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BIOLOGICAL TREATMENT OF SIMULATED HUMIC ACID WASTEWATER IN A LABORATORY SCALE AEROBIC REACTOR

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Abstract

A laboratory study was conducted to determine the feasibility of activated sludge reactor for treating humic acid wastewater and to examine the effects of the presence of glucose as the second carbon source on treatment performance. Activated sludge obtained from a wastewater treatment plant treating domestic wastewater was used as a seed for the reactors. Synthetic wastewaters containing humic acid as the sole carbon source and glucose as the second carbon source were used as feeds for the reactors operated in a fill-and-draw mode. The results showed that the presence of glucose in the wastewater enhanced the production of higher MLSS (Mixed Liquor Suspended Solids) than that of without glucose. The TOC (Total Organic Carbon) concentrations in both reactors fluctuated greatly until the end of the experiment due to inability of keeping the input TOC at desired level. However the decrease in TOC suggested that there are some microorganisms capable of degrading the humic acid. Addition of glucose to the simulated humic acid wastewater improved the capability of microbes in degrading the acids. Most ammonium nitrogen in the wastewaters was converted into nitrate nitrogen. Although the performance was lower compared to that of conventional system, activated sludge process was capable of degrading wastewater containing humic acids.

Keywords: *activated sludge; ammonium nitrogen; fill and draw; glucose; humic acid; wastewater.*

Introduction

The pollution of groundwater with concentrated organic compounds from landfill leachates has been well documented (Husain, *et al.*, 1989). Leachates produced from old landfill usually contain high concentrations of refractory organics which mainly consisted of humic and fulvic acids and ammonium nitrogen (NH_4-N). This kind of leachate is characterized by low ratio of BOD to COD, generally ranging from 0.1 to 0.3 or less (Forgie, 1988).

The presence of humic acids in groundwater, which is a main source used for drinking water, can create many problems in water treatment. A certain amount of trihalomethanes (THMs), mainly chloroform ($CHCl_3$), are formed during chlorine disinfection of raw water containing humic substances. The presence of THMs in the drinking waters is of concerned from health-related aspect, since these compounds have been linked to the occurrence of human cancer in many instances.

Many researchers have suggested the use of physical-chemical approach to treat wastewaters containing humic acids, as they are considered less biodegradable (Chian, 1977; Mendez, *et al.*, 1988). Several investigators have attempted to combine biological and physical means to treat wastewaters containing refractory organics. By biological activated carbon fluidized bed process, Imai *et al.* (1995) was able to remove about 70% of humic substances with a HRT of 24 h. Combination γ-ray irradiation -activated sludge for the treatment of humic acid solution has been investigated by Yamazaki, *et al.* (1983). They found that the use of γ-ray irradiation on humic acid samples improved the total elimination efficiencies in comparison to without the use of γ-ray. However, from technical point of view the use of γ-ray is far from practical.

Little research has been reported with regard to the treatment wastewater containing humic acids by pure biological method. This may be due to low removal efficiency in terms of COD or TOC, as has been shown by several researchers. A mixed culture of activated sludge may contain one or more populations capable of degrading humic acid and nitrogen compounds simultaneously. Gradual acclimation of these microbial populations to an simulated wastewater containing high nitrogen and humic acids may enhance biological degradation of the compounds mentioned. On the basis of this consideration, the present study is conducted to investigate the feasibility of biological degradation of wastewater containing high nitrogen and humic acids using a fill and draw mode activated sludge process.

Materials and Methods

Experimental procedure

The composition of simulated wastewaters for both reactors is shown in Table 1. Activated sludge cultured with the simulated wastewaters was used as seeding microbes. Concentration of the

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activated sludge was approximately 4000 mg MLSS/L at the start of the acclimatization. The sludge was acclimated in both reactors having a 2 L operating volume, respectively, at 25 °C by a fill and draw mode of one cycle per four days. The reactors were aerated with 0.5 L air/min through a sparger placed in the bottom of the reactor. In each cycle, after settled for 30 minutes, 1 L supernatant was removed and the same amount of fresh simulated wastewater was added. Everyday the pH of both reactors was adjusted to 7.0 by addition of 1 N NaOH solution.

Table 1. Characteristics of Simulated Humic Acid Wastewater

Constituents	Reactor A mg/l	Reactor B mg/l
Humic acid	150 as TOC	150 as TOC
Glucose	-	50
$(NH_4)_2SO_4$	125 as N	125 as N
KH_2PO_4	15	15
$MgSO_4.7H_2O$	11.3	11.3
$CaCl_2.2H_2O$	1.4	1.4
$FeCl_3.6H_2O$	0.1	0.1

Sampling and Analysis

Both reactors were periodically sampled and analyzed for TOC, MLSS, pH, and Nitrogen concentrations. The TOC was measured by Total Organic Carbon Analyzer (Shimadzu TOC-500). Microbial concentrations were measured according to Standard Methods (1975). Measurement of pH was performed by a pH meter (TOA HM-20E). Ammonium-N, Nitrate-N, and Nitrite-N were measured by Shimadzu Ion Chromatography.

