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NITRIFICATION OF AMMONICAL WASTEWATERS BY MIXED BACTERIAL CULTURES

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ABSTRACT

The paper deals with nitrification of ammonical nitrogen in synthetic wastewater and coke oven wastewater of Visakhapatnam steel plant. Synthetic wastewater was prepared and coke oven wastewater was collected from the MBC plant of Visakhapatnam steel plant. Nutrients and *Nitrosomonas* and *Nitrobacter* cultures were added to both the wastewaters before the nitrification process. A bench scale experimental set-up was fabricated for the biological nitrification of ammonical wastewater. The experiments were conducted at different flow rates, solid retention and hydraulic residence times. For all the experimental runs MLSS and MLVSS of the nitrification tank were determined. The influent and effluent concentrations of ammonical nitrogen, alkalinity and COD were also determined. The kinetic and decay coefficients of the nitrifying and the heterotrophic bacteria were calculated.

INTRODUCTION

Coal is the main solid fuel being used as energy source and also as a raw material for the production of coke in steel plant, Visakhapatnam. Coke oven gas, generated in the coke making process is cooled for removal of tar, scrubbed for removal of volatile organics and ammonia, and further processed to remove coal chemicals such as benzol fractions, before it is used as fuel gas. Waste water generated from this process is called gas liquor or waste ammonical liquor (WAL). Waste water generating from cooling and scrubbing of coke oven gas is laden with phenol, ammonia, cyanide and thiocyanate. Since these pollutants are toxic to aquatic life, lower the dissolved oxygen, and increase the suspended particulate matter, they should be removed before discharging the waste into environment.

The major contaminants in the coke plant wastes can be divided into two categories namely carbonaceous and nitrogenous compounds. The carbonaceous constituents of major concern are phenols and major nitrogenous constituent is ammonia. The methods used for phenol recovery are distillation, absorption and extraction with solvents such as benzol, butylacetate and methyl isobutylketone, etc. However, these extraction methods are not effective in removing the last traces of the toxicants and are also costly to set-up and to operate. Ammonia compounds in ammonical liquor are recovered as ammonium sulphate by bubbling the gas through dilute sulphuric acid solution in a saturator; the same is also being followed in Visakhapatnam steel plant.

Biological treatment of waste water is recognized as the cheapest method than physico-chemical methods. In biological treatment, destruction of complex chemical compounds is done by the action of microorganisms. In Visakhapatnam, steel plant, waste water treatment unit is referred as mechanical, biological and chemical or MBC plant. In this plant the total ammonia concentration in the treated effluent was higher than the desired level as shown in Table 1. Keeping this problem in view, treatability studies for biological nitrification (Siddiqui 1971) of waste water were undertaken.

MATERIALS AND METHODS

Experimental set up: Biological oxidation unit (Gupta 1983) consists of continuous flow reactor with cellular recycle. The reactor was made of transparent Perspex sheet, the vessel was cubical and has a total capacity of 30 L. A rectangular slit at the side of the reactor formed an outlet for the treated waste. Aquarium pumps provided air to the unit. The air was evenly dispersed by use of four sintered glass diffusers located at base of the aeration chamber. This gave a satisfactory biological floc mixing. The overflow from the oxidation unit was sent to an improvised conical glass vessel of 5 L capacity from where part of the settled solids were re-circulated back into the oxidation unit via a T-joint by means of an air lift mechanism. With this arrangement the recirculation of the settled sludge as well as the sludge wasting could be controlled. The influent flow was controlled with a valve of the storage tank kept at a height of 30cm above the reactor. Temperature fluctuations in the biological reactor were in the range 32 to 35ºC and pH varied from 7.4 to 9.4. The layout of the experimental setup is shown in Fig. 1.

Table 1: MBC plant effluent quality and its comparison with ISI standards for discharging effluent into ocean.

Parameter	Norm	From MBC plant
pH	6-8.5	7.9
COD	250	300
Phenol	1	<1
Free Ammonia	1.5	100
Fixed Ammonia	-	500
Thiocyanate	1	10
Cyanides	0.2	1.5-3.5
Oil and grease	10	25
Temperature, ºC	< 40	35

All the quantities are in ppm except temperature and pH.

Table 2: Composition of synthetic media.

