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Full Length Research Paper

Nutrients requirements in biological industrial wastewater treatment

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Wastewaters from olive mills and pulp and paper mill industries in Jordan have been characterized and treated using laboratory scale anaerobic and aerobic sequencing batch reactors, respectively. Nutrient requirements for these two industrial wastewaters were found to be less than what is usually reported in the literature for C:N:P ratio of 100:5:1 for aerobic treatment and 250:5:1 for anaerobic treatment. This was ascribed to the low biomass observed yield coefficients and relatively low removal efficiencies in these wastewaters. It was found that for anaerobic treatment of olive mills wastewater COD:N:P ratio of about 900:5:1.7 was able to achieve more than 80% COD removal. The observed biomass yield was about 0.06 kg VSS per kg of COD degraded. For extended aeration aerobic treatment of pulp and paper mill wastewater COD:N:P ratio of about 170:5:1.5 was able to achieve more than 75% COD removal. The observed biomass yield was about 0.31 kg VSS per kg of COD degraded. In both these wastewaters nutrients were not added. A simple formula is introduced to calculate nutrient requirements based on removal efficiency and observed biomass yield coefficient.

Key words: Olive mill wastewater, anaerobic treatment, aerobic treatment, sequencing batch reactor, biomass yield, nutrient requirement.

INTRODUCTION

Microorganisms involved in the removal of carbonaceous contaminants from wastewater require nitrogen and phosphorous for growth and reproduction. Microorganisms require nitrogen to form proteins, cell wall components, and nucleic acids (Maier, 1999a). Biomass has been universally accepted to have the chemical formula $C_5H_7NO_2P_{0.074}$ (Droste, 1997).

When treating wastewater, it is usually stated that the ratio of COD:N:P in the wastewater to be treated should be approximately 100:5:1 for aerobic treatment and 250:5:1 for anaerobic treatment (Metcalf and Eddy, 1991; USEPA, 1995; Henze et al., 1997; Maier, 1999 a). For anaerobic treatment, the required nitrogen and phosphorous concentrations is lower than the case for aerobic treatment due to the fact that anaerobic treatment produces only 20% sludge compared to aerobic treatment.

Henze and Harremoes (1983) based the COD:N requirements for anaerobic treatment on loading rates. For highly loaded processes (0.8-1.2 kg COD/kg VSS/d), they recommended a value of 250:5. For lower loading rates, the value can be increased from 250:5 by multiplying it with a factor which equals to the loading rate in kg COD/kg VSS/d divided by 1.2.

In the present study, the effect of both the removal efficiency and observed biomass yield on nutrient requirements for both aerobic and anaerobic treatments is discussed. It is hypothesized that, for industrial wastewater, more accurate determination of nutrient requirements should be based on both removal efficiency and biomass yield.

Abbreviations: COD, Chemical Oxygen Demand; BOD_5 , Five days Biochemical Oxygen Demand; OMW, Olive Mill Wastewater; VSS, Volatile Suspended Solids; MLVSS, Mixed Liquor Volatile Suspended Solids Concentration; *E*, Chemical Oxygen Demand Removal Efficiency; Y_{obs}, Observed Biomass Yield.

MATERIALS AND METHODS

The sequencing batch reactor used in this study had an active volume of 2 L. For anaerobic treatment of olive mills wastewater (OMW), it was mixed and kept at 30± 2^{o}C using a magnetic stirrer/hotplate. After the mixing time was completed, mixing and heating were turned off, and the reactor was kept quiescent for 2 h to allow for anaerobic sludge to settle. After that the calculated volume of the supernatant was removed from the reactor and tested for a number of parameters following Standard Methods for the Examination of Water and Wastewater (APHA, 2000). An equal amount of raw wastewater was added and the whole volume started a new phase of mixing under anaerobic conditions. After the startup phase, the COD of the reactor was kept around 16,000 mg/l by dilution. Sludge wastage was conducted to keep the volatile suspended solids (VSS) concentration in the reactor as constant and as close to 12,000 mg/l as possible. The hydraulic retention time was kept equal to 3 days. pH of the reactor was adjusted to around 7 as found necessary using sodium bicarbonate.

