Utilization of NO_x from Combustion Gases by Biological Processes. A Preliminary Study

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Abstract

A biological system for the removal of NO_x from flue gas was investigated using the cyanobacterium Spirulina platensis. The experiments have been carried out in a labscale plant, consisting of an illuminated Erlenmeyer flask in which a mixture of NO_x and air has been introduced from the bottom; the NO_x excess going out from the plant was entrapped in an absorber, located at the top of the reactor. Under different conditions of gas feeding, namely continuous or fedbatch pulsefeeding, the NO_x removal efficiency was always >92% and scarcely influenced by the inoculum level (0.5- 1.0 g l^{-1}).

Introduction

In the last decades several scientists performed studies about the removal of some gaseous pollutants in the atmosphere, among which nitrogen oxides assume a particular relevance due to their high environmental impact. The primary sources of NO_x (including nitrogen monoxide and dioxide) are the anthropogenic activities: transportation sources (e.g. onroad and offroad motor vehicles and engines, rail), fossilfuelled electric power plants, upstream oil and gas industry (e.g. natural gas plants, oil sands). The natural production of nitrogen oxides occurs by oxidation processes under very hot conditions; for example in the hot part of vegetation fires or oxidation of the molecular nitrogen in lightning or volcano eruptions [1].
The NO_x are generated by direct reaction between oxygen and nitrogen of the air at the combustion temperature (> 1200 °C). Nitrogen dioxide is a reddish brown, highly reactive gas that is formed in the atmosphere by the quick oxidation of NO, which is the major constituent of flue gas (more than 90%). NO_2 dissolves in water vapour to form acids, and interacts with other gases and particles in the atmosphere forming nitrates and other products harmful to the human and animal health and to the environment. It reacts with sunlight and unburned gasoline in a matter of hours to days to produce "photochemical smog" and also can produce nitric acid, which is very soluble and contributes significantly to acid rain.
NO_x is very toxic to humans and animals causing adverse respiratory effects; in particular, NO may induce pulmonary damage [2]. In fact, NO is the most toxic nitrogen oxide, reacting with various biomolecules, directly or via the formation of free radicals.
The chemical processes commonly used for NO_x removal employ ammonia or urea that reduce oxides to inert gaseous nitrogen and water vapour: they are well known as the Selective NonCatalytic Reduction (SNCR) [3] and the Selective Catalytic Reduction (SCR) [4]. SCR is similar to SNCR but the difference between them is the presence in SCR systems of a catalyst, which accelerates the chemical reactions. The catalyst is needed because SCR systems operate at much lower temperatures than SNCR, and the most commonly used catalysts are vanadium/titanium formulation (V_2O_5 stabilized in a TiO_2 base) [5] and zeolite materials. However, the SCR causes problems of poisoning and overloading of the catalyst. The SNCR technology operates at suitably high temperature (about 800-1000 °C) with efficiency of 50-65%, while SCR operates at 300-450 °C with efficiency of 75-90%.
Several authors have studied the possibility to remove NO_x by biological methods [6-9], employing green algae that are able to use nitrate as a nitrogen source: the cells reduce nitrate to nitrite by nitrate reductase, then the nitrite is reduced to ammonium by nitrite reductase, and finally the resulting ammonium is metabolized by the cell [10]. Yoshihara et al. [6] studied the simultaneous elimination of NO and CO_2 from flue gas by means of a marine microalga, strain NOA113, using a long tubular photobioreactor. Nagase et al [7].
investigated the biological removal of NO_x from fuel flue gas using the unicellular microalga *Dunaliella tertiolecta*, and examined the way to improve NO removal by increasing the dissolution of NO in the aqueous phase [8,9].
This study aims at removing the NO_x from the flue gas in a labscale plant, consisting of an illuminated reactor employing a culture of *Spirulina platensis*. Batch experiments were carried out at two inoculum levels (0.5 and 1.0 g l^{-1}), under different feeding conditions in the Schlösser medium [11], where sodium nitrate was replaced by nitrogen oxides from the flue gas as the only nitrogen source.

