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Studies on the Biological Treatment of the Shôchû-Distiller's Slops by the Sea-Water Activated Sludge

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Introduction

Shôchû is a spirituous liquor, containing from 20 to 25 per cent of alcohol, produced by means of distillation of the Shôchû-Moromi, a mash made from Kôji and sweet potatoes, in a distillatory apparatus, excepting a continuous still. Five to eight parts of the Shôchû-distiller's slops at the BOD of 30,000 to 70,000 ppm to one part of alcohol, are drained off from the distillery[1]. If the activated sludge process happened to be applied to the treatment of the Shôchû-distiller's slops, more than 10 parts of fresh water would be required for a dilution medium for a satisfactory treatment of one part of it.

In a region, where there is not enough supply of fresh water for a 1 : 10 dilution of the distiller's slops, the fresh-water activated sludge process cannot be applied, though the sea-water activated sludge process, in which sea-water could be employed for a dilution medium of the distiller's slops, might be available. In any of the treatment-processes, the treated water must flow into the sea at the end. In addition, the treatment-plants in this process might be established in marine environments. The sea-water may have an injurious effect on the fresh-water activated sludge, but it has no such effect on the sea-water activated sludge, formed from a resident microflora in the sea-water by means of feeding the waste water. In order to employ the sea-water in place of the fresh-water for a dilution-medium in a biological treatment of the Shôchû-distiller's slops, the sea-water activated sludge must be formed from the resident microflora in the sea-water.

This report presents the treatment of the Shôchû-distiller's slops by the sea-water activated sludge, and its optimum treating conditions.

Methods and Materials

Shôchû-distiller's slops

The Shôchû-distiller's slops-samples were collected from the Hi'oki plant of Komasa Jôzô Co. The analyses of the distiller's slops were performed according to the directions of the testing methods for Industrial Waste Water, JIS K 0102–1971, Japanese Industrial Standard[2]. The results were summarized in Table 1.

*This report was presented at the Joint Meeting of the Kansai Division and the Nishi-Nippon Division of the Agricultural Chemical Society of Japan, Naha, Abstracts, p. 103, 1974, and at the Annual Meeting of the Agricultural Chemical Society of Japan, Tokyo, Abstracts, p. 21, 1974.

Table 1. Analysis of the distiller's slops of the-Kôme koji-Shironuka-shikomi Shôchû

	slops	supernatant
specific gravity, at 15°C	1.011	1.005
pH	4.2	4.2
dry weight, %	5.39 ～ 5.62	3.45 ～ 3.87
total nitrogen, %	0.454 ～ 0.479	0.148 ～ 0.284
reducing sugar, as glucose, mg/ml	1.76 ～ 1.88	1.20 ～ 2.49
total sugar, as glucose, mg/ml	9.77 ～ 17.60	5.67 ～ 15.81
BOD, ppm	46950 ～ 51800	34150 ～ 40150
COD, ppm	16700 ～ 21100	10400 ～ 18600

*The distiller's slops of the Kome-kôji-sweet potatoes-shikomi Shôchû, total phosphate in the supernatant, 856 ppm.

Table 2. Examples of the Shôchû-mash bills

1) Kôji-sweet potatoes Moromi

	Shubo	2-ji Shikomi	Total*
Kome-koji	600 kg		600 kg
Sweet potatoes		3,000 kg	3,000 kg
Kumimizu	900 kg	1,440 kg	2,340 kg

*An estimated volume: 5338 l.

2) Kôji-Shironuka Moromi

	Shubo	2-ji Shikomi	3-ji Shikomi	Total*
Kome-koji	300kg			300kg
Shironuka		600kg	400kg	1,000kg
Kumimizu	450kg	2,150kg		2,600kg

*An estimated volume: 3548 l.

The Shôchû-Moromi is prepared from such materials as shown in Table 2, which is distilled to give the Shôchû, leaving the distiller's slops[1]. The distiller's slops-sample was centrifuged at 3000 rpm (2000 × g) for 10 minutes, and its supernatant was diluted 1 : 4 with the sea-water or with the tap-water and was adjusted to pH 7.2 to 7.6 before use. The dilutions were served for all the experimental treatments of the Shôchû-distiller's slops.

Formation of the sea-water activated sludge

The supernatant of the slops was added to an equal mixture of the respective sea-water sample collected from the three of the stations of the Kinkô Bay, Kagoshima (one of which is shown in Photo 1), to give the final COD of 300 ppm for a day. Three liter and a half of the mixed liquor in a 5-liter flask was aerated through at an air-flow rate of 3 to 3.5 liter per minute at 25° C, and approximately 6 months were required to obtain the sea-water activated sludge enough to be used for the experimental treatment of the distiller's slops. For comparison, the tap-water activated sludge was formed from the pond water in the

Photo 1 Iso, Kagoshima city, one of the sampling stations from which the sea-water samples had been collected.

Photo 2 Tamari-ike in the Arata campus of Kagoshima University, from which the pond water had been collected.

Arata campus of Kagoshima University in the same way as the one in which the sea-water activated sludge was made. (Photo 2)

Experimental treatments of the distiller's slops

The artificial sewages I and II were also served for the experimental treatments, and they are as follows: artificial sewage I, glucose, polypepton, KH_2PO_4, at a concentration of 300 ppm, each; artificial sewage II, beef extract, glucose, KH_2PO_4, sodium benzoate, at a concentration of 300 ppm, each.

The supernatant of the distiller's slops was added to 3.5 liter of the mixed liquor in a 5-liter of flask to give the final COD of 300 ppm, and the mixed liquor was aerated through at an air-flow rate of more than 670 ml per minute at 25° C. The sea-water activated sludge was compared with the tap-water activated sludge in COD-removal, settling ability, and recovery of phosphate, and various conditions for the treatment of the distiller's slops were also compared in the COD-removal for one hour. Various conditions are shown in Table 3. For the experimental treatments under varying conditions, 1.5 liter of the mixed liquor in a 2-liter of flask was employed, to which the supernatant of the distiller's slops was added, to give the final COD of 300 ppm.

Table 3. Various conditions, under which the experimental treatments were carried out to determine the optimum treatment condition

	sea-water activated sludge	tap-water activated sludge
sludge volume (%)	1.9 3.1 8.4 13.6 19.9 27.8	2.3 4.5 11.4 16.3 21.7 30.9
temperature (°C)	15 20 25 30 35 40	15 20 25 30 35 40
air flow (*l*/min)	0 0.51 0.98 1.75 2.94 4.08	0 0.51 0.98 1.75 2.94 4.08
starting pH	3.80 5.61 6.52 8.40 8.80 9.33	4.02 4.53 6.62 8.60 9.42 9.70
concentration of sodium chloride (%)	0.1 1.2 2.2 3.8 6.3 12.5	0 1.0 2.1 3.5 6.1 12.4

Radioactive assay

The activated sludge was centrifuged at 3000 rpm (2000 × g) for 10 minutes and was washed twice with centrifugation in equal volumes of a suspending medium, tap-water for the tap-water activated sludge, or sea-water for the sea-water activated sludge. The washed activated sludge was re-suspended in the suspending medium to give the sludge-volume of about 11 per cent, and to this was added the 10-fold strength artificial sewage, to give the concentration of 300 ppm to each of the ingredients; and 0.5 ml of the ^{14}C-U-glucose solution or the ^{14}C-U-glutamate solution at a radioactivity of 1 μCi in ml was added also. Two ml of the mixed liquor was pipetted and filtered through a millipore filter, having a pore size of 0.45 μm; and a sludge fraction on a millipore filter and 1 ml of the filtrate were served for radioactive assays in a Gas-flow counter, respectively.