Ingredient	Concentration
Ammonium chloride, ppm	700
Phenol, ppm	1
KH_2PO_4, ppm	375
$Na_2HPO_4.2H_2O$, ppm	375
Thiocyanate, ppm	40
Distilled water, L	1

Experiments with synthetic wastewater: Synthetic wastewater (Luthy et al. 1980) of known composition as shown in Table 2 was prepared. To this synthetic wastewater, nutrients of known composition (Monod 1949) as shown in Table 3 and *Nitrosomonas* and *Nitrobacter* culture were added . This feed was fed to the biological oxidation unit of the nitrification tank. SRT was selected on the basis of literature and laboratory experimentation. The experiment in the laboratory gave an SRT of 17.3 days for a sludge wasting rate of about 6 percent per day. This value gave an idea for choosing a range of appropriate SRT to perform oxidation studies. It is known that nitrification process controls the required HRT, therefore, HRTs were chosen on the basis of nitrifier growth constants. At different HRTs the liquid from the bioreactor was led into the sludge settler for settling the biomass. The average value of influent COD ranged from 1530-2610 mg/L, and value of TKN from 590-700 mg/L. For four different HRTs the influent and effluent concentrations of ammonical nitrogen, alkalinity and COD were determined. At different flow rates, MLSS and MLVSS of the reactor were also determined.

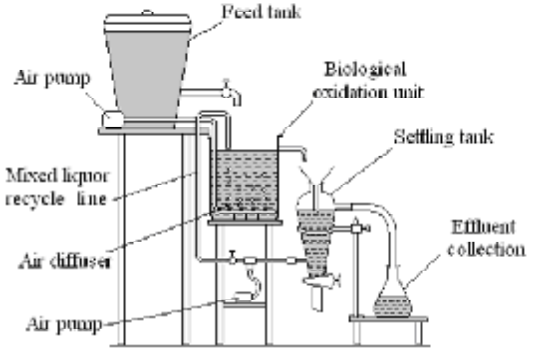

Fig. 1 : Experimental set-up used for Biological oxidation studies.

Experiments with coke oven wastewater with nutrient addition: Coke oven wastewater from the MBC plant was collected and to this nutrients and *Nitrosomonas* and *Nitrobacter* cultures were added. The feed water from the feed tank was then pumped into the bioreactor. The value of influent COD ranged from 1600-2100 mg/L. The value of TKN ranged from 590-730 mg/L. For four different HRTs the influent and effluent concentrations of ammonical nitrogen, alkalinity and COD were determined. At different flow rates MLSS and MLVSS of the reactor were also determined.

Table 3: Composition of nutrient media.

Ingredient	Quantity
NH_4Cl	0.8
$MgSO_4.7H_2O$	0.2
K_2HPO_4	0.016
$CaCl_2.2H_2O$	0.02
Chelated iron	0.001
$MnCl_2.4H_2O$	0.002
$Na_2Mo_4.2H_2O$	0.0001
$ZnSO_4.7H_2O$	0.0001
$CuSO_4.5H_2O$	0.00002
$CaCoCl_2.6H_2O$	0.000002
Distilled water, L	1.0

All the quantities are in ppm except distilled water.

Modelling: The data obtained in the above experiments were fitted into the Monod kinetic model (Lawrence et al. 1970) to evaluate the kinetic coefficients. The detailed model is given as below:

The kinetic model used in the study was based on substrate and cell mass balances, and growth rates of microorganisms. Based on the Monod model of population dynamics, the rate of growth of microorganisms and concentration of rate limiting substrate can be related as:

$$m = \frac{m_{\max} S}{K_S + S} \quad . \qquad ..(1)$$

The specific growth rate for heterotrophic microorganisms in the mixed culture can be related to solid retention time and substrate removal rate as:

$$m_b = \frac{1}{q_C} = g_b q_b - k_d \qquad ...(2)$$

The substrate (COD) removal rate can be expressed as:

$$q_b = \frac{(S_0 - S)}{X_b q} \qquad ...(3)$$

Similarly the specific growth rate for nitrifying bacteria can be related to solid retention time and ammonium nitrogen removal rate as:

$$m_N = \frac{1}{q_C} = g_N q_N - K_{dn} \qquad ...(4)$$

where ammonium nitrogen removal rate can be related as:

$$q_N = \frac{N_0 - N}{X_N q} \qquad ...(5)$$

The nitrifiers are only a fraction of the total biomass present in the system. The unit nitrification rates can be defined as:

$$r_N = q_N f \qquad ...(6)$$

Table 4: Results of nitrification studies with synthetic water.