Materials and methods

Microorganism

The culture of the cyanobacterium *Spirulina platensis* (LB2340) was obtained from the Culture Collection of the University of Texas. Cells were maintained in the medium of Schlösser [11], whose composition was as follows (per liter): 13.61 g $NaHCO_3$, 4.03 g Na_2CO_3, 0.50 g K_2HPO_4, 2.50 g $NaNO_3$, 1.00 g K_2SO_4, 1.00 g NaCl, 0.20 g $MgSO_4 \cdot 7H_2O$, 0.04 g $CaCl_2 \cdot 2H_2O$, pH 9.6. All the nutrients were dissolved in distilled water containing (per liter): 6.0 ml of metal solution (0.750 g Na_2EDTA, 97.0 mg $FeCl_3 \cdot 6H_2O$, 41.0 mg $MnCl_2 \cdot 4H_2O$, 5.0 mg $ZnCl_2$, 2.0 mg $CoCl_2 \cdot 6H_2O$, 4.0 mg $Na_2MoO_4 \cdot 2H_2O$), 1.0 ml of micronutrient solution (50.0 mg Na_2EDTA, 618 mg H_3BO_3, 19.6 mg $CuSO_4 \cdot 5H_2O$, 44.0 mg $ZnSO_4 \cdot 7H_2O$, 20.0 mg $CoCl_2 \cdot 6H_2O$, 12.6 mg $MnCl_2 \cdot 4H_2O$, 12.6 mg $Na_2MoO_4 \cdot 2H_2O$) and 1.0 ml of a 150 $\mu g\ l^{-1}$ B_{12} vitamin solution.
A suspension collected at the exponential growth phase was harvested, filtered, washed with 0.9% NaCl solution, and used to inoculate the photobioreactor.

Photobioreactor

The experiments were carried out in a labscale plant consisting of a 3.0 l-Erlenmeyer flask, with 1.5 l-working volume (Fig. 1). The reactor was illuminated by two fluorescent lamps (2x36 W), located at about 20 cm from the reactor surface, assuring a light intensity of 90 µmol photons $m^{-2}\ s^{-1}$.
The reactor was fed with Schlösser medium without sodium nitrate, which was replaced by nitrogen oxides from the flue gas.
The residual NO_x leaving the plant was transferred to an absorber, located at the top, containing 100 ml of $KMnO_4$ alkaline solution. Periodic distilled water additions in the reactor avoided the volume loss due to evaporation and air stripping.

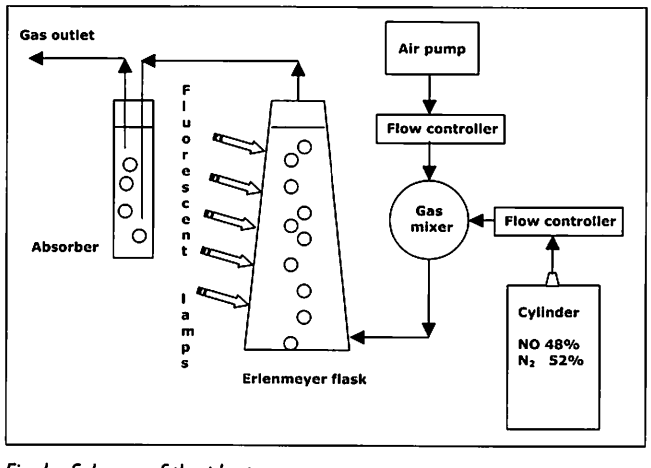


Fig. 1 - Scheme of the plant.

Four runs were carried out at room temperature (about 25 °C) at 0.5 and 1 g l^{-1} inoculum concentration, either insufflating air (20 Nl h^{-1}) or not. Daily, the air stream was mixed with gaseous NO coming from a cylinder containing 48% NO (v/v) and 52% inert N_2 (v/v).
Blank tests were performed to investigate the behaviour of nitrogen oxides in the matrix.