Results and Discussion

Experimental treatment of the distiller's slops

The experimental treatments were carried out for confirmation of the treating capacity of the newly-formed sea-water activated sludge. The supernatant of the distiller's slops was added to the newly-formed sea-water activated sludge to give the final COD of 322, 501, and 1037 ppm, respectively, and two kinds of artificial sewages were also employed for this experiment. Both the sea-water and the tap-water activated sludges could remove 95 per cent of the COD added, within 3 hours when the COD of 322 ppm was given, as shown in Fig's. 1 and 2, and within 5 hours and a half, when the COD of 501 ppm was given, as shown in Fig. 3. When the COD of 1037 ppm was given, the treatment failed to go satisfactorily, as shown in Fig. 4, because the sludge was blown up with bubbles on account of an increase in the viscosity of the mixed liquor, overflowing, as shown in Fig. 5. However, when an aeration into the mixed liquor was still going on, a tardy removal of the COD was observed. Calculated from the aeration time required for removal of the COD given in the batch-wise experimental treatment, the maximum COD loading was assumed to be 2.4 kg of the COD per m^3 for a day, and a semi-continuous treatment seemed to be satisfactory also within the maximum COD loading. In the continuous treatment of the supernatant of the slops in such apparatus as shown in Photo 3, the COD-removal in the effluents was as shown in Table 4. The facts indicate that the sea-water activated sludge is effective for the treatment of the Shôchû-distiller's slops, and the sea-water activated sludge process is probable.

The experimental treatments of the distiller's slops under various conditions such as varying concentrations of the sludge, temperatures, air-flow rates, starting pH's and concentrations of sodium chloride, were carried out and the conditions were compared in the COD-removal for an hour. An optimum concentration of the sea-water activated sludge was noted to be less than 14 per cent (*v*/*v*), but there was no significant difference in the COD-removals at various temperatures, ranging 20° C to 40° C, and in those at various air-flow rates of 0.7 to 2.7 liter per liter of the mixed liquor per minute at 25° C, as shown in Fig's. 6, 7, and 8. Effect of the pH of the mixed liquor on the removal of the COD of the slops done with the activated sludge, was investigated. To determine the optimum hydrogen ion concentration for the treatment of the Shôchû distiller's slops, the mixed liquors were adjusted to varying pH with 6 N hydrochloric acid or with 4 N sodium hydroxide solution.

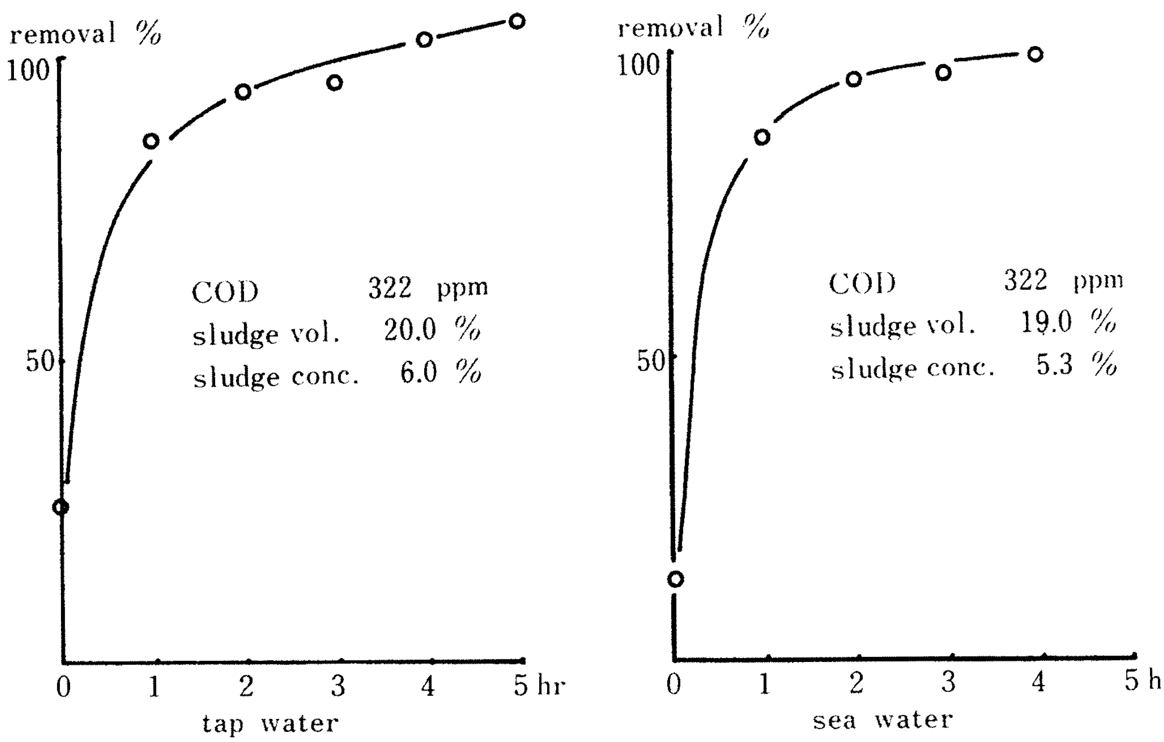


Fig. 1. Removal of the C OD in the Shôchû-distiller's slops at 322 ppm by the activated sludge.

The starting pH and the final pH of the mixed liquors were checked on the pH meter, and the COD at the respective pH was determined. As shown in Fig. 9, removal of the COD of the distiller's slops was done satisfactorily both by the tap-water activated sludge and by the sea-water activated sludge, with the starting pH of the mixed liquor ranging 5 to 9. Then, the pH of the mixed liquor seemed to have come up to about 7.5 with one hour-aeration. When the starting pH of the mixed liquor was adjusted to 4.0, removal of the COD was unsatisfactory, with its pH hardly rising up with one hour-aeration. The results show