Chemicals

Humic acid was obtained from commercial source (Waco Chemical Co.). Preparation of humic acid stock solution followed the procedure in Grasso *et. al.* (1980). Humic acid stock solution was prepared by adding specified amounts of humic acid to distilled water, and raising the pH to 11 with 1.0 *N* NaOH to facilitate the dissolution. After 24 hours of agitation, the pH was readjusted to 7.0 with 1.0 *N* HCl, and the solution was centrifuged and filtered to remove fraction that may have precipitated. The other chemicals were of commercial grade.

Result And Discussion

Figure 1 shows MLSS variations in both reactors, reactor A (without glucose) and reactor B (with glucose). The microbial concentration in both reactors decreased steadily up to 28 days. Beyond these days, the concentration declined slowly and reached closely to steady state after 56 days of culturing. At the end of the acclimatization period, the concentrations were 775 mg MLSS/l in reactor A and 835 mg MLSS/l in reactor B, respectively. These values are lower than that of suggested for conventional activated sludge system. However, the presence of glucose in the reactor B slightly enhanced the production of higher MLSS compared to that of the reactor A (without glucose). The degree of enhancement in terms of MLSS was small which probably due to low concentration of glucose (50 mg/l) in the simulated wastewater in the reactor B.

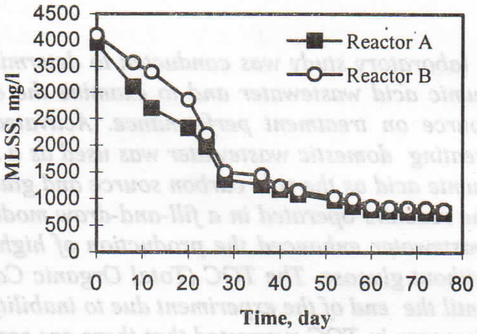

Figure 1. Variation of microbial concentrations in the reactor A (without glucose) and in the reactor B (with glucose)

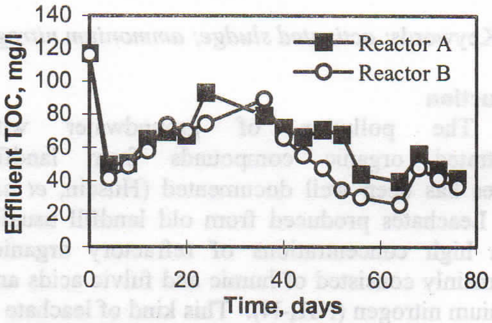

Figure 2. Variation of microbial concentrations in the reactor A (without glucose) and in the reactor B (with glucose)

Figure 2 shows variation of effluent TOC in the Reactor A and B during the acclimatization period. In the first cycle, the TOC decreased sharply. This decrease was partly contributed by physical adsorption of TOC by activated sludge. It showed that the TOC concentrations in both reactors fluctuated greatly until the end of the experiment, even though the MLSS tended to be constant at the end of the experiment. This fluctuation was due to inability of keeping the input TOC constantly at desired level. Up to 76 days of culturing, complete degradation of humic acid in the reactors was not achieved. However, the decrease in TOC suggested that there are some microorganisms capable of degrading the humic acid.

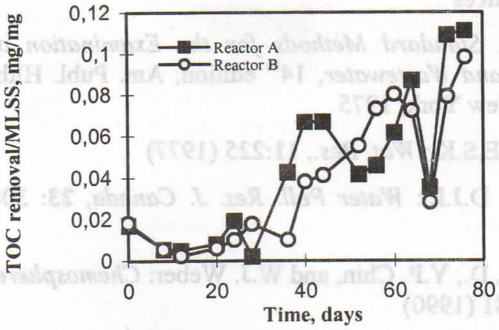

Figure 3. Removal of TOC per mg MLSS in Reactors A and B versus time

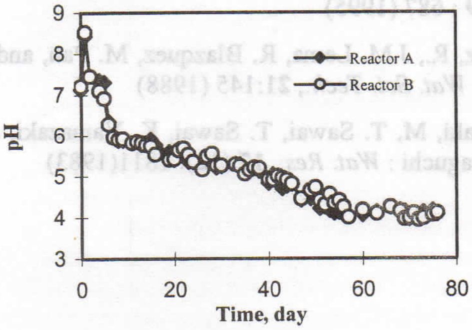

Figure 4. Daily pH variations in Reactor A and B during acclimatization period

Figure 3 showed the relationship between TOC removal per mg MLSS and time. Although data greatly fluctuated, it was observed that the capability of biomass in both reactors increased from time to time. The fluctuation of data was affected by influent substrate concentrations. As the influent substrate affects the biomass in the reactor and eventually will affect the amount of TOC removal for every mg MLSS in the Reactor. The presence of glucose in the reactor B resulted in higher capability of biomass in removing the TOC compared to the one without glucose in the Reactor A.

