Evaluation of the performance of the process of nitrification in the wastewater treatment plant of Settat

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ABSTRACT: This research has attempted to assess the effects of operating parameters (hydraulic retention time T and the C / N ratio) affecting the conversion of ammonium ions of wastewater in the City of SETTAT and optimization of the process conditions of nitrification.

The strategy is based on building a statistical model through an experimental Box-Behnken design that accounts for variations in the rate of removal of ammonium based on the C / N ratio and time hydraulic retention T.

The process parameters namely, the C / N ratio and hydraulic retention time are optimized using response surface methodology (RSM) from curve resulting polynomial equation of the plane of iso-response experiments designed to find the optimal point.

The optimization results predicted by the model showed that the maximum ammonium removal rate is 51.6%, it was achieved to the optimal condition of C / N = 15 and a hydraulic retention time of 39.5 Days

Under optimal conditions through using kinetic equations and monitoring over time of concentration of various nitrogen species (NH4 +, NO2 and NO3), variation curves of concentration of compounds nitrogen function of time and to study the kinetics of the nitrogenous material in the waste water SETTAT by calculating apparent kinetic constants K2 related K1 and nitrification.

Keywords: nitrification; experimental design; response surface; optimization; kinetic behavior

1. INTRODUCTION:

The exceeding discharge limits identified in particular for nitrogen compounds values is a major problem the wastewater treatment stations face.
Referring to the 1991 directive of the European Community [1] and Order No. 1276-1201 of 17 October 2002 laying down quality standards for water intended for irrigation (Morocco) [2], the maximum permissible discharges of urban waste water treatment plants are regulated concentrations ; when one is dealing with the treatment plants of urban waste water of over 100,000 population equivalent (as in the city of SETTAT), we have to descend under concentrations of 10 mg N / l for total nitrogen (in other words a reduction of 70% of N).
Urban discharges from the city of SETTAT often lead to large quantities of ammonium whose concentration varies between 21.5 and 45.7 mg NH4 + .L-1.
There are many methods for the treatment of nitrogen, in particular NH4 +-N, but it is generally accepted that biological nitrification is the most practical method of removal of ammonia in the water [3]
According JULIASTUTI [4], nitrification is the most sensitive method among the biological nutrient removal in wastewater process.

Recall that biological nitrification is a process of conversion of nitrogen in the form of oxidized compounds (nitrites and nitrates).

The main steps of nitrification are given by the following two equations:

$NH_4^+ + \frac{3}{4} O_2 \rightarrow NO_2^- + H_2O + 2H^+$

$NO_2^- + \frac{1}{2} O_2 \rightarrow NO_3^-$

First, the ammonium is oxidized to nitrite with the release of H + ions, so it is a reaction of acidification.
In the second step the nitrite is oxidized to nitrate ion. The oxidation of ammonium and nitrite ions is caused respectively by Nitrosomonas and Nitrobacter species. Nitrosomonas and Nitrobacter are aerobic and autotrophic bacteria and are characterized by low specific growth rates. [5]
According HENZE [6], there are many factors that influence nitrification such as temperature, pH, dissolved oxygen, alkalinity and energy sources.
In addition, account must be taken of the responses of nitrifying bacteria to a combination of factors, such as temperature, pH, oxygen concentration and the substrate concentration [7]
Nitrifying bacteria grow optimally at slightly alkaline pH (7.2 to 8.2) and temperatures between 25 and 35 ° C. [8]

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The pH has a significant impact on the metabolic activity of nitrifying populations is a key parameter for monitoring nitrification.

The temperature has a direct influence on the metabolism (assimilation rate, respiration, photosynthesis) and therefore on the rate of growth of phytoplankton [9]

Dissolved oxygen (DO) is recognized as a key variable often used in real applications. A suitable level of oxygen concentration must be maintained so that the organic material is degraded and the ammonium is converted into nitrate.

The dissolved oxygen and ammonia nitrogen are essential reagents for carrying out the nitrification. When present in non-limiting amount, the growth of autotrophic bacteria is maximum.

In practice, it is generally accepted that higher values to 2.0 mg • L-1 [10] or from 2 to 3.0 mg • L-1 [11] does not limit the nitrification.

The aim of this study was to use an experimental design and response surface methodology to assess the impact at different hydraulic retention time (T) C / N adjusted to the biological removal of nitrogen effluent of the WWTP SETTAT and to optimize the process of nitrification.

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2. MATERIALS AND METHODOLOGY

2.1. Study Site

SETTAT is the capital of the region of Chaouia Ouardigha and prefecture of the province of SETTAT.

