Concentration reduction of ammonia in industrial oil residue of an oil refinery

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ABSTRACT

Water is one of the main natural resources, upon which the diversity of aquatic and terrestrial life depends, including mankind. Despite the industrial development and the urban area enlargement, aquatic environment is still the most available vehicle for soluble wastes. As a consequence, rivers, streams and the sea receive high organic and inorganic content waters from different sources. Ammonia is considered a pollutant substance in water, when in concentrations higher than 5mg/L. Since ammonia concentration in the studied refinery was beyond Brazilian environmental legislation limits, this study aimed its reduction in the refinery wastewater. The problem was studied in reactors of fixed and suspended biomass in order to reach the best nitrification performance. The results, expressed in percentage of ammonia removal, were considered satisfactory when the continued flux reactor system was applied, with the addition of bacterial inoculum. In the end, the ammonia concentration reduction observed was below the line established by the legislation in effect.

KEYWORDS: residue treatment, ammonia, nitrification, pollution, microorganisms.

INTRODUCTION

Water is a natural resource essential to life, to the economical development and to the social welfare. However, each day potable water is becoming scarce due to the high index of discharge of pollutants from urban, industrial and agricultural origin that are discharged in water. The availability of water, both quantitatively and qualitatively, to the human needs depend on policies for the protection and prevention of the natural hydric sources; the survival of all terrestrial and water organisms depends on water.

With the increase of the urban area and the industrial development the hydric sources, natural receptors for domestic wastewater and soluble industrial dejects, became more and more polluted. In this regard, presently, rivers that were supposed to be important source of water collection are no more than vehicles for transmission of diseases. It is necessary to improve the systems for treatment of wastewater making water free of pathogens and other substances harmful to life.

Special attention should be paid to the aqueous ecosystem since most of the substances released in the air and in the soil may affect it, in its original or modified form, leading to direct contamination of the water bodies (CAMPBELL, 1977). Among the problems for the treatment of wastewater there are those related to the organic and inorganic pollutants. The organic compounds derivate from oil are degraded generating biomass, gas and non-biodegradable molecules. The inorganic material, in its turn, may be deposited along the watercourses or, when dissolved, it can be absorbed by the biota.

The search for new technologies to the treatment of hydric effluents has become an issue of interest for industries since the agencies for environmental control are more proactive as the society request improvements in the quality of life. In Brazil and other countries there is an increasing concern from industries regarding the destination of their residues. Oil industries are building large areas for the treatment of solid residues close to their plants aiming to recover water.

Ammonia is one of the products resulting from purification of oil, which is under serious control by environment agencies due to its toxic potential. The maximum amount allowed is 5.0mg of NH_3/L of effluent (CONAMA, 1986) since ammonia, when dissolved in water, is harmful to animal and vegetal life, mainly to young forms (larves, spores and cysts) and sprouting seeds. The removal of ammonia follows a determined cycle of biochemical transformations know as “The Nitrogen Cycle”. In this cycle, microorganisms, mainly bacteria, take an active part in the conversion of N_2 into NH_3 (ammonification) and of NH_3 into N_2 (nitrification and later on, denitrification).

Many studies have been conducted to control the ammonia concentration into acceptable ambiental patterns and to diminish it in residual waters. The aim of this study is to present a condition to decrease the concentration of ammonia in the industrial effluent of an oil industry, measured through the microbial activity, taking into consideration the reduction of the pollu-

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tion of the Atibaia river (Rio Piracicaba basin - SP), through improvements in the quality of waste water by biological treatment of the effluent in systems of continuous flow reactors and immobilized cells in bioreactors.

MATERIAL AND METHODS

Samples were collected in plastic flasks from the industry's stabilization lagoon and transported to the Department of Biochemistry and Microbiology, UNESP-Rio Claro, SP.

