INFLUENCE OF OPERATING PARAMETERS ON BIODEGRADATION PROCESS OF PHENOLIC WASTEWATERS

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A fost studiată tratarea apelor reziduale cu compuşi fenolici într-o instalație de la o platformă petrochimică. Scopul lucrării a fost identificarea parametrilor care influențează procesul de biodegradare a compuşilor fenolici din apele reziduale şi determinarea valorilor optime ale acestora. Instalația industrială a fost monitorizată peste o mie de zile când a fost urmărit răspunsul sistemului la modificarea pH-ului, a concentrației biomasei şi a concentrației agentului nutritiv. S-a determinat randamentul de defenolare şi implicit concentrația finală a compuşilor fenolici la modificarea celor trei parametrii. În final, a fost determinat un interval optim de funcționare al sistemului. Condițiile analizei simultane a efectului pH-ului, concentrației biomasei şi a concentrației agentului nutritiv au considerat funcționarea instalației la randamente mari şi concentrație finală a compuşilor fenolici, sub limita maximă admisă la deversarea în emisar (0,3 ppm).

The treatment by biodegradation of phenols wastewaters resulted from a petrochemical platform was studied. The purpose of this work was to establish the parameters that influence the phenols biodegradation process and to find out the optimum points for system working. During more than one thousand days of experiments was obtained the system answer at changing of the pH, biomass concentration and nutrient concentration. It was settled the phenols removal efficiency and the final phenols concentration at the changing of the parameters above mentioned. In the end, it was established an optimum running unit interval related to the pH, biomass concentration and nutrient concentration for running the system in conditions of best phenols removal efficiency and final phenols concentration below the maximum admissible phenols concentration (0.3 ppm). .

Keywords: phenols, biodegradation, phenolic wastewaters

1. Introduction

Aromatic compounds such as phenols occur in wastewater of a number of industries such as petroleum refining, resins and plastics and high temperature coal conversion. These aromatic compounds can be toxic when present at elevated levels and are known or suspected to be carcinogens. Thus, the removal of such

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chemicals from industrial effluents is of great importance. Current methods for removing phenolic from wastewaters include microbial degradation.

The effluents are treated in a sludge biodegradation process. It are very sensitive on variation of phenols concentration, biomass concentration, pH and nutrients composition.[1-6]

The aim of this study is to investigate the parameters that present a major influence on the biotreatment process, in order to analyse their variation range and to establish the optimal (nominal) working conditions, leading to ensure the best removal efficiency and a phenol concentration in effluent below the maximum admissible limit of 0.3 ppm (i.e. below the regulation threshold).

2. Experimental part

An industrial-scale process has been studied, by taking into account wastewaters from a petrochemical platform with initial phenols concentration up to 15-20 mg/L and a final imposed phenols concentration less than 0.3 ppm. During three years of experiments, the biological phenols compounds degradation was monitored, the recorded parameters being the followings: initial phenols concentration, temperature, pH, nutrient concentration, flow rate, sludge concentration, final phenols concentration etc. Table 1 presents a small set of the recorded data.

Table 1

A few experimental data from the industrial petrochemical process

	Output from mechanical step Input to biological step		Biological step I (Output) Biological Reactor 1 (R1)						Biological step II (Output) Biological Reactor 2 (R2)					
Exp. No.	Ga (m3/h)	C_{S0} (mg/L)	pH	T (C)	C_S (mg/L)	C_X (mg/L)	C_{NH4} (mg/L)	η (%)	pH	T (C)	C_S (mg/L)	C_X (mg/L)	C_{NH4} (mg/L)	(%)
0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	750	0.9	7.1	30	0.330	7.0	8.5	65	7.4	28	0.0928	1.3	7.72	72
2.	500	0.9	7.4	12	0.440	8.8	3.5	52	7.6	12	0.0250	9.6	0.77	94
3.	800	1.4	6.6	18	0.200	9.5	4.1	86	7.2	17	0.0270	9.7	3.20	87
4.	800	1.6	7.8	19	0.231	9.5	6.4	86	7.5	18	0.0124	9.4	5.15	95
5.	800	1.6	8.4	20	0.440	7.0	5.5	73	8.1	20	0.0070	6.7	3.21	98
6.	400	1.6	8.4	20	0.440	7.0	5.5	73	8.1	20	0.0070	6.7	3.21	98
7.	700	1.7	6.9	34	0.184	8.5	1.3	89	7.1	31	0.0560	1.2	1.03	70
8.	800	1.7	7.1	39	0.081	3.9	5.9	95	7.3	31	0.0290	1.4	3.86	64
9.	600	1.9	7.6	18	0.136	9.3	9.5	93	7.6	20	0.0270	9.3	7.90	80
10.	1000	3.1	6.4	20	2.590	2.2	8.4	17	11.4	19	0.0105	4.0	4.24	100
11.	800	3.2	6.8	30	0.160	9.0	10.8	95	6.9	27	0.0195	2.5	4.38	88