Operating Data		Experimental runs			
		I	II	III	IV
Flow in L/day		9.96	7.65	6.02	5.77
MLSS, ppm		2235	2410	3150	4200
MLVSS, ppm		1630	1830	2390	3270
Solid Retention Time, days		17.3	25.0	29.8	40.3
Hydraulic Residence Time, days		3.012	3.92	4.98	5.19
Alkalinity, ppm	Influent	2880	2650	3000	2900
	Effluent	400	330	390	250
COD removal rate, per day, ppm		0.399	0.2980	0.2550	0.2063
COD, ppm	Influent	1530	1600	2450	2610
	Effluent	106	94	70	58
Ammonical nitrogen removal rate, ppm		0.4137	0.2596	0.1976	0.1300
Ammonical Nitrogen, ppm	Influent	673	590	695	630
	Effluent	118	82	43	27

Table 5: Results of nitrification studies with coke oven wastewater.

Operating Data		Experimental runs			
		I	II	III	IV
Flow in L/day		10	8.0	6.0	5.7
MLSS, ppm		2335	2510	3250	4300
MLVSS, ppm		1730	1990	2450	3350
Solid Retention Time, days		17.3	25.0	29.8	40.3
Hydraulic Residence Time, days		3.0	3.75	5.0	5.263
Alkalinity, ppm	Influent	2600	2700	2750	3100
	Effluent	345	350	340	325
COD removal rate, per day, mg/L		0.4800	0.3650	0.2520	0.1985
COD, ppm	Influent	1600	2450	2610	2750
	Effluent	94	70	58	30
Ammonical nitrogen removal rate, ppm		0.4309	0.2850	0.1500	0.1253
Ammonical Nitrogen, ppm	Influent	730	590	685	630
	Effluent	120	82	43	27

The fraction of nitrifiers in the system at equilibrium can be calculated by:

$$f = \frac{1}{\frac{S_0 g_b}{N_0 g_N} + 1} \qquad ...(7)$$

Rate of substrate utilization (organic matter) can be obtained by:

$$r_{su} = \frac{kX_b S}{K_S + S} = -\frac{S_0 - S}{q} \qquad ...(8)$$

The linearized form of equation (8), obtained by taking its inverse, is

$$\frac{X_b q}{S_0 - S} = \frac{K_S}{kS} + \frac{1}{k} \qquad ...(9)$$

A similar equation can be obtained, when ammonium nitrogen is considered as substrate

$$\frac{X_N q}{(N_0 - N)} = \frac{K_N}{k_n N} + \frac{1}{k_n} \quad ...(10)$$

The mean hydraulic retention time θ, in days is V/Q.

The cell wasting rate from recycle line, Q_w, in L/day

$$Q_W = V_X / \theta_C X_r \quad ...(12)$$

The concentration of nitrifiers can be calculated by:

$$X_n = f \times MLVSS \quad ...(13)$$

The concentration of heterotrophs can be calculated by:

$$X_n = MLVSS - X_b \quad ...(14)$$

The type of kinetic model reviewed has been used successfully by various researchers for designing activated sludge units for substrate removal. The steady state in the biological reactor was ascertained on the basis of SRT rather than HRT.

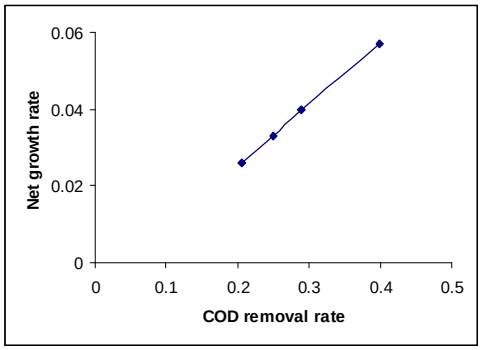

Fig. 2: COD removal rate Vs. net growth rate.