Analytical procedures

Cell concentration was determined by dry weight, after filtration through Millipore filters (0.45µm pore diameter) and washing with 3.0 N acetic acid solution to eliminate precipitates. The filter was dried at 80 °C overnight until constant weight. In the medium, nitrite and nitrate were determined by the sodium salicylate colorimetric method and the Griess reactive method [12], respectively. Nitrogen entrapped in the absorber was determined as nitrite and nitrate by means of ionic chromatograph (Metrohm CI MSM compact 761) [13].

Results

Blank test, performed to evaluate the behaviour of NO_x in the system, showed that the nitrogen stripping in the atmosphere due to air insufflation was negligible (less than 8% with respect to the inlet one) and the nitrogen insufflated into the reactor was almost completely oxidized to nitrite and/or nitrate. In fact, by comparison between the amount of insufflated nitrogen (79.9 mg_N) and that present in the reactor as nitrate and nitrite (data not shown), it has been calculated that almost all the fed nitrogen was oxidized, being the dissolved amounts of NO_2^- and NO_3^- in the ranges 39-54 and 22-33 mg_N, respectively. This result is in agreement with those of Komiyama and Inoue [14], who found that the most important reactions between gaseous nitrogen oxides in the presence of water (at atmospheric pressure and temperature) lead only to nitrate and nitrite and that the equilibrium/absorption under alkaline conditions (like in the Schlösser medium) is completely shifted to right (reactions c and d):

- $2NO_2 \longrightarrow N_2O_4$ (a)
- $NO + NO_2 \longrightarrow N_2O_3$ (b)
- $N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$ (c)
- $N_2O_3 + H_2O \longrightarrow 2HNO_2$ (d)

Hence, on the basis of these considerations, we expected a massive depletion of nitrogen (as NO_2^- and/or NO_3^-) in the inoculated medium.
Figures 2 and 3 show the trends of biomass growth and nitrogen content, calculated as sum of dissolved nitrite and nitrate, in the reactor v/s time, during runs carried out at two different inoculum levels (0.5 and 1.0 g l^{-1}) with air and without air, respectively.

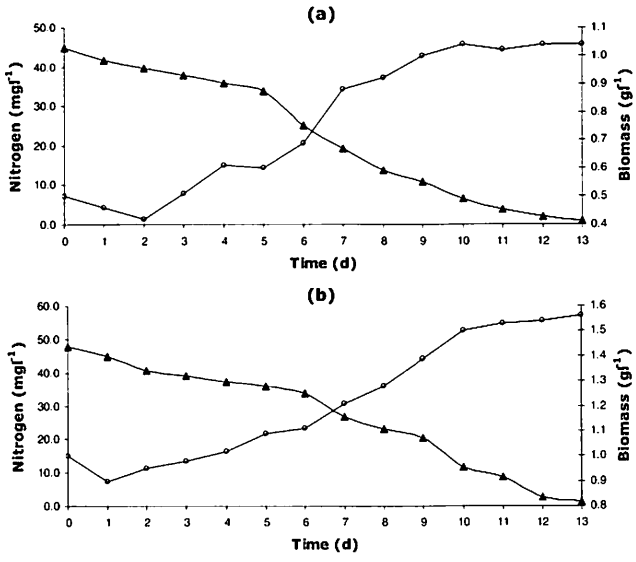
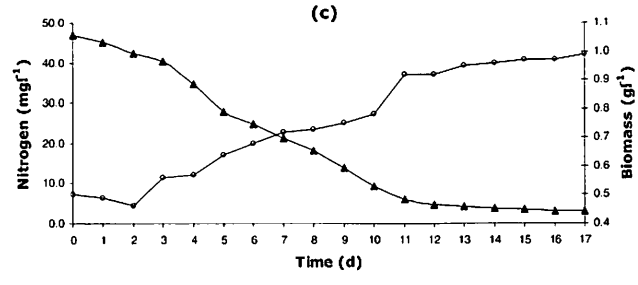


Fig. 2 - Concentrations of biomass (O) and nitrogen (▲) versus time during batch cultivation of S. platensis using NOx as nitrogen source with 20 Nl h^{-1} air flow at different initial biomass concentrations (X_o) a = 0.5 g l^{-1} and b = 1.0 g l^{-1}

The biomass growth, after a lag phase, shows a regular trend reaching a maximum concentration varying from 1 up to 1.5 g l^{-1}, depending on the inoculum concentration and aeration conditions. The nitrogen concentration at the end of the runs, was about 0.9-3.0 mg_N l^{-1}, thus suggesting that the dissolved NO_2^- and NO_3^- were almost completely consumed.



