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Denitrification of Wastewater Using Sludge and Methanol as a Carbon Source

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Abstract:

External carbon sources can enhance denitrification rates and thus improve nitrogen removal in wastewater treatment plants. When external carbon sources are added, no severe effect could be observed from an operational point of view. Denitrification is a process in which the oxidized nitrogen substances, i.e. nitrates and nitrites are reduced to nitrogen gas, such as N_2O and N_2, when a proton donor (energy source) is available. Nitrogen in groundwater results from human excreta, ground garbage and industrial effluents, particularly from food processing plants. The addition of external carbon source helps in increasing denitrification rates and enhances the nitrogen removal. In most biological denitrification systems, the nitrate polluted wastewater (e.g. domestic sewage) contains sufficient carbon source to provide the energy source for the conversion of nitrate to nitrogen gas by the denitrifying bacteria. The groundwater, in which the nitrate contents may be as high as 100 mg/L with low dissolved carbon content, an additional proton acceptor is required. This project work discusses the successful implementation of methanol as carbon sources for Wastewater Treatment Facility utilizing upflow deep bed continuous filter. This work will describe the methodology employed to implement methanol carbon sources, the modifications required to utilize methanol carbon sources in deep bed filter technologies.

Keywords: Carbon, Denitrification, Effluent Treatment Plant, Sludge Wastewater

1.0 Introduction

Our day to day activities are totally depends on the various manufactured items e.g. we use clothing which is the output of textile industries. Fertilizers are required in big quantity are the product of fertilizer industries. Like this we are depend on the different type of industries like textiles, mineral processing, fertilizers, metal finishing. As this type of industries provides the output which fulfill our requirement simultaneous they also generate the unwanted material which is in the form of wastewater, smoke, noise etc.(Choudary*et.al,*2014.) Different types of industries are responsible for different type of pollutions. Industries such as textiles, mineral processing, fertilizers, metal finishing are more contributing industries in wastewater generation and contributing in the water pollution. Wastewaters discharged by several industrial activities, such as synthetic fibers, mineral processing, fertilizers, metal finishing, and ammunitions and explosives industries, have an high-salinity content and are characterized by a very high concentration of nitrates (more than 3 g/L). Leaching of the nitrogen leads to eutrophication of the surface water and the contamination of drinking water. Increasing biological production in the surface waters consumes dissolved oxygen Algae present in the waters with excess nitrates (mainly leached nitrogen and phosphorus form soil erosion) grow rapidly and consume most of the oxygen preventing development of other forms of life, e.g. fishes. In some cases eutrophication can lead to the total extinction of life in the waters and can make surface waters unusable.

The treatment of these wastewaters generally deals in an anoxic biological process performed in activated sludge reactors (ASR). Due to the practical absence of an organic component, the treatment involves the addition of an external source of carbon, as electron donor for denitrification reactions. In addition, explosives industries

wastewaters are characterized by low pH (2-3), since nitrates are generally discharged as nitric acid, and this induces a further difficulty in reactor operation, due to the extreme sensitivity of denitrifying biomass to pH conditions. Biological nitrification and denitrification have been applied to tertiary treatment of low-strength municipal wastewaters, with nitrogen concentrations typically <50 mgIL. Limited studies have shown the potential of these processes to treat nitrogen concentrations> 1,000 mg/L efficiently, particularly in the absence of significant amounts of biodegradable organic matter. Several industries activities produce large quantities of nitrates as by-product. Synthetic fibers, mineral processing, fertilizers, metal finishing, and ammunitions and explosives industries wastewaters are indeed highly concentrated in nitrates (Cyplik *et al.*, 2012), present in a concentration higher than 1 g/L and generally accompanied by large amounts of other inorganic ions (sulphates, chlorides, etc.) (McAdam *et al.*, 2009).The treatment of these wastewaters generally deals in an anoxic biological process performed in activated sludge reactors (ASR) (Shen *et al.,* 2009), though other technologies are currently under investigation as microwave-assisted degradation (Halasz *et al,.* 2010) and reductive transformation by pyrite and magnetite (Oh *et al.,* 2008). Due to the practical absence of organic compounds in the wastewaters, the treatment involves the addition of an external source of carbon as electron donor for denitrification reactions. In particular, explosives industries wastewaters are also characterized by low pH (2-3), since nitrates are generally discharged as nitric acid, and this induces a further difficulty in reactor operation, due to the extreme sensitivity of denitrifying biomass to pH conditions. It was in fact already shown that under strong acidic conditions denitrification of wastewaters with high concentration of nitrates can be severely inhibited (Eusebi *et al.,* 2009).