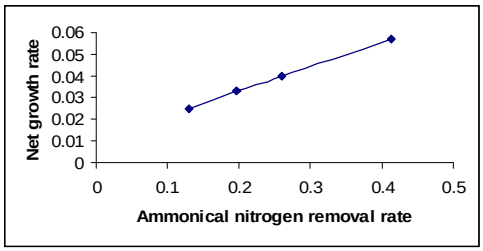

Fig. 3: Net growth rate Vs. ammonical nitrogen removal rate

RESULTS AND DISCUSSION

The results obtained with synthetic wastewater and coke oven wastewater are given in Tables 4 and 5. For synthetic wastewater, the COD removal efficiency increased from 84 to 88% and the TKN efficiency increased from 84 to 95% with decrease in ammonical nitrogen removal rates from 0.4137 to 0.1300 per day. Net growth rate was calculated for all SRTs and was plotted against COD removal rate for the heterotrophic bacteria as shown in Fig. 2, where the slope gives the yield coefficient, $\gamma_b = 0.18$ and the intercept, gives the decay coefficient, $K_d = 0.01$. Similarly for nitrifying bacteria the net growth rate was plotted against ammonical nitrogen removal rate (Fig. 3); the slope gives the yield coefficient, $\gamma_N = 0.12$ and the intercept, gives the decay coefficient, $K_d = 0.01$. For coke oven wastewater, the COD removal efficiency increased from 79.6 to 84.3% and the TKN efficiency from 93 to 99% with decrease in ammonical nitrogen removal rates from 0.4309 to 0.1253 per day. Net growth rate was calculated for all SRTs and was plotted against COD removal rate for the heterotrophic bacteria, (Fig. 4); the slope gives the yield coefficient ,$\gamma_b = 0.093$ and the intercept, gives the decay coefficient, $K_d = 0.008$. Similarly for nitrifying bacteria, the net growth rate was plotted against ammonical nitrogen removal rate (Fig. 5); the slope gives the yield coefficient, $\gamma_N = 0.136$ and the intercept, gives the decay coefficient, $K_d = 0.008$.

Both γ_N and γ_b values obtained were lower than those reported in literature. While γ_N values showed smaller decrease than the γ_b values indicating distinct departure from those found in literature. This indicates that the method adopted is more efficient than that being practised under the MBC plant operation.

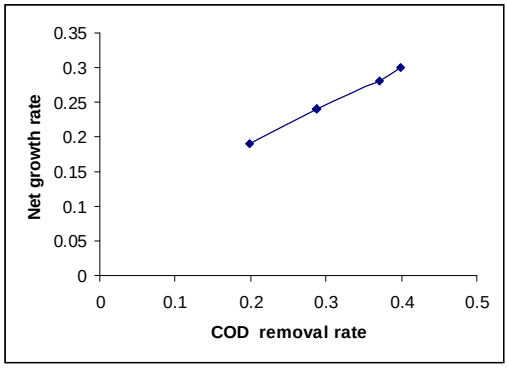

Fig. 4: COD removal rate Vs. net growth rate.

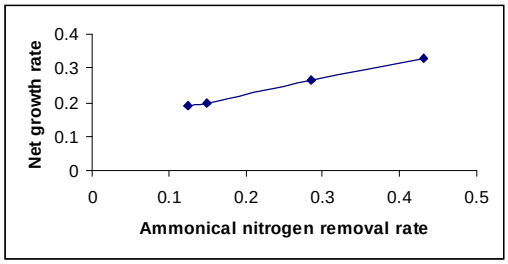

Fig. 5: Ammonical nitrogen removal rate Vs. net growth rate.

NOMENCLATURE

μ	Specific growth rate
μ_{max}	Maximum specific growth rate
S	Substrate concentration
K_S	Half saturation constant for organic matter (COD)
μ_b	Specific growth rate for heterotrophic bacteria
θ_C	Solid retention time
γ_b	Yield coefficient for heterotrophic bacteria
q_b	COD removal rate
K_d	Decay coefficient for heterotrophic bacteria
S_0	Initial substrate concentration
X_b	Concentration of heterotrophic bacteria
θ	Hydraulic residence time
μ_N	Specific growth rate for nitrifying bacteria
γ_N	Yield coefficient for nitrifying bacteria
q_N	Ammonium nitrogen removal rate
K_{dn}	Decay coefficient for nitrifying bacteria
N_o	Influent TKN concentration
N	Effluent TKN concentration
X_N	Concentration of nitrifying bacteria
r_N	Nitrification rate
f	Nitrifier fraction of the mixed liquor solids
r_{su}	Substrate utilization rate

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