It is characterized by mild, wet winters (average 10 ° C) and dry but cool summers much (23 ° C on average), precipitation remains low with an average of 350 mm (Water Basin Agency Bouregreg-Chaouia , 2004).

The population of the city is 116570 SETTAT in 2004, 24,303 households, 95% are supplied with drinking water by the Autonomous Administration of Distribution the Water and Electricity Chaouia (RADEEC).

The purification SETTAT station is a facility for waste stabilization ponds. It is connected to a network of collection unit which handles very long in a raw effluent essentially domestic nature. The plant is designed to process 13,500 m3.d-1 of wastewater collected from the city of SETTAT daily.

The effluent from the treatment plant is transferred to agricultural land to be used for irrigation.

2.2. Characterization of treated effluent

The experimental aim is studying the behavior of the system for the removal of COD and also nitrification during aerobic and anaerobic phases.

Table 1 shows the results of the consumption of organic matter evaluated by COD and nitrogen removal assessed by determining the forms of nitrogen + NH4, NO2 and NO3 and the mean values for the other parameters monitored during the experimental procedure, the pH, temperature.

	Units	Entry wastewater	Anaerobic pond outlet	Facultative pond outlet	Maturation pond outlet
Residence time	J	0	4,5	22	39, 5
Ph		7,1	7,7	8	8, 2
dissolved Oxygen	mg/l	0	0	4,6	7,1
DCO	mg/l	703	294	224	140
DBO_5	mg/l	301	134	95	91
$N\text{-}NH_4^+$	mg/l	26,4	24,8	19,4	15,2
$N\text{-}NO_3^-$	mg/l	0	0, 4	6,1	10,5
$N\text{-}NO_2^-$	mg/l	0,	1,2	0.9	0.7

TABLE 1: *Annual averages of main physico-chemical characteristics of raw waste water at the inlet and treated water at the outlet of each of the three components of the wastewater treatment plant of SETTAT*

2.3. Experimental design and mathematical model

2.3.1. Evaluation of the variables :

To evaluate the effect of the ammonium concentration in the nitrification process, the experiments were performed in batches.

In this study, the ratio (C / N) and the hydraulic retention time (T) have been chosen as the independent operation and the most critical factors.

The other environment variables namely the initial concentration of the substrate (NH4 + concentration at the inlet was maintained at a concentration of 26.4 mg L-1) and the dissolved oxygen DO was constantly monitored values determined experimentally to be optimal. The system was maintained at 30 ° C (± 1 ° C) and at a controlled pH of about 7.5.

The dissolved oxygen concentration in the aerobic phase is more than 3 mg L-1, whereas the concentration in the anoxic phase is close to zero. The efficiency of elimination of ammonium (%) was calculated using the following expression: Removal efficiency (in%) = (1 - C / C 0) × 100 Where C0 and C are the ammonium concentrations at time 0 and t, respectively

2.3.2. Design of Experiments

An experiment Box Benhken plane was conducted to optimize the effect on the parameter by removing ammonium through biological nitrification.

The main objective of this plan has been adapted to explore the response surface

The ranges of the experimental variables related to the elimination of ammonium are summarized in Table 2:

Variables	Coded levels		
	-1	0	+1
T(d)	4,5	22	39,5
C/N	10	15	20

TABLE 2: *Range of values for the variables in the experimental design*

2.3.3. Mathematical modeling

The studied process can be described by polynomial empirical model of second order:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i \right)^2 + \sum_{i=1}^{n-1} \sum_{i=i+1}^{n} b_{ij} x_i x_j$$

Where Y is the predicted response and the dependent variable studied (ammonium removal) b0 is a constant coefficient, bi are linear coefficients, bij are coefficients of interaction and bii are quadratic coefficients. Furthermore, xi and xj are the coded values for the experimental parameters.

In this design, the two factors (independent variables): T and C / N were evaluated, each at three levels, and experimental trials were conducted in all possible combinations.

The terms of models were selected or rejected based on the probability (P) value with a confidence level of 95%. The results were analyzed using analysis of variance completely (ANOVA) by software design (Statgraphics).

The response surface plot and the respective contours were obtained based on the effect of levels of two factors, the simultaneous interaction of the two factors on the response was studied. Optimum region was also identified. The experimental conditions and the results are shown in Table 3.

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Experience matrix:

T(d)	C/N	Y(%)
-1,0	0,0	48,1
-1,0	-1,0	45,9
0,0	1,0	49,1
1,0	0,0	51,6
1,0	-1,0	49,6
-1,0	1,0	46,9
0,0	0,0	50,3
0,0	-1,0	48,1
1,0	1,0	50,6

TABLE 3: Experimental conditions and results of the factorial design

2.4. Chemical analysis

Measurements of NO3-, NO2-, NH4 +, were performed according to the standard method APHA 2005.