However, there is lack of information about the treatment of very high nitrate wastewaters (above 3 g/L), such as the explosives and ammunitions industries wastewaters, and, in particular, about the extent of nitrite accumulation and its dependence upon the type and amount of the carbon source. Considering above all it is essential to enhance the denitrification process, study the denitrification rates, kinetics etc. This study aims to determine and compare the denitrification rates, kinetics, and growth rates among acclimatized biomass with sewage + methanol and methanol as a carbon source for denitrification at laboratory-scale sequencing batch reactors (SBRs).

2.0 Materials and Methods:

Experiment was carried out on the effluent generated from Fertilizer industries. Effluent was collected from Mumbai base fertilizer industries.

2.1 Chemicals/Reagents

The chemical/reagents were used in the experimental work on quantification were invariably of Analytical Reagent (AR) grade. Methanol, were from Fisher Scientific. Standard solutions and reagents were prepared in distilled water from distillation unit.

2.2 Denitrifying Biomass and Sewage.

Denitrifying biomass is full-scale activated sludge which is tested for comparison between Methanol and Sewage. Full-Scale Activated Sewage Sludge was from the municipal Sewage WWTP with secondary clarification followed by denitrification sand filters and UV disinfection. The plant did not use any external carbon source, and the sludge samples were taken from the Aerobic zone. Methanol and Sewage as Carbon-source-specific and also denitrifying biomasses were acclimatized fully for over 2 months before the beginning of batch testing in laboratory-scale Sequencing Batch Reactor (SBR) with methanol and Sewage using the same Full-Scale Activated Sludge. Several models have been developed in the past to describe denitrification kinetic in both open and closed system (Wild *et al.,* 1995). The reduction pathway in biological denitrification systems involves a two step mechanism: in the first step nitrate reduction to nitrites occurs, through the reaction:

$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O$ (1)

while, in the second step, the above formed nitrites are reduced to molecular nitrogen, by the reaction:

$NO_2^- + 3e^- + 4H^+ \rightarrow 0.5\ N_2 + H_2O$ (2)

Both reactions require a carbon source as electron donor.(Sözen*et al.,* 1999)

2.3 Lab Scale Sequencing Batch Reactor:

The Sequencing Batch Reactor (SBR) system had an influent flow of 9 l/day and was operated with an SRT of 7 days and 3 daily cycles, which included a 1 hours anoxic phase, 30 minutes of feeding, and 4 hour aerobic period. The chemical oxygen demand (COD), ammonia (NH_4), nitrate (NO_3), and nitrite (NO_2) were examined on a weekly basis to monitor the general functioning of the system. Total and volatile suspended solids (TSS and VSS, respectively) were maintained at concentrations between 700 and 1100 mg/l. The temperature was in the range 20 to 23^{0}C, and the oxygen concentration during the aerobic phase was approximately 5 to 7 mg/L. The pH was kept in the optimal range of 6.5 to 7.5.In pilot scale study, Denitrification of wastewater using biomass with methanol and Methanol + sewage was carried out on pilot plant having dimension of 65m^3 area. Where different ratio of Methanol and sewage was added to observed the significant denitrification rate.