The behaviour of pH in both reactors is quite similar, as shown in Figure 4. Even if the pH was adjusted to 7.0 once a day, the pH slowly decreased day by day and reached to a nearly constant level of 4.0 after 57 days. The decrease in pH exhibited that the biomass in both reactors produced acidic substances as part of its metabolic activity. Most probably part of humic acid may have been degraded into fulvic acid and the fulvic acid contained in the wastewater was degraded into lower molecular substances (less than 1000 of molecular weight). The occurrence of nitrification may also contributed to the decrease of pH, as nitrification produces acidity.

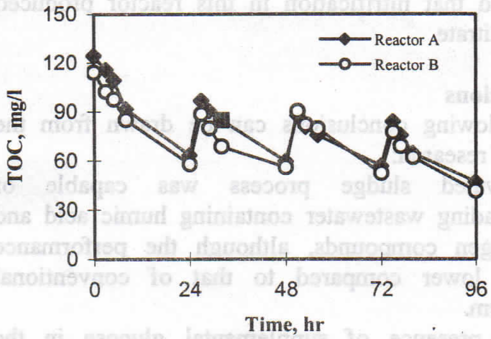

Figure 5. Variation in TOC in Reactors A and B during one cycle started at day 72 of acclimatization period.

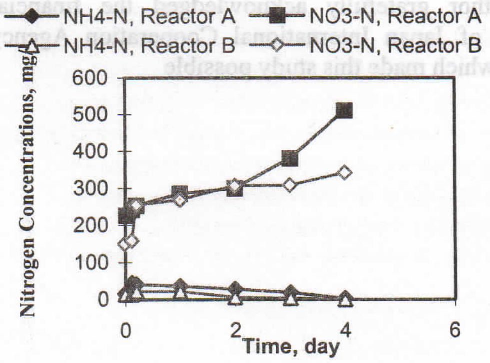

Figure 6. Variation in nitrogen concentration in Reactors A and B during one cycle started at day 72 of acclimatization period

The observation of TOC variation in one cycle, as shown in Figure 5, was started at day 72 of the acclimatization time. Although the TOC in the Reactor B was slightly lower than that of the Reactor A, the variation of TOC during one cycle was quite similar. During the first 24 hours the TOC in both reactors steadily decreased. The next day the TOC increased to approximately 100 mg/l. Similar case also occurred after 48 and 72 hours during one cycle study. The reason behind the above phenomena is that as the operation reached 24 hours, the pH in the reactor decreased to about 4.0. At this point, some portion of humic acid may have been precipitated. As the pH of the reactors was adjusted to 7.0 after 24, 48, and 72 hr of operation, the precipitated portion dissolved again to the bulk solution which then contributed to the increase of TOC.

Ammonium nitrogen in both reactors decreased gradually reaching to an undetected level at the end of the cycle (day 4). High nitrate-N concentrations, as shown in Figure 6, at the beginning of the cycle came from nitrate-N build-up of the previous cycle. It is seen that the nitrate-N tended to accumulate in the reactors, as the profile in one cycle increased steadily. However, nitrite-N was undetectable during one cycle measurement which suggested that nitrification in this reactor produced mostly nitrate.

Conclusions

The following conclusions can be drawn from the result of research:

1. Activated sludge process was capable of degrading wastewater containing humic acid and nitrogen compounds, although the performance was lower compared to that of conventional system.
2. The presence of supplemental glucose in the wastewater enhanced the capability of microbes in degrading the humic acids.

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References

APHA: *Standard Methods for the Examination of Water and Wastewater*, 14th edition, Am. Publ. Hlth. Ass., New York, 1975

Chian, E.S.K.: *Wat. Res.*, **11**:225 (1977)

Forgie, D.J.L.: *Water Poll. Res. J. Canada*, **23**: 308 (1988)

Grasso, D., Y.P. Chin, and W.J. Weber: *Chemosphere*, **21**: 1181 (1990)

Husain, T., A. Hoda, and R. Khan: *Wat. Air Soil Pollut.* **45**: 191 (1989)

Imai, A., K. Onuma, Y. Inamori, and R. Sudo: *Wat. Res.*, **29** : 687 (1995)

Mendez, R., J.M. Lema, R. Blazquez, M. Pan, and C. Forjan: *Wat. Sci. Tech.*, **21**:145 (1988)

Yamazaki, M, T. Sawai, T. Sawai, K. Yamazaki, and S. Kawaguchi : *Wat. Res.*, **17** (12): 1811(1983)