the refuse layer

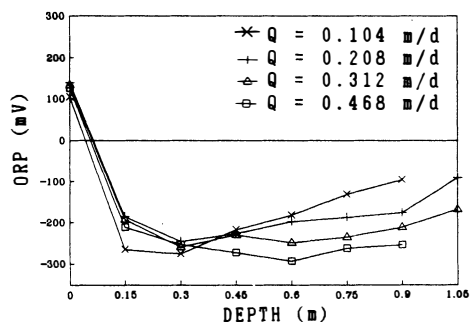


Fig. 9. Variation of ORP with depth in the refuse layer

SUMMARY AND CONCLUSIONS

This study demonstrates that stabilized refuse has a great capacity to treat brewery wastewater. The 90 cm refuse layer reduced the wastewater COD from 6011 mg/l to 60 mg/l at a surface loading of $0.104 \text{ m}^3/\text{m}^2/\text{d}$ or an organic loading of $0.596 \text{ kg COD}/\text{m}^3 \text{ refuse}/\text{d}$. The following equation was found to perfectly simulate COD removal:

$$\text{Se}/\text{So} = \exp(-1.3835\text{DQ}^{-0.5873}) \quad (6)$$

The value of 'n' in this refuse system was close to those found in trickling filters. Acidogenesis occurred quickly in the first 15 cm of the refuse layer, resulting in a low pH, high VFAs concentration, and low alkalinity. As the flow rate increased, acidogenesis occurred at a deeper level and the rate of recovery

became slower. The ORP dropped to as low as -290 mV, indicating the anaerobic conditions occurring in the system. The BOD/COD ratio decreased gradually from 0.87 to 0.3 through the reactor.

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