In addition to these parameters, pH and temperature were also monitored with a multiparameter probe (modèleHI769828, Hanna Instruments).

The dissolved oxygen concentration (DO) in the waste water was determined using an oxygen sensor.

3. RESULTS AND DISCUSSION:

3.1. Statistical Analysis

The analysis of variance (ANOVA) results in removal of ammonium nitrification process is summarized in Table4.

Analysis of variance of the response was performed to estimate the significance (at the risk 5%) of the effects of C / N ratio of the medium and the hydraulic retention time T.

All data were processed using the software Statgraphics

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
A : T	19,8017	1	19,8017	317,67	0,0000
B : C/N	1,5	1	1,5	24,06	0,0045
BB	5,33556	1	5,33556	85,60	0,0002
Total error	0,311667	5	0,0623333		
Total (corr.)	26,9489	8			

TABLE 4: *Analysis of variance results of removing ammonium by nitrification*

The response data were analyzed by default. Based on statistical analysis, the models are highly significant with values of very low probability

The square of the correlation coefficient for the response was calculated as the coefficient of determination (R2) with a confidence level of 95%.

R2 = 98.8435%

R2 (adjusted) = 98% in 1496

Standard error. = 0.249666

Mean absolute error = 0.17037

A polynomial model was used to model the effects of two factors. The coefficients of the polynomial were determined by a multilinear regression calculation using the least squares criterion.

A relationship between the dependent and independent variables based on factors encoded was established.

The quadratic model fitted to the data is:

Y (elimination of ammonium %) =

50,0 + 1,81667*T + 0,5*C/N - 1,63333*C/N^2

3.2. Process analysis and modeling:

3.2.1. Interactive effects and optimization of operating parameters

The removal of total inorganic nitrogen was significantly affected (p-value <0.05) by the linear effect of the hydraulic retention time T and the quadratic effect of the ratio (C / N) of 95% confidence .

A response surface and the two-dimensional graphic outline were plotted against the model equation obtained to evaluate the interaction between the parameters and to determine the optimum values of every parameter. The effects of temperature, C / N ratio in the ammonium removal are shown in Figure1.

As it can be seen in Figure 1a, the ammonium removal efficiency increases with the increase in the C / N ratio as well as the efficiency increases as the hydraulic retention time increase

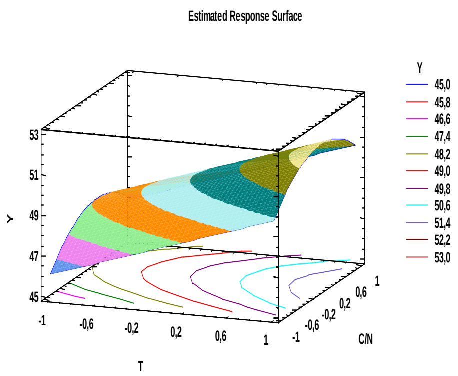


Figure 1a : *surface of estimated repons*

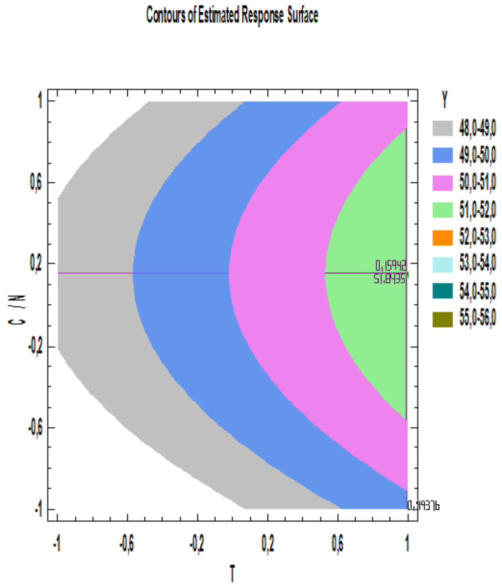


Figure 1b : Contour surface of estimated response

The C / N ratio plays a significant role in stabilizing pH and to avoid the accumulation of nitrite

Therefore, optimizing the C / N ratio can be significant for ammonium oxidation.

Other terms of the model the interactions T * C / N and T * T are not significant (with a value greater than 0.05 probability) indicating that their effects on the removal of ammonium are negligible.

