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DENITRIFICATION OF A HIGH NITRATE CONTAINING INDUSTRIAL WASTEWATER IN A SUSPENDED GROWTH SYSTEM

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ABSTRACT

The aim of this study is to evaluate the possibility of direct denitrification of concentrated wastewater, NO_3-N concentrations of 1200-1760 mg/li. Special consideration was given to inhibition effects due to highly concentrated nature of the wastewater. Based on this study a design for full scale application was made. Chemostat trials were performed employing a 2 day residence time and batch trials were carried out to determine kinetic parameters k_s and μ_s. Sludge from an existing oxidation ditch plant was used as innoculant. Initial results in the chemostat trials showed inhibition occurring at 30% dilution of the wastewater. At high dilution ratios, equivalent to 60% dilution, washout occurred. Various trials were used to determine the inhibiting component in the wastewater. The carbon source was primarily ethylene glycol. Various interventions were investigated in order to overcome the inhibitory effect of which only dilution was seen as effective. The inhibitory effect was assumed to be due to the effect of the carbon source. Both the mono and di-ethylene glycol species were present in the wastewater of which the mono-ethylene glycol made up 80% of the total. The glycol effect may be seen as affecting the microbial cells by increasing the osmotic pressure. To overcome the glycol effect, it is necessary to dilute the wastewater. A two reactor system was proposed to achieve denitrification while providing a source for dilution water. The effluent from the first reactor, a denitrification reactor, was fed to an aerobic reactor where the remaining COD as glycol is oxidized and the effluent from this reactor is split and part is fed back to the denitrification reactor as dilution water and part is disposed of as final effluent. A mathematical model was proposed using both Monod and inhibition kinetics. Design charts at different dilution ratios were made from the resulting mathematical model. The results show substantial denitrification results in the two reactor system depending on the dilution ratio employed. It shows the possibility of direct denitrification by using a two reactor system while at the same time substantially decreasing the COD in the wastewater.

I. Introduction

To prevent excessive eutrophication of receiving waters, nutrient removal standards are becoming much stricter in Europe. More stringent Nitrogen standards are to be implemented by 1998 requiring a total Nitrogen effluent concentration of 10 ppm. Typical Nitrate concentration of domestic wastewater range from 20 to 100 ppm. Nitrogen removal through Nitrification/Denitrification of domestic wastewater is a well-studied system which is implemented in many wastewater treatment plants to achieve strict effluent Nitrogen standards.

In this study, the denitrification of a specific industrial wastewater with very high levels of nitrate will be investigated. Industrial effluent from the production of Tertiary-butyl acetate (TBA) contains elevated levels of Nitric Acid (HNO_3). The Nitric Acid is used as a rinsing solvent for the polymeric product. The wastewater leaves the process as part of the bottoms fraction of a distillation unit and will be referred to as TBA Bottoms. The nitrate concentration in the effluent ranges from 600-1200 mM or approximately 8 -17 g NO_3-N/liter. This wastewater is treated in an oxidation ditch "Carousel" plant which has aerobic and anoxic stages. A low degree of denitrification is achieved in the carousel plant.