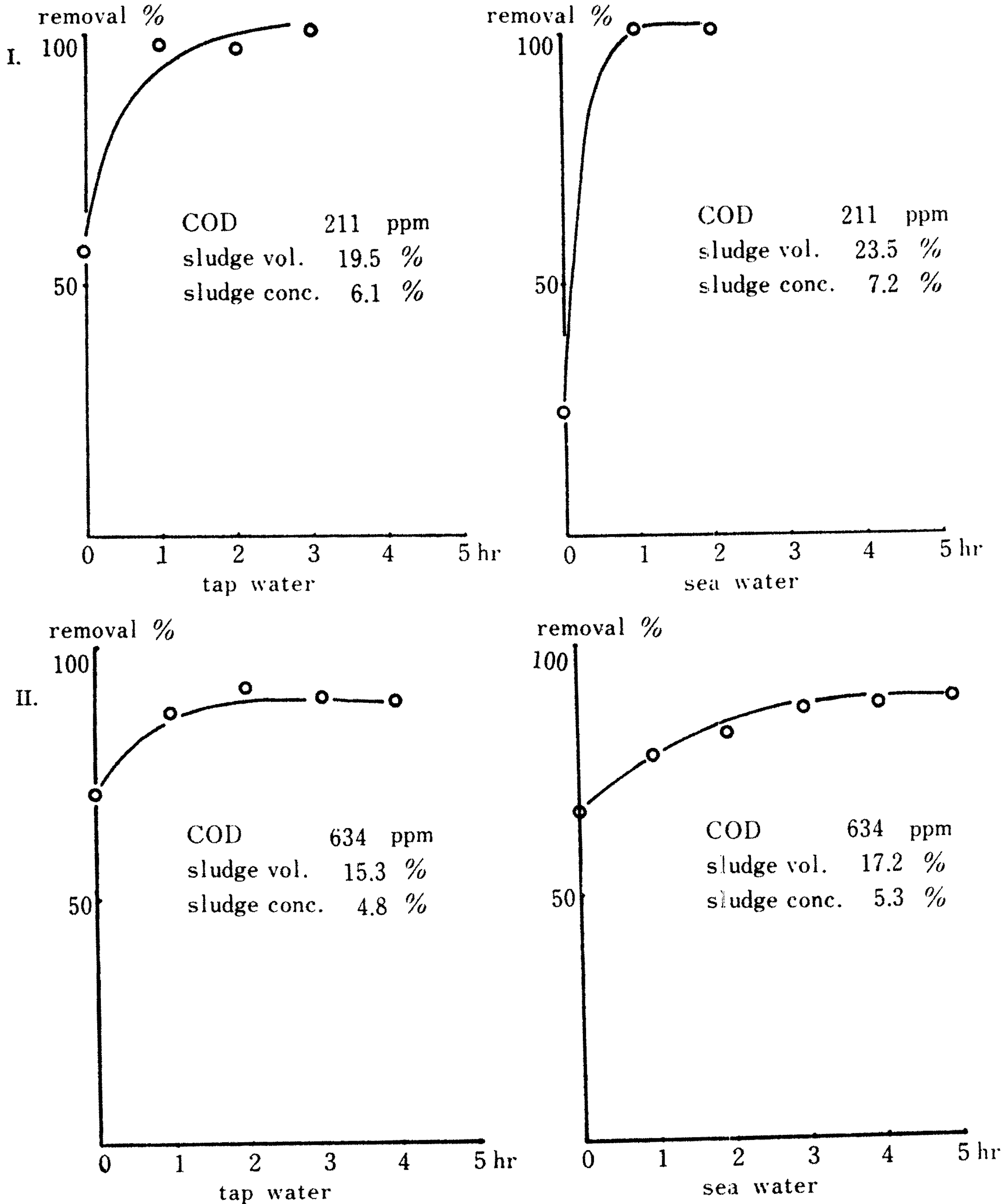


Fig. 2. Removal of the COD in the artificial sewages I and II by the activated sludge.

that the optimum pH for the treatment with the activated sludge might be about 7.5.

To determine the optimum concentration of sodium chloride for the treatment of the Shôchû-distiller's slops with either the tap-water activated sludge or with the sea-water activated sludge, the removal of the COD of the distiller's slops with one hour-aeration at

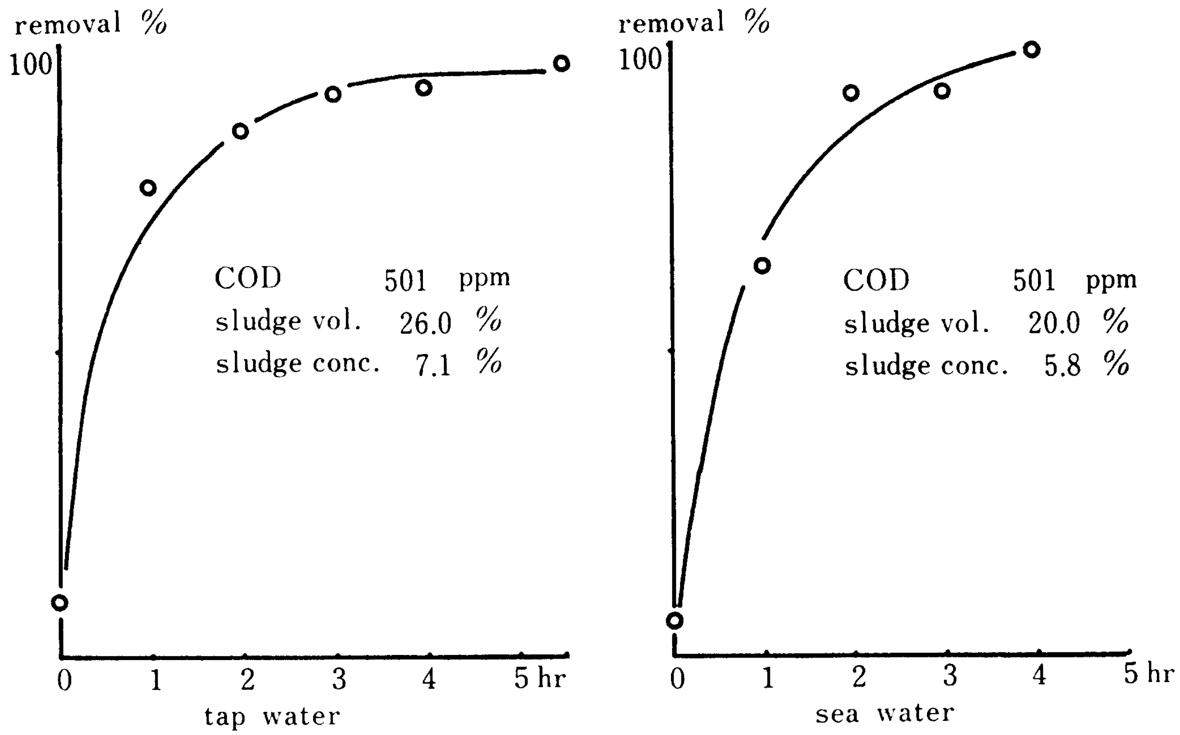


Fig. 3. Removal of the COD in the Shôchû-distiller's slops at 501 ppm by the activated sludge.

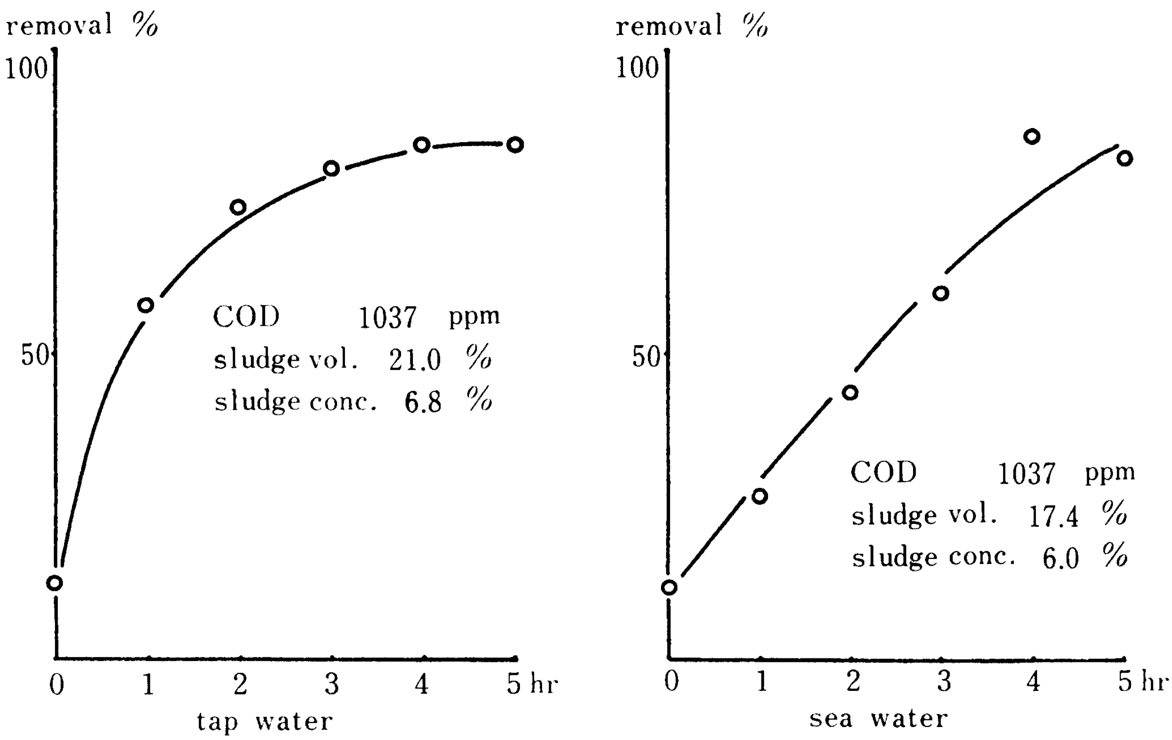


Fig. 4. Removal of the COD in the Shôchû-distiller's slops at 1037 ppm by the activated sludge

various concentrations of sodium chloride in the mixed liquor was measured. As shown in Fig. 10, the optimum concentration of sodium chloride for the treatment of the distiller's