It must be noted that with a time longer hydraulic retention, nutrient medium becomes a limiting factor for bacterial growth. Bacteria having exhausted the organic matter in the water die and thereby cause the resulting decline in DBO5. We can conclude that the optimization of variables T and C / N with the response surface methodology is satisfactory, providing optimal conditions for the removal of nitrogen from the effluent; optimum values of nitrogen removal was obtained with 39.5 days and C / N ratio of 15.8, which have been validated experimentally.

So, this effluent can be considered as a potential source of nitrogen and organic material for the production of proteins of unicellular organisms.

3.3. Kinetic study of the activity of nitrification

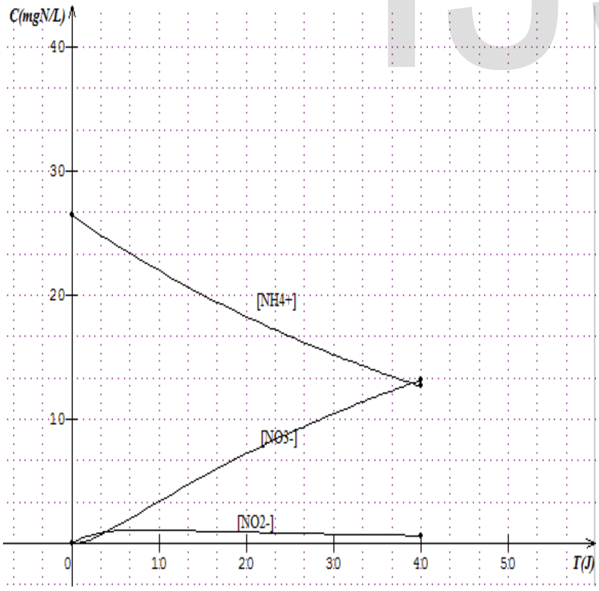
3.3.1 Kinetic modeling

The kinetics of removal of ammonium is often approximated by a first order kinetics [12]
The nitrification activity was estimated by determining the kinetic parameters K1 and K2, based on the establishment of the kinetic models represented by equations substrate consumption NH4 + according to the production of oxidized forms (NO2 - and NO3 -) in steps of nitration

[NH4 +] = [NH4 +] 0 e-K1T

[NO2-] = k1 [NH4 +] 0 / k2 - k1 {e-e-k1t- K2T}
[NO3-] = [NH4 +] 0-[NH4 +] - [NO2-]

Figure 2 illustrates the changes in concentrations of ammonium NH4 +, NO3-N -, N-NO 2 - over time,



The analysis shows that the consumption of ammonia nitrogen (NH4 +) was more pronounced. In this period, there was a progressive increase in the concentration of nitrate (NO3 -), 0 to 12 mg.L-1 7.
Therefore, the accumulation of nitrite was negligible throughout the experimental period. Low accumulation of nitrite indicated that the ammonium oxidizing bacteria have a high affinity for ammonium. In the normal process of nitrification, the ammonium conversion result primarily first order kinetics.
The kinetics of the nitrification is governed by that of the slowest stage.
Table 5 shows the average estimated values of the constants K1 and K2.
The table displays the average estimated values of constantesK1 and K2.

UNIT	K1	K2
d^{-1}	0,0184	0,391

A ratio K1 / K2 of 0.0465 indicates that the conversion of ammonia nitrogen into nitrite is not the limiting stage of the method. As was expected; the rate of nitration was larger and the accumulation of nitrite is low, Intermediate NO-2 being consumed by a rapid response and cannot accumulate. Its maximum concentration remains low and almost constant. They say we are in a quasi-steady state
The average value of nitrate recorded at the outlet of the treatment plant wastewater is between 12mg / L and 15 mg / L. This value is within the limits allowed by the OMS (2006).
By the End of of nitrification, the ammonium conversion rate is between 45% and 52%
As regards the pH, according to [10], the microorganisms responsible for nitrification grow best under slightly alkaline conditions, in the range of 7.2 to 8.0. [13]

4. Conclusion

In this study, a process of biological nitrification in continuous mode optimized the removal of ammonium in wastewater station SETTAT.
The response surface analysis were performed according to the ratio C/N and the retention time.
This study allowed us first, to appreciate that the C / N ratio and the retention time were determined to be the most

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effective operational factors on the performance of the system to remove nutrients.

These two factors have shown an influence as well as their interactive effects on the response.

On the other hand, this study allowed us to see that the performance of the system remains in a steady state when the process is operated under appropriate conditions; in particular, the control of pH and the concentrations of substrates because of the affinity for the microorganisms of the substrate appears to decreases with the reduction of pH.

The natural lagoon is an effective and controllable process to remove nutrients (N and P) from wastewater.

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