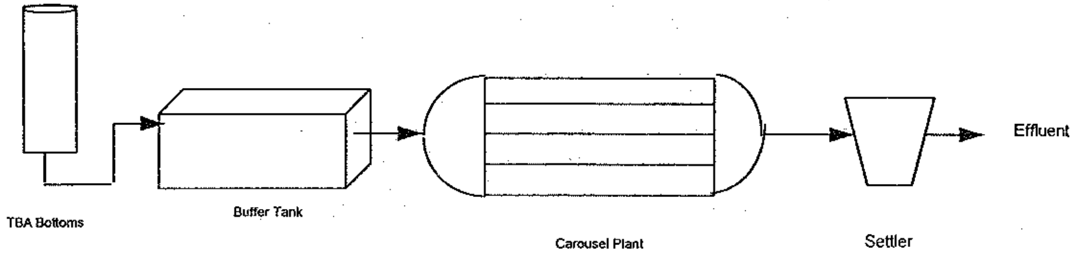

Figure 1. Wastewater treatment facility

It is planned to upgrade the water treatment system in order to achieve higher levels of carbonaceous COD removal and at the same time achieve higher nitrogen removal rates. The very high nitrate concentration present in the TBA Bottoms does not allow the carousel system to significantly decrease the nitrate levels. Therefore an anoxic denitrification process is needed within the process. An existing buffer tank with a hydraulic residence time of 2 days is to be used as a pre-denitrification reactor before carbonaceous COD removal. In this way denitrification can be carried out without the addition of an external carbon source. The use of industrial effluent as an external carbon source has been reported in literature [3]. In our case the carbon source is composed mostly of mono and di-ethylene glycols, about 80% of total carbon content on a COD basis. The glycols are a by-product of processes involving ethylene oxide .

A new wet air oxidation system is to be implemented as the carbonaceous COD removal process as shown below. The Wet Air Oxidation System will eventually replace the Carousel plant.

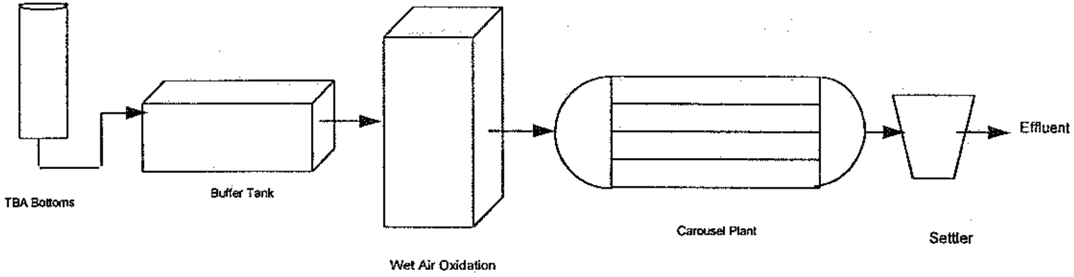

Figure 2. Proposed wastewater treatment scheme with Wet Air Oxidation System

The present wastewater treatment plant occupies a large area. Treating full strength wastewater in the buffer tank, followed by wet air oxidation would require much less space. There is sufficient COD in the wastewater to act as the carbon source for denitrification. The high COD content of the wastewater, about 110 g/li, means there will be no need for biomass retention. Without retention, 20g VSS/li is formed. This would mean less space, simple installation and operation. No make-up water will be required for dilution. The wet air oxidation unit would take care of COD removal.

The company has done a previous study on the denitrification of the wastewater using sludge from the carousel plant. Denitrifrying microorganisms are facultative and hence are found in the sludge from the carousel plant. Using this sludge also has the advantage of obtaining bacteria which are exposed to the specific conditions of the wastewater. In that study, various dilutions of the TBA bottoms were placed under denitrifying conditions i.e. anoxic, with sludge from the carousel plant. The limiting dilution rate was 50%, above which denitrifying activity ceased. Evidence of this was seen from the cessation of gas production and increasing Nitrate concentration in the reactor. That study was done under batch conditions, without pH or temperature control.

Work on the denitrification of highly concentrated NO_3^- wastewater (sometimes referred to as high rate denitrification) has been done by several groups. Bode, et.al. (1986) reported "high rate denitrification" as an extremely efficient process both in the thermophilic and mesophilic range. The concentrations involved were 1200-1760 mg/li NO_3 -N [1]. Mahne, et.al (1996) worked with waste water from an animal production plant having nitrate concentrations of 3500 mg/li. [2] A nitrification step was followed by a denitrification process which reduced nitrogen concentrations of 100 mg/li. Bernet, et.al. (1996) used Wine distillery wastes as an external carbon source in the denitrification of high strength synthetic wastewater NO_3 -N = 150,000 mg/l.[3] The high NO_3 -N concentrations in the last paper approaches the values we encounter in the current study. In all three studies, the carbon source was seen as the most important factor in determining the specific kinetics of the process.