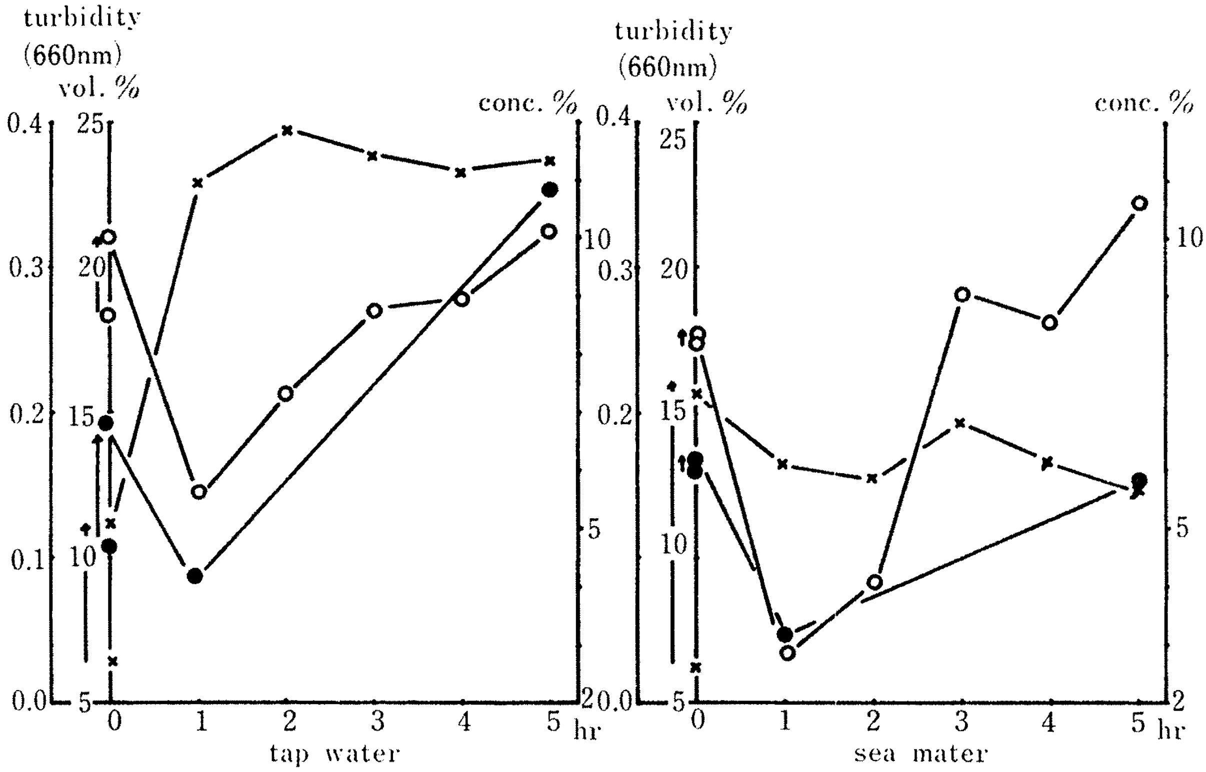


Fig. 5. Time course of changes in the sludge volume, sludge concentration and turbidity of the mixed liquor in the removal of the COD in the Shôchû-distiller's slops at 1037 ppm by the activated sludge.

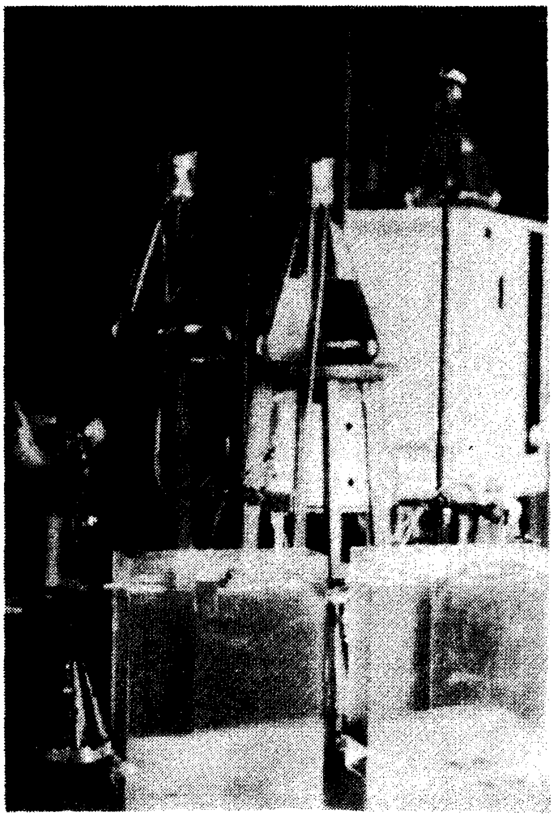


Table 4. Continuous treatment of the distiller's slops in such apparatus as shown in Photo 3

	sea-water activated sludge	tap-water activated sludge
sludge volume (%)	12.0	10.1
sludge volume index	159	81
flow rate (ml/min)	31	30
COD loading (kg/m /day)	1.5	1.2
COD (ppm) influent	184	139
effluent	14–46	8–36
COD removal (%)	75–92	74–94

⇦Photo 3 The apparatuses for continuous treatment of the waste water.

slops seemed to be 2.2 per cent for the sea-water activated sludge, and 0 per cent (21 ppm in chlorinity) for the tap-water activated sludge. The capacities of both the activated sludges to treat the distiller's slops and to settle, were not affected at the concentration of sodium chloride of 3.5 per cent, which was equivalent to that of the sea-water, but the temporary increase of the COD was observed in the mixed liquor of the tap-water activated sludge at a concentration of 12.4 per cent, because of a probable shock of the sludge caused by a high concentration of soldium chloride.

Recovery of phosphate in the distiller's slops by the activated sludge

Total phosphate amounted to more than 800 ppm in the distiller's slops of Kome-koji-sweet potatoes Moromi as shown in Table 1; and it was assumed to be one of the initiators, inducing the red water. Fig. 11 shows that one third of the total phosphate added remained in the treated water treated by the sea-water activated sludge when the distiller's slops were added to give the total phosphate concentration of 10 to 30 ppm in the mixed liquor. We should pay attention to this problem from the point of view of the treatment by the algal sludge, into which a normal sludge turns in a starved cultivation in light or from that of the treatment by such green algae as *Spirogyra* and *Hydrodictyon.*

Distribution of the radioactivity of ^{14}*C-U-glucose and* ^{14}*C-U-glutamate in the activated sludge fraction*

The incorporation of ^{14}C-U-glucose and ^{14}C-U-glutamate as substrates into the sea-