The bacterial cultures used were isolated by Brito (1997) and it was also used bacterial cultures isolated from the refinery and preserved in Agar-nutrient (NA) maintained in the Department of Biochemistry and Microbiology, UNESP-Rio Claro, SP. The bacterial cultures were reactivated in a nutrient broth and associated among them forming a pool. To this mixture it was added 0.1% glucose, 0.1% yeast extract and 0.02% of potassium phosphate. Then, the mixture was incubated at 36°C for activation and growth of autochthones bacteria. During the experiment, the inoculum was reactivated every 12h, thus avoiding bacterial death due to shortage or lack of nutrient.

For the evaluation of the decrease of ammonia concentration it was used a system of four reactors made of PVC, each one with total volume of 3.8L, 3.9L, 4.0L and 4.0L respectively, totaling 15.7L (FIGURE 1). In the four reactors it was introduced 300g of expanded clay containing previously immobilized cells of the inoculum.

The experiment of continuous flow was conducted under pH of 6.0 during 192 hours at an average temperature of 30°C. The effluent of the stabilization lagoon was introduced in the first reactor by gravity in a flow out of circa 900mL/h. It was added to it the bacterial inoculum consisting of autochthones bacteria containing circa 10^8 cells quantified in CFU/mL (Colonies forming units) and cane sugar molasses at 8° Brix keeping the systems with air injection. The period of hydraulic retention was circa 17.4 hours, being this considered as ideal in regards to the amount of effluent produced by the refinery. Linked to the exit of the fourth reactor was a sampler collector flask where the dosage of ammonia and the measurements of the pH were done.

The number of bacteria, in CFU/ml, was checked daily, removing samples from the first reactor and from the exit of the system. Later, bacteria were suspended in a solution of NaCl 0.85% in decimal dilutions and evaluated by the pour plate technique. The concentration of dissolved oxygen (DO) was evaluated daily in the reactors by direct reading made with a DIGIMED-Model DM 4 oxymeter.

The quantification of ammonia was monitored by the potentiometric method using selective electrodes for ammonia (ORION – Model 95-12) according to Clesceri et al. (1989).

The period of hydraulic retention was 17.4 h, a period suggested by the studied refinery, which produces near 500m^3/hour of effluent continuously.