II. Objective

The aim of this study is to evaluate the possibility of direct denitrification of the concentrated wastewater. Special attention was given to inhibition effects due to the highly concentrated nature of the wastewater. Based on this study a design for full scale application was made.

An initial study was conducted by the author using the following set-up.

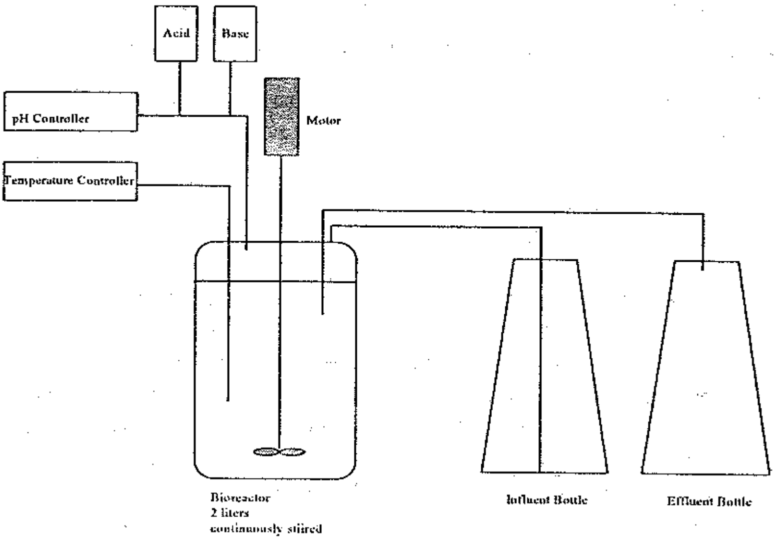

Figure 3. Experimental set-up

An Applikon jacketed bioreactor was used as a chemostat with temperature and pH control as shown in Figure 3. The following conditions were maintained in the reactor.

pH = 7 -7.5
Temp = 35 ^{O}C (mesophilic range)
Airtight reactor (Maintain anoxic conditions)
Continuous stirring (350 rpm)
Addition of phosphate (1 g/li)
Addition of $MgSO_4$ (0.3 g/li)
Hydraulic retention time = 2 days
No sludge recycle

III. Calculations

$[NO_3^-]_{in}$ = influent NO_3^- concentration (mM)
TOC = Total Organic Carbon (ppm)
$[NO_3^-]_{out}$ = influent NO_3^- concentration (mM)
$TOC_{con} = TOC_{consumed} = (TOC_{influent} - TOC_{effluent}) * Q$
Q = flowrate
V_{eff} = Volume of Effluent
% Conversion = $(\{[NO_3^-]_{in} - [NO_3^-]_{out}\} / [NO_3^-]_{in}) * 100$
Carbon to Nitrogen Ratio (C/N) = $TOC_{con} / \{([NO_3^-]_{in} - [NO_3^-]_{out}) * Q\,)$
Acid Consumption Rate = $(V_{acid} * 2.5\ N) / \{([NO_3^-]_{in} - [NO_3^-]_{out}) * V_{eff}$

IV. Results

Sludge from the Carousel plant was obtained from the company and mixed with a 10% solution of the TBA bottoms. Phosphate was added in the form of NaH_2PO_4 at 1 gram/li influent. Two reactors where charged with the same influent. The denitrifying capacity of the sludge was immediately evident from the vigorous evolution of gas. Due to the presence of anoxic sections in the carousel sludge, denitrifying enzymes are already present in the sludge. pH was maintained at 7 and the temperature at 35°C. These were kept at batch conditions for two days and were then fed with a 10% solution of the wastewater. The Hydraulic Residence Time (HRT = SRT) was kept at 2 days. This initial stage allowed the selection of the appropriate microbial population i.e. denitrifiers.