For aerobic treatment of pulp and paper mill wastewater, dissolved oxygen concentrations were kept between 2 and 4 mg/l. The treatment mode was extended aeration, because the yield coefficient in this mode is lower than the conventional activated sludge process. Average hydraulic retention time was 24 h. The reactor was fed three times daily each with about 670 ml. Mixed liquor volatile suspended solids concentration (MLVSS) was kept about 2500 mg/l.

Table 1. Average olive mill and pulp and paper mill wastewater characteristics during the study period.

Parameter	Average concentration/ value (Olive Mill Wastewater)	Average concentration/ value (Pulp and paper mill Wastewater)
BOD_5 (mg/l)	30,600	230
COD (mg/l)	97,000	420
Total Nitrogen (mg/l)	532	13
Total-P (mg/l)	182	4

RESULTS AND DISCUSSION

Wastewater Characteristics

Wastewater from olive mills and paper and pulp industries, have a wide range of characteristics. Table (1) shows the average value of a number of wastewater characteristics for these wastewaters. The table shows that the COD value for olive mills wastewater is very high and therefore anaerobic treatment is necessary for such wastewater. The average ratios of COD to nitrogen (COD: N) and phosphorous concentrations (COD: P) are equal to about 180 and 530, respectively. The COD: N: P ratio then equals 911: 5: 1.7. The maximum ratio that is usually reported in the literature as the required ratio is 250:5:1 to 500:5:1 depending on the extent of loading or COD influent concentrations (Droste, 1997; USEPA, 1995). The present ratio suggests that the concentrations of nitrogen and phosphorous are lower than what is required for anaerobic treatment of such wastewater. Therefore, and according to these figures, nutrients, especially nitrogen, have to be added to the OMW.

Similarly, for the pulp and paper mill wastewater, the ratio of C:N:P is lower than what is usually reported in the literature. This suggests that both nitrogen and phosphorous have to be added to the wastewater for effective biological treatment.

COD Removal

Despite the low nitrogen and phosphorous concentrations, the anaerobic reactor treating olive mill wastewater performed at a high level of efficiency as was observed from the low and stable concentration of fatty acids (between 50-90 mg/l), and the high removal of COD (about 80% at 3 days retention time).

Sludge wastage was conducted whenever the VSS exceeded 13000 mg/l, about every 6 to 9 days. The average sludge age at these conditions would be around 45 days. At 3 days retention time, the COD removal efficiency averaged a value of about 83%. This was achieved without the need for nutrients addition. At these conditions, the observed yield was found to be around 0.06 kg VSS per kg COD removed.

Similarly, for pulp and paper mill wastewater, removal efficiency of COD was higher than 75% without the addition of any nutrients. The sludge yield coefficient was found to be equal to about 0.31 kg VSS per kg COD removed.

Nutrient Requirements

Nutrient concentrations in the wastewaters reported in this study were lower than that reported in the literature. However, they achieved high removal efficiencies without the need for nutrient addition. So how were nitrogen and phosphorous sufficient for the treatment at this low concentration?

The C:N:P ratios listed in the literature (100:5:1 and 250:5:1 for aerobic and anaerobic treatments, respectively) were based on the following theoretical background. Carbonaceous organic matter is simplified as glucose and is given the formula $C_6H_{12}O_6$ while the biomass is given the formula $C_5H_7NO_2$. Upon degradation of organic matter, biomass is produced. The mass of biomass produced divided by the mass of the organic matter is termed the yield coefficient. In the biomass formula, the amount of nitrogen is 12.3% of the biomass. The degradation is given in the following equation:

$$C_6H_{12}O_6 + NH_3 + O_2 \rightarrow C_5H_7NO_2 + CO_2 + H_2O$$

In the above equation, the required ratio of C: N in the wastewater becomes 100: 5 when the yield coefficient is 0.41. If phosphorous is introduced and assumed 20% of nitrogen mass, the biomass chemical formula becomes

$C_5H_7NO_2P_{0.074}$ (Droste, 1997), and the required ratio becomes 100:5:1. For anaerobic processes and assuming that sludge production rate is 40 to 20% of aerobic sludge production, the ratio becomes 250:5:1 to 500:5:1, respectively.