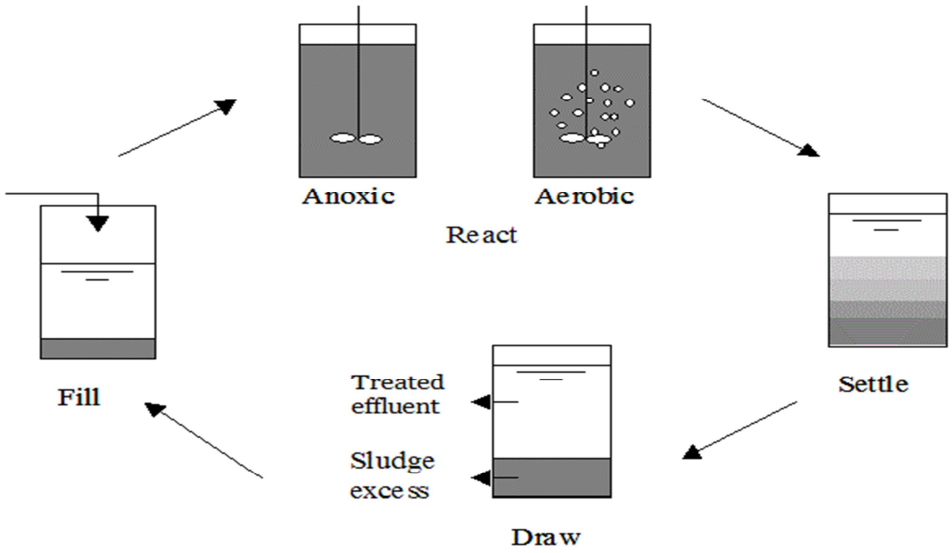

Fig.1: Lab Scale Sequencing Batch reactor

2.4 Analytical Measurements.

For the completion of the aimed object Nitrate, nitrite, ammonia, volatile and total suspended solids were analyzed according to Standard Methods of APHA. Dissolved oxygen meter was used to monitor the extent of aeration. pH and temperature were checked using a Thermo Orion 230 meter (Thermo Fisher scientific).Dichromate acid digestion was used to determine the total COD equivalent and duplicates of different dilution series were conducted to obtain statistically confident values. Total Carbon and Total Phosphate were also analyzed according to Standard Methods of APHA .

2.5 Denitrification Rates and Kinetics.

2.5.1 Denitrification Batch Tests

A series of denitrification batch tests was conducted to determine the denitrification rates and kinetics with biomass that was acclimated with sewage + methanol and with methanol. Denitrification rates were determined at various carbon concentrations (0 to 300 mg COD/L) and with an adequate initial nitrate concentration (20 to 40 mg/L)

The method proposed by Doldetal. (2005) was applied to estimate the maximum specific growth rates of each carbon-specific denitrifying culture and to estimate the carbon-to-nitrogen ratio (C/N) during denitrification. Kinetic parameters were determined by fitting the nitrate uptake rate versus time using the equation presented in using statistical software SPSS 14.0, as follows:

$$\mathrm{SNOx} = \mathrm{SNOx}, 0 - \frac{1 - YHD}{2.86} * \frac{\mu\mathrm{max.\,X0}}{YHD.\,(\mu\mathrm{max} - \mathrm{bH})} * (e(\mu\mathrm{max} - \mathrm{bH})\mathrm{t} - 1)$$

3.0 Results and Discussion:

Table 1: Physicochemical characteristics of wastewater

Parameter	Results(mg/l, except pH)
Total N	35.8 ± 3.2
Inorganic N	10 ± 1.2
Organic N	25.6 ±2.1
Total P	5.1± 0.12
Total C	242.5± 34.2
COD	453.7± 43.5
BOD	318± 20.53
pH	7.6± 1.3

± S.D. for five experimental observations

3.1 Physico-chemical characteristics of Wastewater at Source Unit:

Physico-chemical characteristics of wastewater at each processing ETP unit are provided by the laboratory authority of industry (table 1).