Vishniac spore solution was added to the reactors beginning day 13 in order to stabilize the reaction. In this trial the TBA bottoms concentration was steadily increased from 10% dilution to 50% dilution. Percent NO_3^- conversion for the initial dilution of 10-30% were high, from 90-100% conversion as seen in the chart below. As the TBA bottoms component of the influent was increased to 40% and 50%, the percent conversion steadily decreased eventually leading to a washout on day 42. From day 34 to day 43, NO_2^- levels in the reactor increased coinciding with an impending reactor washout.

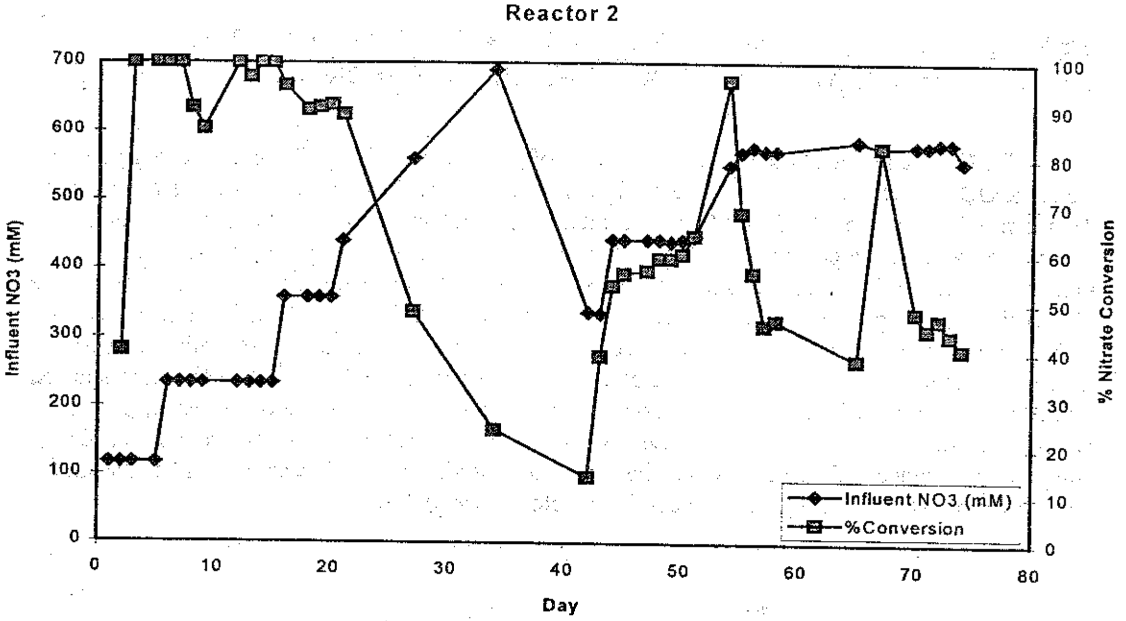

Figure 4. Percent Nitrate Conversion

Reactor 2 was then fed with a 30% TBA Bottoms influent and sludge from reactor 1 was added. On day 44 NO_2^- levels had decreased back to normal levels (2 -10 ppm) and percent NO_3^- conversion was about 50-60%. A carbon to Nitrogen ration of 3.42 and 5.23 mg TOC/mg NO_3-N was observed. Acid consumption rate was 1.59×10^{-4} and 1.48×10^{-4} moles H^+/mole NO_3 consumed.

Several more trials were performed to determine the actual TBA bottoms dilution rate which could support the denitrifying microorganisms. All the trials showed consistently that above a 30% dilution of the TBA Bottoms, inhibition begins to take effect. At 60% dilution denitrification is unstable and washout likely. When the microorganisms are thriving and denitrification is proceeding, nitrite concentration remains low, around 5-20 ppm. At the onset of inhibition, nitrite concentration increases beyond 100 ppm.