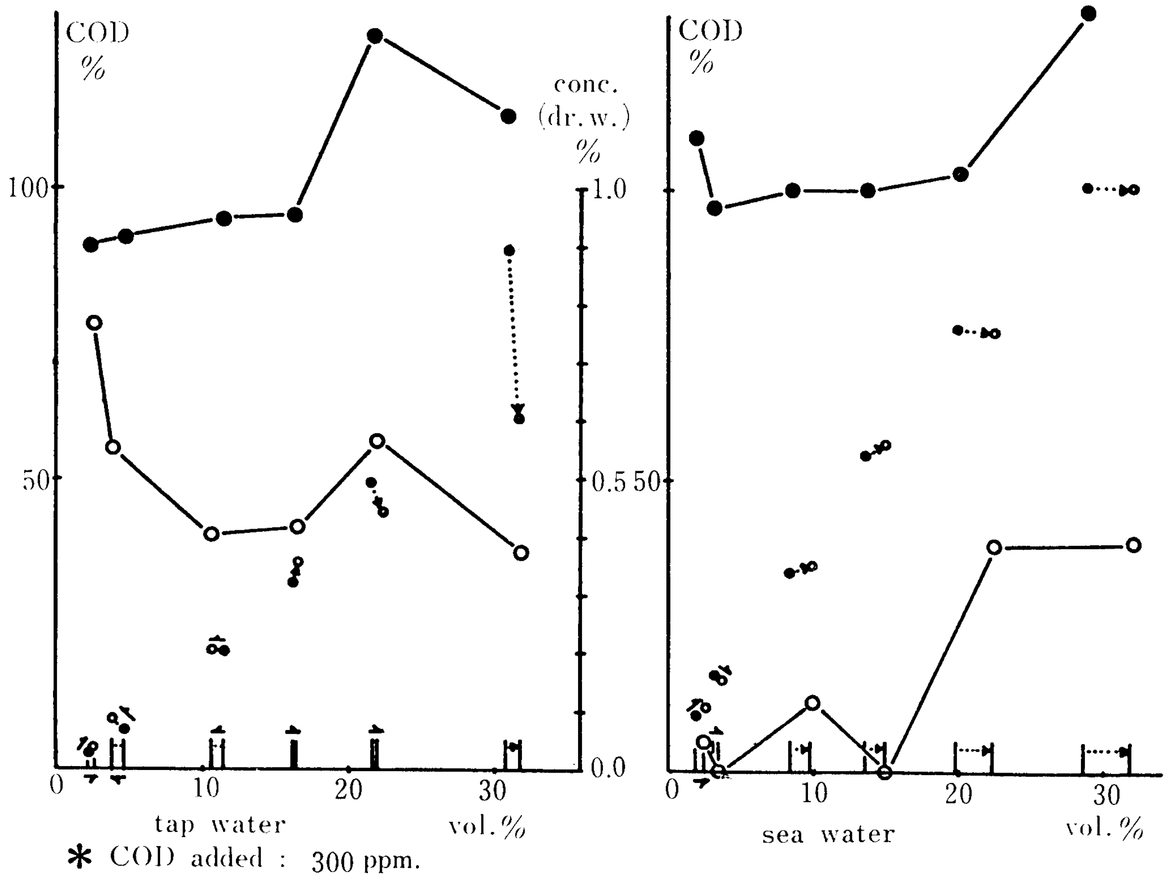
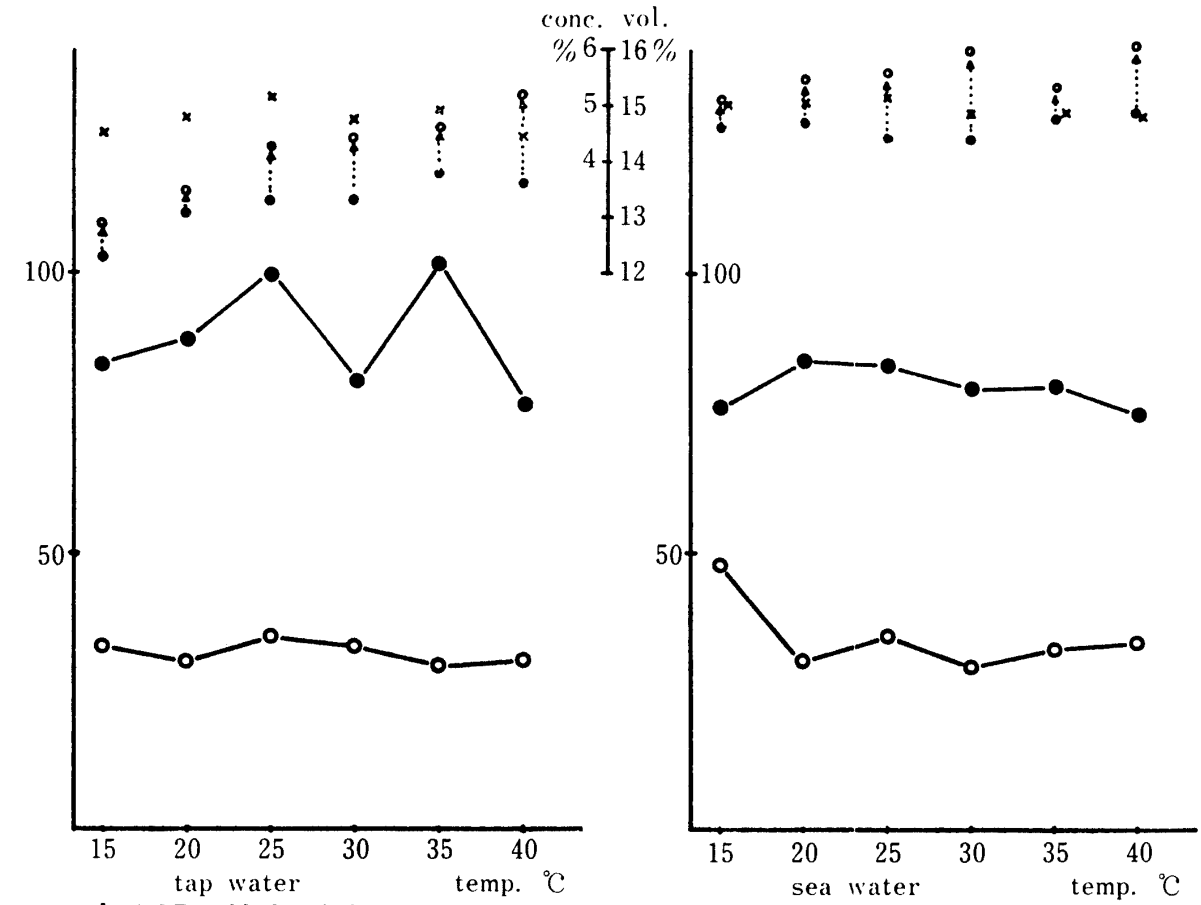
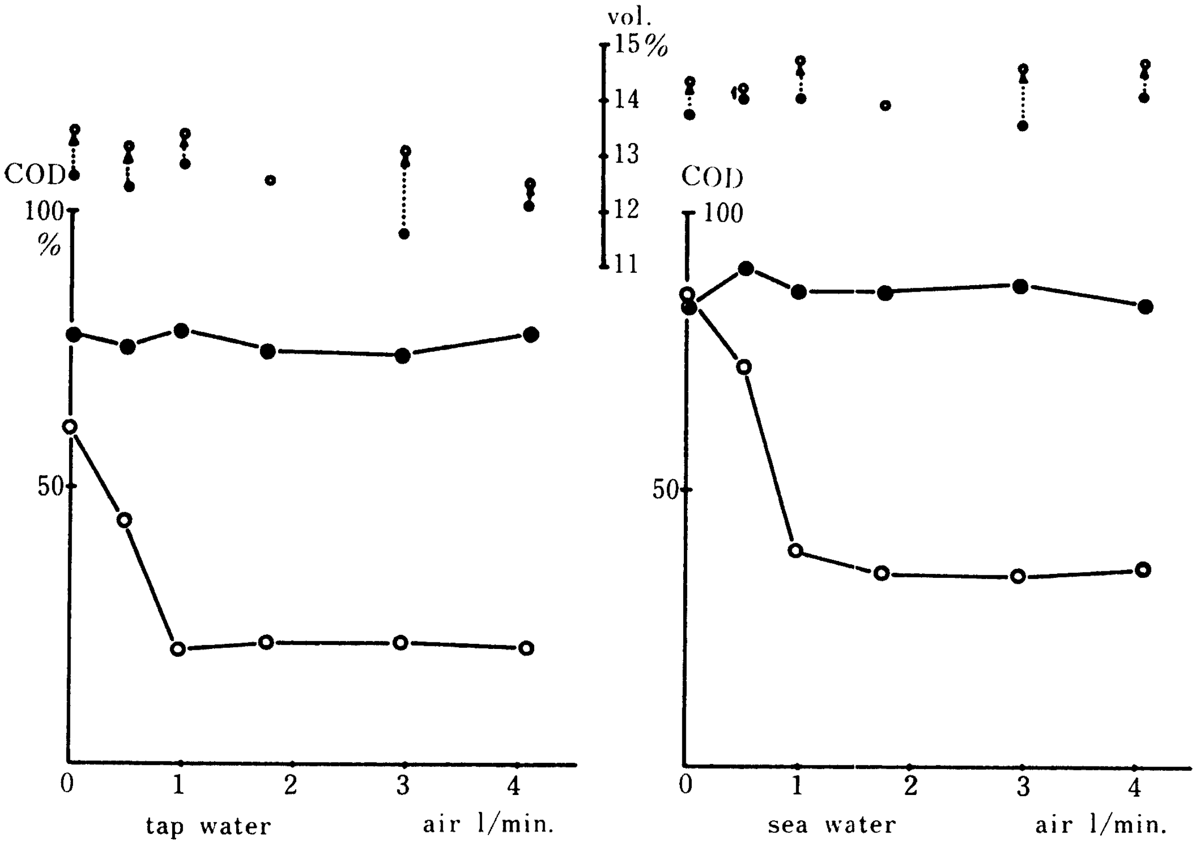