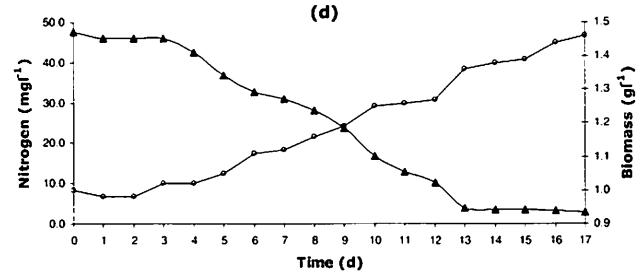


Fig. 3 - Concentrations of biomass (O) and nitrogen (▲) versus time during batch cultivation of S. platensis using NO_x as nitrogen source without air flow at different initial biomass concentrations (X_o) c = 0.5 g l^{-1} and d = 1.0 g l^{-1}.

A significant parameter to evaluate the cell growth is the specific growth rate (μ), which is defined as [15]:

$$\mu = \frac{t}{X}\frac{dX}{dt}$$

where X is the biomass concentration (g l^{-1}). The way to calculate the specific growth rate of microalgae has been largely described [16]. The most commonly used equation is:

$$\mu = \frac{\ln X_f - \ln X_0}{t_f - t_0}$$

where X_0 and X_f are biomass concentrations (g l^{-1}) at the beginning (t_o) and the end (t_f) of each run, respectively. Table 1 shows the main growth and nitrogen removal parameters under different operating conditions. For a given inoculum level the specific growth rate was higher, when air was furnished to fluidize the culture; moreover, this parameter as well as the cell productivity was higher at the lower initial biomass concentration. The nitrogen removal efficiency, calculated as the percentage between the inlet and outlet nitrogen levels, was always >92%.

X_o (g l^{-1})	Nitrogen outlet (mg l^{-1})	Nitrogen removal yield (%)	Q_x[a] (mg l^{-1} d^{-1})	μ (d^{-1})
0.5*	3.0	94.4	29.0	0.040
1.0*	2.3	95.7	27.1	0.022
0.5°	4.0	92.5	41.5	0.056
1.0°	3.6	93.3	43.1	0.034

* Air flow rate (20 Nl h^{-1}) NO_x feeding.
° Air flow rate (20 Nl h^{-1}) for 24h.
[a] Q_x=Cell productivity

Table 1 - Comparison of the main growth and nitrogen removal parameters under different conditions.

Discussion

The feasibility of NO_x removal from flue gas by means of the cyanobacterium *Spirulina platensis* has been demonstrated in this work. Different operating conditions either of gas feeding (continuous or fed-batch pulse-feeding) or inoculum level (0.5-1.0 g l^{-1}) allowed a removal efficiency always higher than 92% (Tab.1), which is a quite promising result, if compared with those obtained by means of the traditional chemical abatement techniques (75-90%).

In particular, the best results in terms of NO_x removal and biomass growth rate (Tab.1) have been obtained with continuous air flow and 0.5 g l^{-1} inoculum, i.e. conditions that allowed the suited fluidizing and lighting of the culture.

The results of this study taken together show that, under the applied conditions, cell growth was not influenced by the concentration of NO_x supplied, even if it should be taken into consideration the toxic effect of NO_2^- in future investigation at higher levels of inlet NO_x.

Further development of the research might consist in the employment of a tubular reactor to improve the growth conditions, feeding a mixture of NO_x and CO_2 which, as well known, are the main components of a flue gas.

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