Two Reactor System

The results of the initial trials show an inhibitory effect on the denitrifying microorganisms. This effect has been seen as the TBA Bottoms concentration goes above a 30% dilution of the wastewater. The most likely reason for the inhibition is the high glycol concentration. The TBA Bottoms contains mono and di-ethylene glycols, by-products in the processing of ethylene oxide. The COD value of the TBA bottoms further reveals that glycol is the main carbon source in the wastewater, about 80% of the COD is due to the glycol. Analysis of the glycols by HPLC did not permit the differentiation between the mono and the di-ethylene species. Glycol concentrations are therefore reported as total glycol concentration. The concentration of the combined glycols in the TBA bottoms is 65 g/li. This same wastewater has a COD value of about 110,000 mg/li. The stoichiometry of the oxidation of the glycols are as follows:

ethylene glycol $C_2H_6O_2$ $2NO_3^- + HOCH_2CH_2OH \rightarrow N_2 + 2CO_2\ 2H_2O + 2OH^-$
diethylene glycol $C_4H_{10}O_3$ $4NO_3^- + HOCH_2CH_2OCH_2CH_2OH \rightarrow 2N_2 + 4CO_2 + 3H_2O + 4OH^-$

The COD equivalents of these two species of glycols are 1.29 gCOD/g ethylene glycol and 1.509 gCOD/g di-ethylene glycol. The COD equivalent of the TBA bottoms is therefore between 83 g/li to 98 g/li or about 75%-89% of the total COD content of the wastewater. Therefore the wastewater would have primarily glycols as their carbon source in the denitrification process. The inhibitory effect of the glycols is due to the increase in osmotic pressure in the mother liquor. The high colligative property of glycols tends to lower the water activity in the liquid and hence exerts a high osmotic pressure on the microbial cells. The inhibitory effect of osmotic pressure on microorganisms has been reported in literature such as the study of Park, et al. [4] which showed inhibition of cell growth in a molasses fermentation process. To overcome the effect of glycols, it is necessary to dilute the wastewater. Dilution with makeup water is a costly proposition for the company and hence a 2-reactor system has been proposed. In this 2-reactor system, an anoxic denitrification reactor is coupled to an aerobic reactor as shown below.

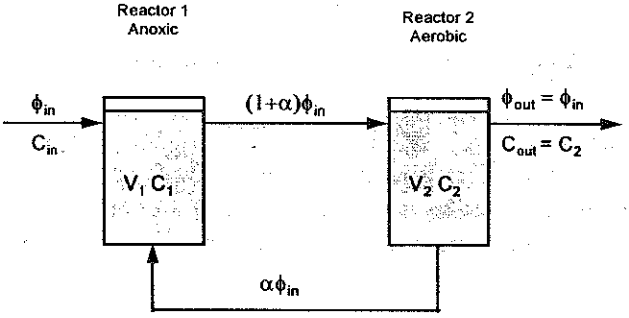

Figure 5. Two reactor system

With the aim of eliminating the need of using make-up water for dilution, an aerobic reactor has been added. The wastewater (TBA Bottoms) is introduced into the denitrification reactor at the rate of 300 ml/day. At the same time 700 ml/day is pumped out of the denitrifying reactor into the aerobic reactor where the glycols are oxidized and COD is reduced. The same volume is then pumped back into the denitrifying reactor to achieve dilution of the incoming glycol rich TBA Bottoms.

Glycols have been used as a carbon source for denitrification. Watanable, Okabe, Hirata and Matsuda, have reported that Ethylene Glycol was efficiently utilized as a carbon source for denitrification. [5] Various groups have shown that glycols primarily ethylene glycol is degradable [6} and follows a first order model [7} and exhibits Monod Kinetics [8].