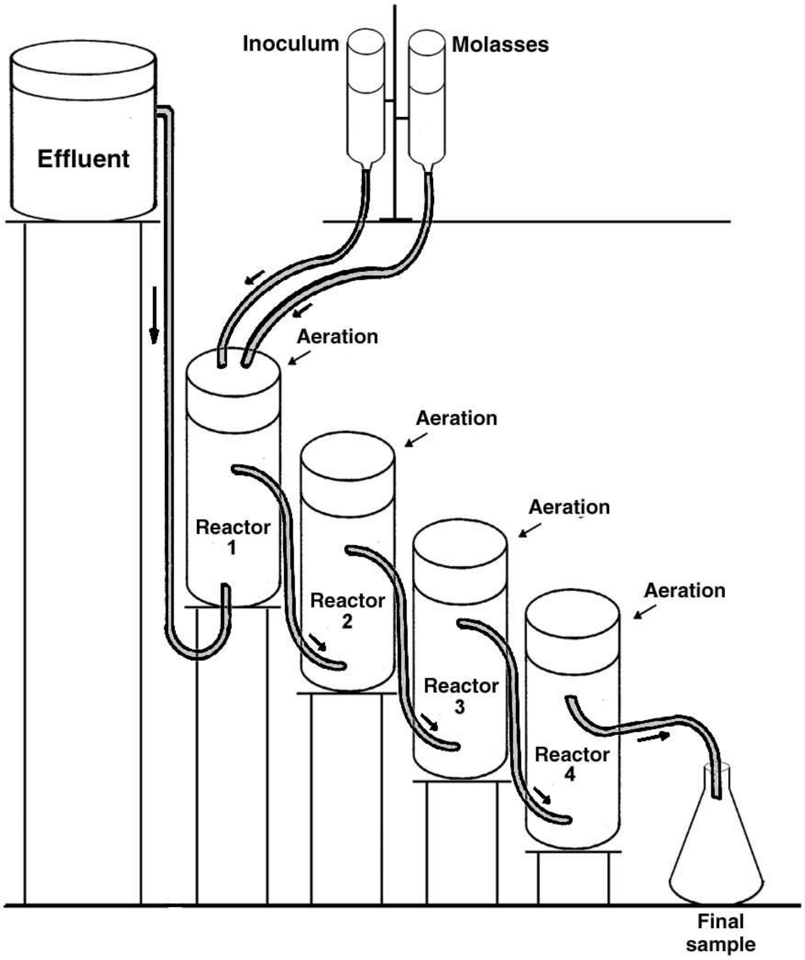

FIGURE 1: System of reactors for the continuous flow experiment, made of PVC, with a volume totaling 15.7L.

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RESULTS AND DISCUSSION

FIGURE 2 shows the average results in the decrease of ammonia concentration in an average temperature of 36°C with a pH of 6.0. Within the first 28 hours the decrease in ammonia concentration was at a 44% rate, obtaining 19.72mg of NH_3/L if compared to the initial concentration of ammonia (reservoir of effluent supplying the reactors) and 11.07 mg of NH_3/L to the final ammonia concentration (exit of the reactors, in the sampler collector flask). From this point on the decrease in concentration reached 4% and it was necessary to add cane-sugar molasses at 9° Brix in a outflow of 5.5 mL/h, introduced in the first reactor, as a source of carbon to activate the metabolism of bacteria.

After 48h it was obtained a 98% decrease in the concentration of ammonia (the final concentration was 0.35mg of NH_3/L). The decrease was significant considering the legal standard of the environmental con-

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trol agency – Resolution CONAMA N.º 20. Reducing the flow of cane-sugar molasses in the reactors, at the point of 100 h, the decrease in ammonia remained near 96% and maintained in low level for 24h. However, this level was not constant although it was kept below 50% until the end of the experiment (192h).

It is possible to see that the bacterial inoculum added to the first reactor was able to promote ammonia oxidization, decreasing its concentration after going through the system of continuous flow reactor. According to Madigan et al. (2000), nitrogen may be present in residual waters as nitrate, nitrite, ammonia our organic nitrogen. The inorganic nitric compounds more commonly used as electron donors are ammonia (NH_3) and nitrite (NO_2^-) when oxidized aerobically by nitrifying bacteria. These bacteria are extensively distributed in the soil and water. Initially, the *Nitrosomonas* oxidize ammonia into nitrite and later on the *Nitrobacter* oxidize the nitrite into nitrate while the denitrifying bacteria, under anaerobic conditions, are able to degrade the nitrate into gaseous nitrogen (HAMMER; HAMMER Jr., 1996). Most inorganic nitric compounds are electron receptors in the anaerobic respiration (MADIGAN et al. 2000).

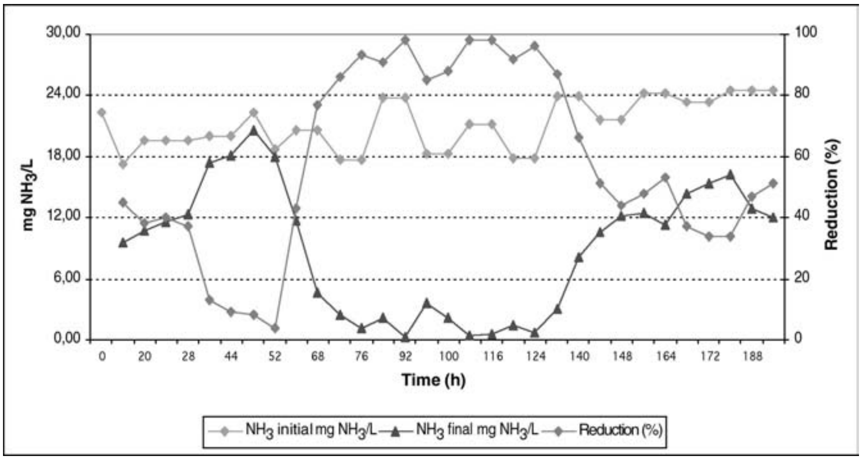

FIGURE 2: Decrease in concentration of NH_3 in the industrial effluent when submitted to continuous flow in a reactor system for a period of 165 hours with outflow of near 900mL/h.