In deriving these ratios, it was assumed that the efficiency of removal is 100%. The fact that different wastewaters have different biomass yields was not taken into account. Therefore when addressing nutrient needs, one should take into account both the microbial yield and the efficiency of COD removal. Giving a ratio between COD:N:P is misleading as this does not take into account the previously mentioned factors (biomass yield and efficiency). This is especially true for industrial wastewaters that have low removal efficiency and yield. For example, biomass treating pentachlorophenol aerobically has a very low cell yield of approximately 0.05 (Maier, 1999b). On the other hand octadecane has a cell yield as high as 1.49 (Maier, 1999b).

As mentioned above, for aerobic treatment, the required ratio of C:N:P in the wastewater should be 100:5:1 when it is assumed that COD removal is 100%, that nitrogen content of biomass is 12.3%, and that the observed yield coefficient is 0.41. In case the observed yield (Y_{obs}) is different than the 0.41, and removal efficiency (E) is different than 100%, the COD: N ratio required in the wastewater would be $0.41(100)/EY_{obs}$:5, or $41/EY_{obs}$:5. If phosphorous content is assumed 20% of nitrogen content then the required ratio of COD: N: P in an aerobic reactor should be calculated from the following formula $41/EY_{obs}$:5 :1.

For anaerobic treatment, the value of C: N: P ratio of 250: 5: 1 is observed at an observed yield value of 0.16 and 100% removal efficiency. At an observed yield value of 0.08, the ratio becomes 500: 5: 1 at 100% removal efficiency. For different observed biomass yield and different than 100% removal, the same formula ($41/EY_{obs}$:5 :1) can be used.

In the present study, the observed yield factor for aerobic biomass treating pulp and paper mill wastewater was equal to 0.31 while the removal efficiency was about 75%. For such treatment, the required C:N:P ratio should be (41/0.75(0.31)): 5:1, which is equal to 176:5:1. The COD:N:P ratio in the present study was a little bit higher than these values (161:5:1.5).

The observed yield for the anaerobic biomass treating olive mills wastewater was found to be equal to 0.06 and efficiency of COD removal was equal to 83%. The required COD:N:P ratio will then be equal to (41/(0.83)(0.06)): 5: 1, which is equal to 823:5:1. The concentration of nitrogen in the olive mills wastewater is lower than what is required by this formula. It should be noted, however, that for industrial wastewater, the usual sludge age used is very high, especially with low degradable wastewater. For this reason, the usual nitrogen content in biomass is lower than 12.3% (Eckenfelder, 1989). This suggests that in anaerobic treatment even lower nitrogen and phosphorous concentrations can be used than those calculated by the above formula. If nitrogen content is assumed 11% instead of 12.3%, the nitrogen content in the wastewater would then be sufficient. However, the above formula still gives a conservative value and therefore should be used. This formula should be used instead of using a constant value such as 250:5:1 or 500:5:1 for all wastewaters regardless of the removal efficiency or biomass yield.

In applying Henze and Harremoes (1983) criteria for COD:N requirements for the present study, the following were obtained. For a loading rate of 0.44 kg COD/kg VSS/d, for the olive mills wastewater, the COD:N ratio required would be 682:5 ((1.2/0.44)250:5). According to their method, nitrogen should be added to the wastewater. This method also depends on influent COD concentration, and does not differentiate between different removal efficiencies. Biomas yield is also not considered. Therefore, the use of loading rates for nutrient requirement determination is as misleading as the use of constant ratios of COD to nitrogen and phosphorous. More accurate determination of nutrient requirements should be based on both removal efficiency and biomass yield as suggested above.

The following conclusions can be drawn from the present study: (1) Olive mills wastewater and pulp and paper mill wastewater in Jordan have sufficient nitrogen and phosphorous concentrations that addition of such nutrients was not necessary, and (2) the COD:N:P ratio required for aerobic and anaerobic treatment of industrial wastewater should be calculated from a formula that take account of the removal efficiency and observed yield for the wastewater in concern ($41/EY_{obs}$:5:1) instead of using a constant value for all different wastewaters, or based on loading rate.

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