3.2 Lab scale Study of Wastewater after addition of Sewage + Methanol in SBR:

Addition of Methanol+ sewage with biomass to treat wastewater shows significant results. Lab scale study shows results as compared to initial results are given in table 2.

Table 2. Lab scale Study of Wastewater after addition of Sewage + Methanol in SBR results are expressed in mg/l

Addition of Methanol (48%) Liters/Day	Sewage Addition Started In DN-I Tank (M^3/Day)	pH	TSS	TDS	MLSS	MLVSS	Phosphate	Ammonical Nitrogen	Nitrate Nitrogen	Total Kjeldahl Nitrogen	COD
1200	**0**	**7.6**	**75**	**1850**	**2879**	**1800**	**4.2**	**25**	**5**	**30±2.1**	**199**
1100	75	7.6	80	1780	3370	1900	4.6	39	7	46**±0.5**	181
800	80	7.3	85	1700	4017	2100	4.1	40	7	47**±1.6**	175
750	78	7.3	70	1660	4713	2747	4.3	39	6	45**±1.4**	123
700	82	7.5	65	1539	4923	3393	4.2	38	5	43**±0.7**	125
AVG= 910	**63**	**7.5**	**75**	**1706**	**3980**	**2388**	**4.28**	36	6	42**±0.4**	**161**

± S.D for five experimental observations

3.3 Denitrification kinetic coefficients for different carbon sources

Table 3.Calculated denitrification kinetic coefficients for different carbon source are as follows

	K_{dmax}mgN/g VSS/h (25^0C)	K_S (mg COD/L)	COD/N (mg COD/mgN)	$Yield_{obs}$ (mgVSS/mgCOD)	μ_{max}
Sewage + Methanol	5.9 ± 3.2	15.2 ± 10.1	4.5 ± 1.2	0.36	0.4
Methanol	6.3 ± 0.5	38.5 ± 28.1	6.2 ±3.2	0.54	1.1

± S.D for five experimental observations

The denitrification rates were determined and compared at temperatures 25^0C. The maximum nitrate uptake rate shown in above table found for Sewage+Methanol (5.9 mgN/gVSS/h) is comparable with that obtained with methanol (6.3 mgN/gVSS/h), and therefore shows the feasibility of using Sewage+Methanol as an alternative external carbon source to methanol for denitrification. A wide range of values has been reported in literature for the observed specific denitrification rates for methanol, ranging from 3.3 mgN/gVSS/h to 21 mgN/gVSS/h .

4.0 Conclusion:

Our study results have led to the following conclusions:

The maximum specific denitrification rates obtained with Methanol were comparable with those obtained with methanol + sewage, indicating that Methanol can effectively support denitrification while methanol + sewage show slightly.

1) Comparison of denitrification rates obtained with Methanol + sewage -acclimated or non-acclimated biomass yielded similar rates, suggesting that the denitrifying microbial population capable of using Methanol + sewage is present in typical WWTPs; therefore, acclimatization to Methanol + sewage may not be needed.

2) The maximum growth rates (mmax) estimated for Methanol- acclimated culture was nearly two times greater than the one found for methanol + sewage at 20 and This implies that a longer anoxic SRT and larger post-denitrification reactor volume would be required using methanol + sewage than that using Methanol, to prevent the slow-growing populations from washing-out from the system, especially at colder temperatures.

3) Evaluation of the capability of a specific carbon-acclimated sludge to instantly use other carbon sources showed that Methanol sludge can readily use all the substrates tested, including methanol and methanol + sewage.

The results indicated that, with equivalent COD dosage, application of Methanol leads to slightly better performance than methanol + sewage , especially for the post-denitrification process and under lower temperature conditions. However, the results also showed that the difference in yield did not translate into a significant difference in sludge production.

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