TABLE 1 shows the results for the concentration of dissolved oxygen (DO). It is possible to observe that in the period with greater decrease in the concentration of ammonia in the industrial effluent the reading for DO was zero indicating an intense bacterial activity. Nitrification is a strictly aerobic process that depends on the condition of the oxygen in the environment and has a significant effect in the speed in the growth rate of nitrifying bacteria (aerobias).

TABLE 1: Concentration of diluted oxygen in the four rectors in the experiment of continuous flow during 192 hours at 30ºC.

Time (hours)	mg O_2/L			
	Reactor 1	Reactor 2	Reactor 3	Reactor 4
24	8.5	8.9	9.8	9.9
48	8.2	9.8	9.8	9.9
72	0.0	0.0	6.4	7.0
96	0.0	0.0	0.0	0.0
120	0.0	3.0	2.7	4.0
144	3.0	9.2	6.6	4.7
168	0.0	7.6	7.3	7.2
192	0.0	4.4	7.8	8.0

Wezernaz e Gannon (1967) proposed a consumption of 4.33 g of O_2 per gram of oxidized nitrogen being 3.22g in the oxidization of the ammoniacal nitrogen and 1.11g in the oxidation of nitrite. In 1975 the Environmental Protection Agency proposed the consumption of 4.20g of O_2/g of oxidized nitrogen. Recent studies suggest that the concentration of DO in the liquid should be maintained at 70% of the saturation concentration. According to Santiago (1994) the concentration of DO needed for nitrification ranges from 0.5 to 2.5mg/L both in suspended biomass or fixed biomass systems in condition of stationary state, depending on the period of cell residence. In cases of low concentration of O_2 it may be necessary a high period of cell residence to achieve a complete nitrification. Both autotrophyc and heterotrophyc bacteria are able to promote the oxidization of the ammoniacal nitrogen. The classification as autotrophyc bacteria is due to the fact that these organisms obtain energy for growth from the oxidization of the inorganic nitrogen. Another important feature is that these bacteria use CO_2 and not organic carbon, as most other do.

TABLE 2 shows the result of the bacterial counting in CFU/mL in the samples collected daily from reactor 1 and in the exit system during the experiment.

According to TABLE 2 there was an increase in the number of bacteria in the reactor 1 just after the addition of molasses (48h) when it was formed a biofilm in the inner part of the reactors (bacterial colonization of the expanded clay). The formation of the biofilm in the reactors indicates also the fixation of microorganisms in a substract, which depend also on the microorganism, on the environmental condition and on the substrate itself where they will adhere to (VILLAVERDE et al., 2000).

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TABLE 2: Quantification of the Colony Formation Units/ml (CFU/mL) from samples of the continuous flow experiment during 192 hours at average temperature of 30ºC.

Period (Hours)	CFU/mL		
	Inoculum (10^8)	Reactor (10^6)	Exit of the system (10^6)
0	4.50	0.20	-
24	3.12	2.19	0.14
48	3.40	1.85	0.50
72	2.67	2.85	9.61
96	3.27	42.90	5.80
120	3.17	23.40	68.10
144	3.55	2.69	5.85
168	3.58	0.19	0.19
192	2.40	1.18	0.76

CONCLUSIONS

The results from this study may lead to the following conclusions:

- The system of bioreactors used favors the decrease in the concentration of ammonia;
- Molasses is an important source of carbon. Also it is easily incorporated and the amount required is minimal;
- The decrease in the concentration of ammonia in the effluent is associated to various factors: source of carbon, pH, dissolved oxygen, temperature, characteristic and number of microorganisms, being the later fundamental since it may vary according to the collection;
- The effluent has organic carbon, however it is not available to bacteria and thus it does no allow the occurrence of metabolism needed to remove the nitrogen.

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