Mathematical Model

Substrate, NO_3^- and Biomass Balances

Reactor 1

Substrate and NO_3^- Balance

$$V_1 \frac{dC}{dt} = C_{in} * \phi_{in} + C_{out} * \alpha * \phi_{in} - (1+\alpha)\phi_{in} * C_i - q_{s,anox} * C_i * V_1 = 0$$

$$\mu_{s,anox} = \mu_{\max,anox} * \frac{C_{x,1}}{k_i + C_{x,1}} * \frac{C_{NO3}}{k_{NO3} + C_{NO3}} * \frac{k}{C_{x,1} + k_i}$$

$$q_s = \mu_s / Y_{sx}$$

Biomass Balance

$$V_1 \frac{dC_x}{dt} = C_{x,out} * \alpha * \phi_{in} - (1+\alpha)\phi_{in} * C_{x,1} + \mu * C_{x,1} * V_1$$

Reactor 2

Substrate and NO_3^- Balance

$$V_2 \frac{dC}{dt} = (1+\alpha)\phi_{in} * C_1 - \phi_{out} * C_{out} - \alpha * \phi_{in} * C_{out} - q_{s,aer} * C_{out} * V_2 = 0$$

$$\mu_{s,aer} = \mu_{aerobic,\max} * \frac{C_{out}}{k_s + C_{out}} * \frac{C_{NO3,out}}{k_{NO3} + C_{NO3,out}} * \frac{k_i}{C_{out} + k_i}$$

Biomass Balance

$$V_2 \frac{C_x}{dt} = (1+\alpha) * \phi_{in} * C_{x,1} - \alpha * \phi_{in} * C_{x,out} - \phi_{out} * C_{x,out} + \mu * C_{x,2} * V_2$$

Steady State

The proposed two reactor system is to be run with undiluted influent (TBA Bottoms). An appropriate recirculation ratio α is to be employed to obtain an effective dilution of the incoming TBA Bottoms influent of not more than 30% or about 300 mM NO_3^-. At steady state the following parameters have been established (see Appendix 1):

$Y_{s/x,\ anoxic} = 0.26$ $Y_{N/x,\ anoxic} = 0.16$ $Y_{s/x,\ aerobic} = 0.16$ (yields are given in terms of COD)
$\mu_{anox,\ max} = 0.151$ hour^{-1}
$\mu_{aerobic,max} = 0.117$ hour^{-1}
$K_i = 20$ g/li (anoxic and aerobic)
$C_{NO3,\ in} = 44000$ ppm COD
$C_{s,in} = 110000$ ppm COD
$V_1 = V_2 = 2$ li

Seven unknown variables are to be solved through a system of six equations. The seven unknown variables are $C_{s,1}$, $C_{s,2}$, $C_{NO3,1}$, $C_{NO3,2}$, $C_{x,1}$, $C_{x,2}$, and α.

The following values were assumed

$K_s = 1000$ ppm $k_{NO3} = 1000$ ppm $\mu_{anox,\ max} = \mu_{aerobic,max} = 0.02$ hour

$Y_{s/x,\ aerobic} = Y_{s/x,\ anoxic} = 0.26$ $Y_{N/x,\ anoxic} = \dfrac{k_i}{C_{out} + k_i}$

The model allows us to predict the effluent COD and NO_3^- concentrations based on the recirculation ratio α and dilution ratio.

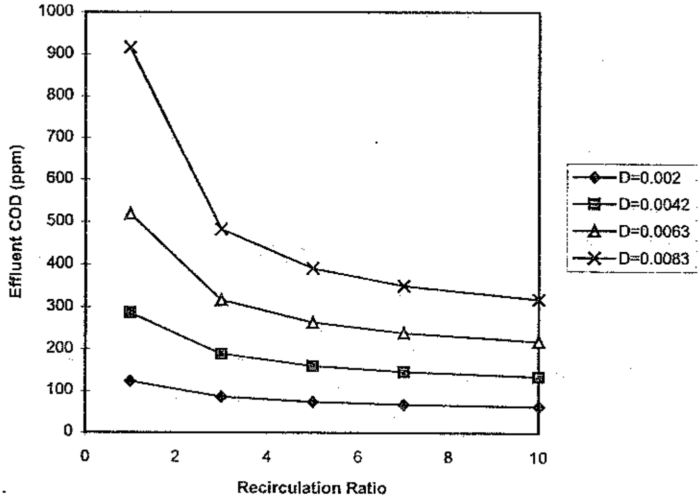

Figure 6. Effluent Substrate Concentration vs. Recirculation Ratio at Different Dilution Ratios