Fig. 6. COD removal at various concentrations of the sludge.
Large circles: COD. Small circles: dry weight of the sludge, %.
Black circles: values at the start of treatment.
Blank circles: values after one hour-treatment.



* COD added : 349 ppm.

Fig. 7. COD removal at various temperatures of the mixed liquor.
Large circles: COD. Small circles: sludge volume.



* COD added : 368 ppm.

Fig. 8. COD removal at various air-flows.
Large circles: COD. Small circles: sludge volume.

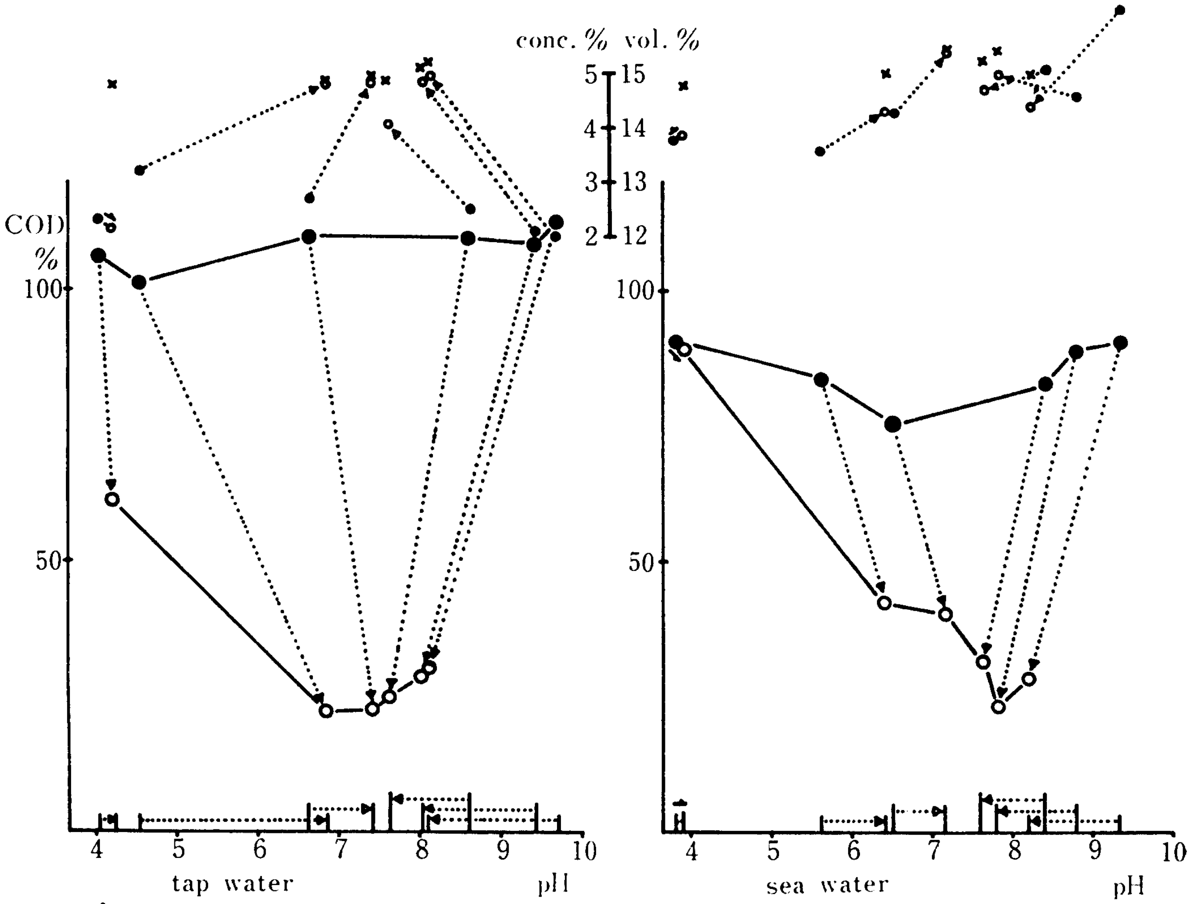


Fig. 9. COD removal at various values of pH.

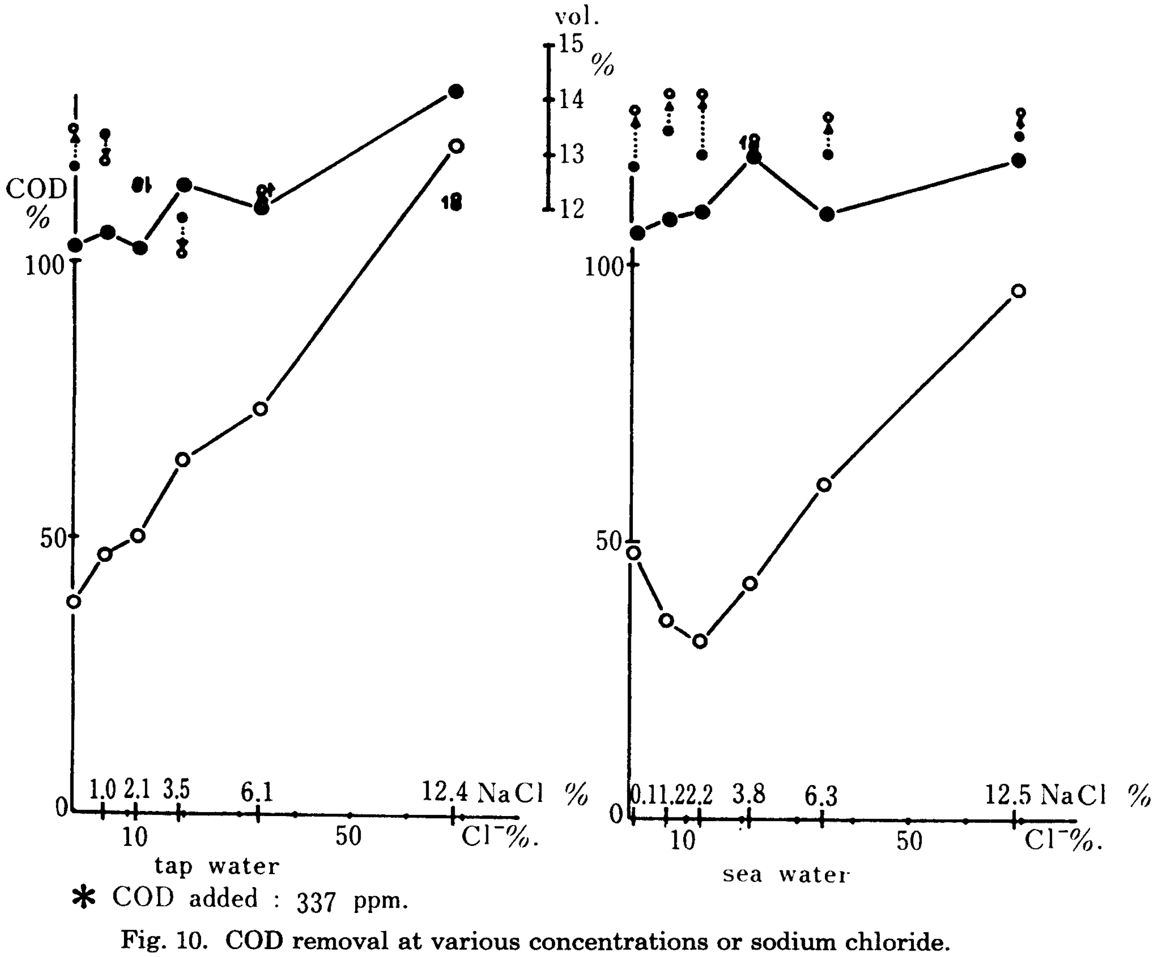


Fig. 10. COD removal at various concentrations or sodium chloride.

water activated sludge was compared with those into the tap-water activated sludge fraction, as shown in Fig.'s 12 and 13. Most of the radioactivity of ^{14}C-U-glucose, or ^{14}C-U-glutamate added was incorporated into the activated sludge fraction within a few hours. Subsequently, a rapid initial reduction in radioactivity was observed, which might be caused by the respiration of the sludge microorganisms. After this reduction, a further rapid reduction was not observed during the incubation without supply of the artificial

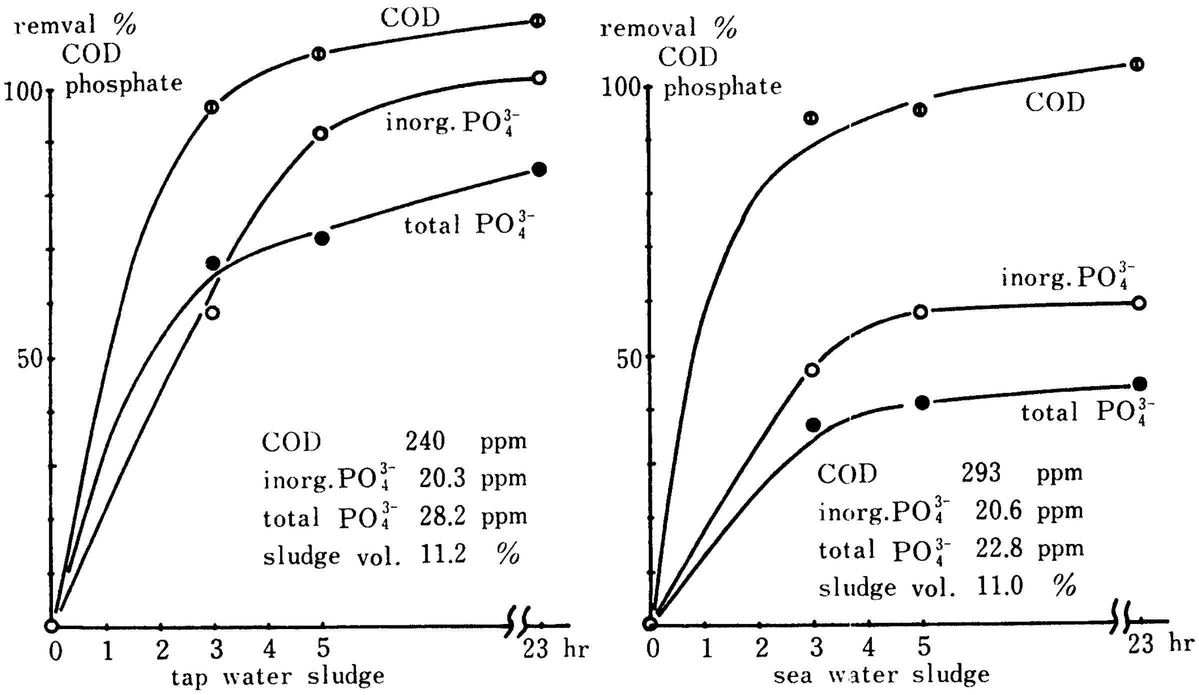


Fig. 11. Removal of COD, inorganic phosphate, and total phosphate in the distiller's slops by the activated sludges.

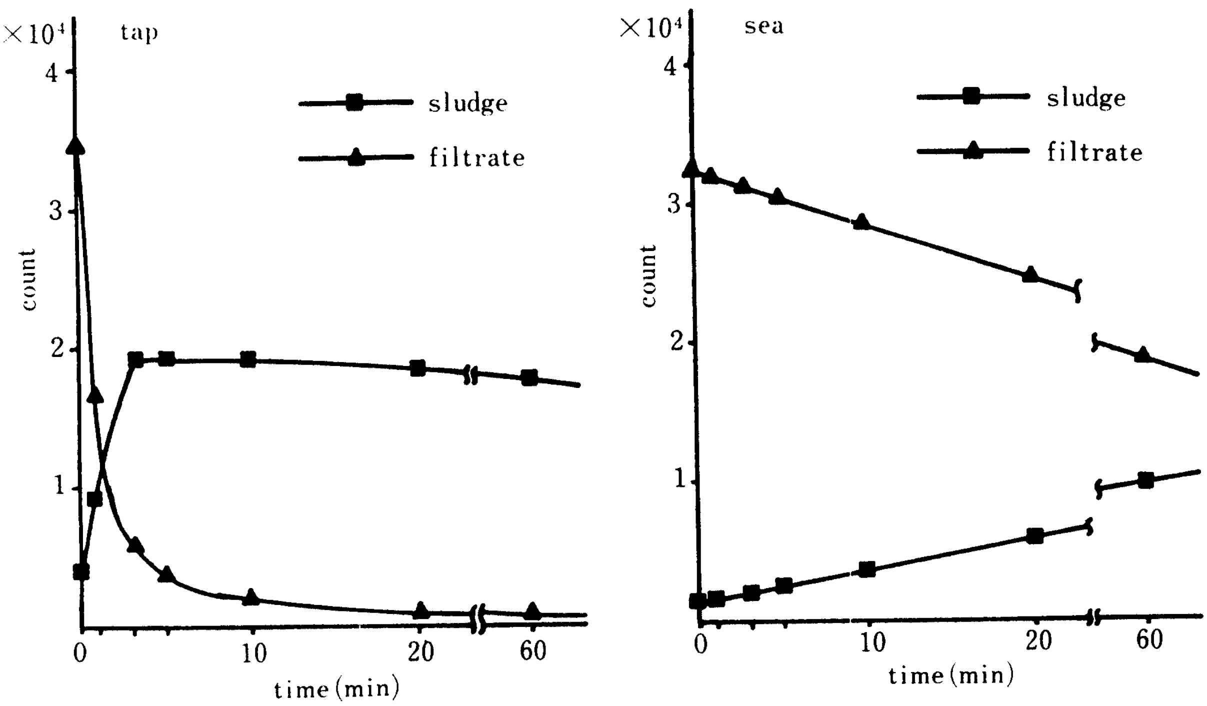


Fig. 12. Distribution of the radioactivity of ^{14}C-U-glucose in the activated sludge.

sewage I, as shown in Fig. 14 A. Only the artificial sewage I was added to the mixed liquor at 24th hour and 48th hour, but a slight dilution of radioactivity in the sludge-fraction