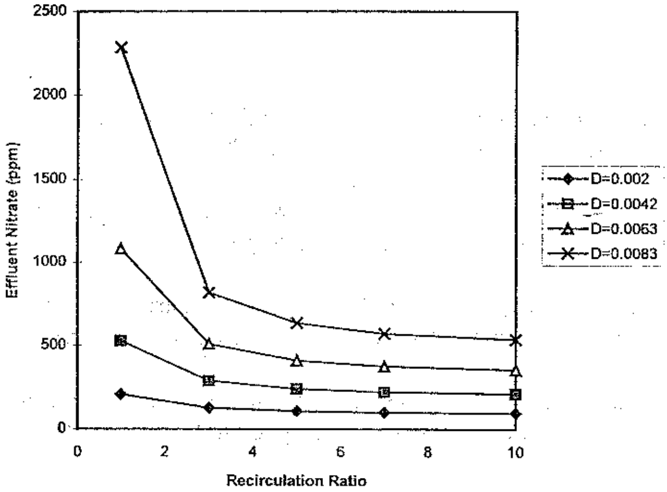

Figure 7. Effluent Nitrate Concentration vs. Recirculation Ratio at Different Dilution Ratios

V. Discussion

Comparison of Glycol consumption and COD consumption in the anoxic reactor of the batch experiment performed showed that the COD equivalent of mono-ethylene glycol consumed corresponded to 98% of the actual COD consumed. This shows that mono-ethylene glycol is the main carbon source in the system.

From the proposed model, a design chart relating effluent NO_3^- and effluent substrate concentrations with different recirculation ratios and dilution ratios. The charts show the results for dilution ratios between 0.002 to 0.0083. At recirculation ratios higher than 0.0083 the model predicts a washout solution for low recirculation rates. As expected, a higher dilution ratio gives a higher effluent concentration for NO_3^- and substrate. Appendix IV shows the design charts for a lower assumed Yield $Y_{s/x,\ anox} = 0.150$. At a lower yield, the model obtains more design curves for higher dilution ratios without washout. At these higher dilution ratios, low recirculation ratios (e.g. α=1 to 3) lead to a washout solution. The predicted effluent levels though are not much different from the higher Yield $Y_{s/x,\ anox} = 0.26$.

VI. Conclusion

The specific wastewater in this study contains very high levels of NO_3^- and glycols. In treating this wastewater both Monod and Inhibition kinetics are involved. To overcome the inhibition due to a component of the wastewater, the wastewater needs to be effectively diluted to about 30% of its original concentration. The proposed two reactor system achieves this required dilution without the need of make-up water. The model for this system shows that at higher dilution rates a without will occur. The design charts derived from the model may be used in designing reactor volumes based on desired effluent concentrations and recirculation ratios. More precise measurements of the kinetic parameters may be needed to further fine tune the model.

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Nomenclature

$C = C_{COD}$ COD concentration (ppm)
C_{NO3} NO_3 concentration (ppm)
C_x microorganism concentration (ppm)
$V_1 =$ Volume of Anoxic Reactor (li)
$V_2 =$ Volume of Aerobic Reactor (li)
$C_{in} =$ Concentration at inflow stream (ppm)
$C_{out} = C_2$ - Concentration at effluent stream (ppm)
$\phi_{in} = \phi_{out}$ - Volumetric Flowrate of incoming steam (li/hr)
α - recirculation ratio
μ_S = Specific reaction rate constant (hr^{-1})
$\mu_{anox, max}$ - Maximum reaction rate constant anoxic (hr^{-1})
$\mu_{aerobic, max}$ - Maximum reaction rate constant aerobic (hr^{-1})
K_S - Half reaction rate constant, substrate (ppm) = 0.1
K_i - Inhibition constant (ppm)
K_{NO3} - Half reaction rate NO_3^- (ppm) = 0.1
q_S - Observed Yield
$Y_{S/X}$ - Yield Coefficient