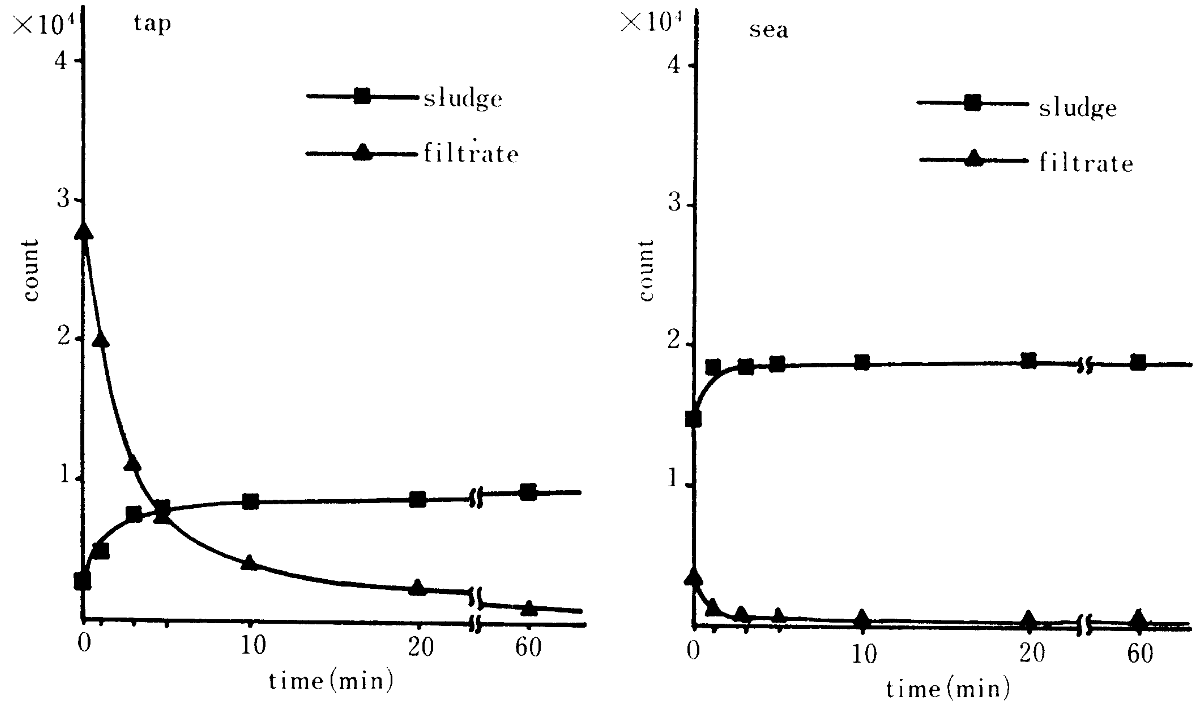


Fig. 13. Distribution of the radioactivity of ^{14}C-U-glutamate in the activated sludge.

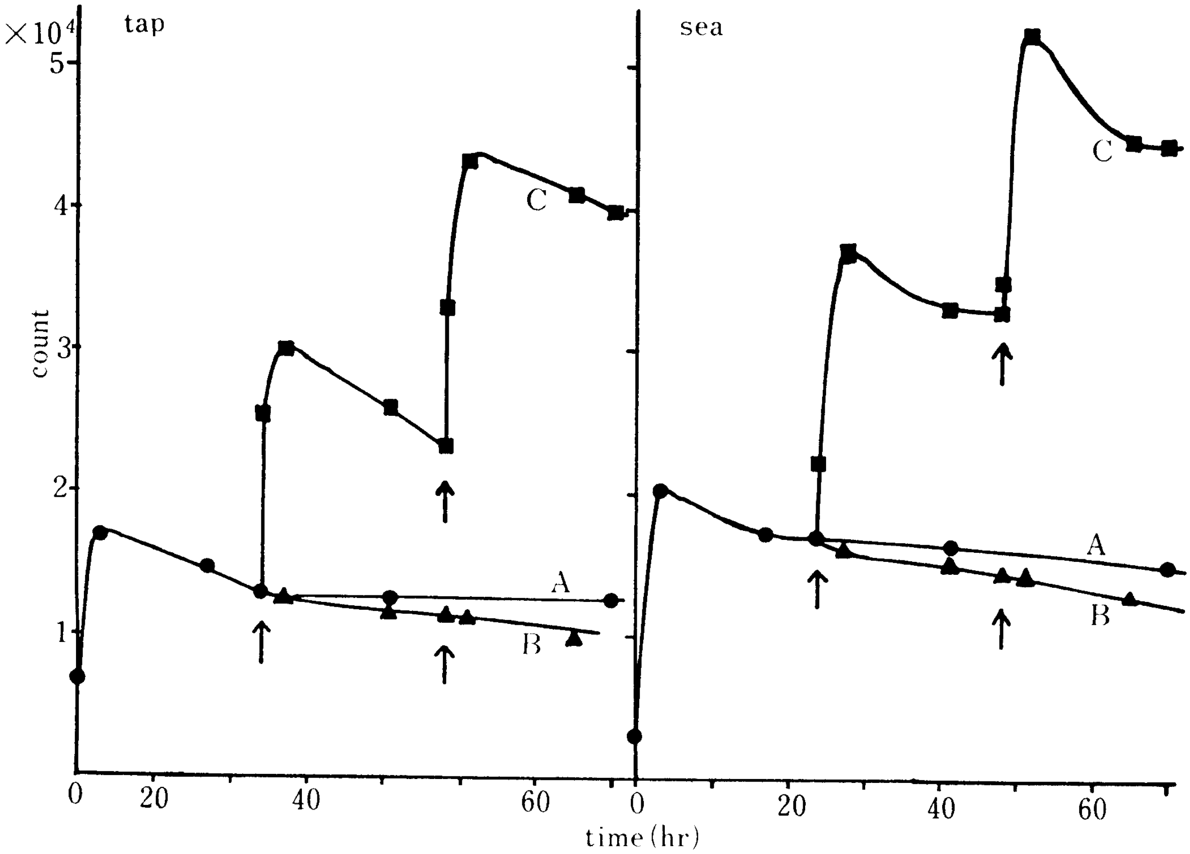


Fig. 14. Distribution of the radioactivity of ^{14}C-U-glucose in the activated sludge.

might be found by uptake of unlabeled ingredients of the artificial sewage I, as shown in Fig. 14 B. Both the artificial sewage I and ^{14}C-U-glucose were supplied to the mixed liquor every day, and an accumulation of radioactivity in the sludge-fraction was going on, as shown in Fig. 14 C. The facts indicate that such substances as glucose and L-glutamic acid seems to be incorporated readily into the sludge, and all of which will not be consumed as a respiration substrate by the sludge microorganisms, but some considerable amount of which may be employed for the formation of the activated sludge.

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Summary

In order to employ sea-water in place of fresh-water as a dilution medium in the biological treatment of the Shôchû-distiller's slops, the sea-water activated sludge must be formed from the resident microflora in the sea-water.

In the batch-wise experimental treatment, the newly-formed sea-water activated sludge equaled the tap-water activated sludge in the COD removal from the Shôchû-distiller's slops and two kinds of artificial sewages and in the settling capacity. The maximum COD-loading might be 2.4 kg of the COD per m^3 for a day, and the continuous treatment seemed to go on satisfactorily also. A desirable condition for the treatment of the Shôchû-distiller's slops by the sea-water activated sludge was as follows: sludge concentration, 12 to 14 per cent (v/v); air-flow rate, more than 0.7 liter of air per liter of the mixed liquor for a minute; pH, in the region of 7.5; salinity, 2.2 per cent; temperature, 25° to 30° C.

In the recovery of phosphate in the distiller's slops by the sea-water activated sludge, one third of the total phosphate added, remained in the treated water.

In the radioactive assay on the uptake of glucose and L-glutamic acid, these seemed to be incorporated readily into the sludge, and all of which might not be consumed as a respiration substrate by the sludge microorganisms, but some considerable amount of which was assumed to be employed for the formation of the activated sludge.

References

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2) Japanese Industrial Standards Committee, *Testing Methods for Industrial Waste Water, JIS K* **0102-1971**.