12.	800	3.3	7.0	18	0.625	9.5	3.7	81	7.8	15	0.0120	2.5	2.57	98
13.	750	3.9	6.9	30	0.031	8.7	2.6	99	7.1	30	0.0159	1.8	1.80	49
14.	800	4.1	7.6	19	0.700	9.5	8.0	83	7.6	19	0.0180	8.3	4.35	97
15.	800	4.2	6.8	32	0.130	9.0	4.4	97	7.1	31	0.0320	1.4	0.90	99
16.	800	4.3	7.7	30	0.560	9.5	6.4	87	7.6	28	0.0140	8.7	5.40	98
17.	700	5.8	6.6	19	0.104	8.6	4.3	98	6.9	18	0.0304	9.3	2.51	71
18.	800	6.5	7.0	32	0.086	9.0	14.9	99	7.1	30	0.0097	2.6	4.30	89
19.	1000	6.7	7.7	19	5.160	5.2	8.0	22	8.1	19	0.0360	4.8	4.63	99
20.	600	7.2	8.1	28	5.340	9.0	10.9	26	7.6	28	0.0420	4.8	8.75	99
21.	700	7.3	6.9	27	0.740	9.2	13.5	90	7.0	26	0.0290	5.2	9.90	96
22.	700	7.3	6.9	27	0.740	9.2	13.5	90	7.0	26	0.0290	5.2	9.90	96
23.	800	8.2	8.1	18	0.103	9.0	2.6	99	7.9	15	0.0132	9.3	1.93	87
24.	700	8.5	7.1	33	0.580	6.4	30.9	93	7.0	31	0.0100	1.8	10.30	98
25.	800	10.8	6.9	27	0.480	8.0	9.2	96	6.8	26	0.0290	4.4	2.57	94
26.	800	12.7	7.4	31	0.559	9.0	13.9	96	7.2	30	0.0019	2.6	2.06	100
27.	800	13.0	7.7	26	0.110	9.0	14.8	99	7.0	24	0.0240	4.2	9.66	78
28.	800	13.4	9.3	20	7.900	6.4	32.4	41	7.6	20	0.0170	2.	23.60	100
29.	400	17.6	9.1	17	17.180	6.5	14.0	2	8.1	17	0.0830	8.6	5.15	100
30.	700	18.5	8.5	19	12.400	8.5	8.8	33	8.1	19	0.0240	8.7	6.43	100
31.	700	19.5	7.0	22	0.087	7.5	14.0	100	7.3	24	0.0192	8.0	7.30	78
32.	800	19.9	8.5	27	0.220	9.0	9.7	99	7.8	27	0.0200	6.0	8.30	91
33.	800	21.2	7.5	29	0.149	9.0	14.2	99	7.4	31	0.0126	8.5	6.40	92
34.	800	23.4	7.5	29	17.480	9.0	14.0	25	7.5	30	0.0270	9.0	6.50	100
35.	800	25.8	5.9	30	17.480	7.1	7.7	32	7.6	29	0.0270	5.5	4.30	100
36.	775	32.7	9.4	32	31.770	7.0	26.7	3	8.2	33	0.0740	5.0	24.40	100
37.	450	33.6	8.9	28	21.000	3.8	31.2	38	8.9	28	0.0520	6.0	24.46	100
38.	500	34.5	9.2	22	34.300	9.2	15.2	1	7.9	21	0.0240	9.7	10.95	100
39.	300	62.5	6.9	30	59.000	6.5	46.8	6	7.8	29	0.0060	4.3	30.90	100

The real petrochemical wastewaters biodegradation process used an active sludge recycling bioreactor type basin composed of two reactors working in series. The nutrient agents were urea and phosphate. The oxygen was introduced directly from the atmospheric air into the basin. Inside the bioreactor the oxygen was uniformly distributed by using perforate panels located on the bottom of the basin [7].

3. Results and discussions

The reported experiments have the first purpose the establishing of pH influence on efficiency of the process and the final phenols concentration before water discharging in an industrial effluent. Thus, the pH was measured in different locations of the system (at the input of the mechanical step, the output of the mechanical step and the input of the biological step, the input of the two biological reactors and the output of the biological station) before the discharging into the effluent. The pH was varied between 6 and 8, maintaining constant the feed flow-rate (G_a), the biomass concentration (C_X) and also the nitrogen nutrient concentration (C_{NH4}). During the pH variation, the phenol concentrations in the two bioreactors, R1 and R2, have been continuously recorded. In order to establish the efficiency of the process was calculated the phenols removal efficiency, η as follows:

$$\eta = \frac{(C_{S0} - C_S)}{C_{S0}} \cdot 100$$

The final paper aim was to establish the optimum working pH for both reactors, in order to obtain a high removal efficiency of phenol, while keeping the effluent concentration below the imposed threshold concentration of 0.3 ppm.

In the figures 1 and 2 is presented the variation of phenols removal efficiency with the pH on the first biological reactor, R1.

The figure 1 shows that the variation of the pH between 6.8 and 7.5 produces an increase of the phenols removal efficiency, resulting high rates within 95 and 99.5%. Also, we can note that the biomass registers high values of 9 mg/L. In the same figure we can observe that increasing the pH at values up to 7.5, the phenols removal efficiency starts to slowly decrease.

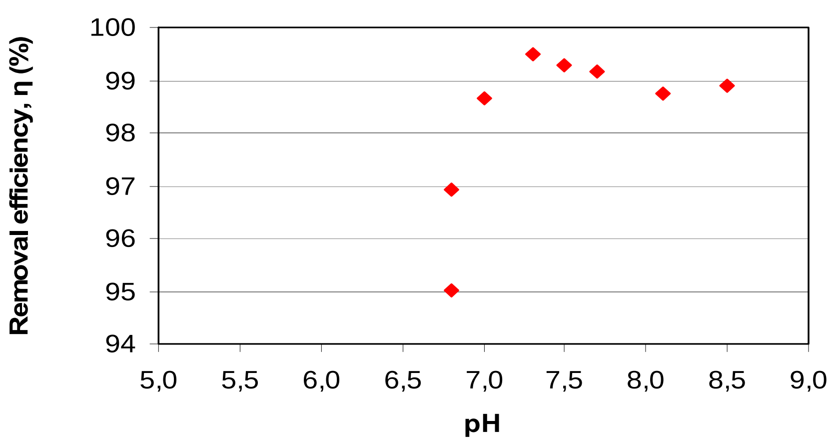

Fig.1. PH effect on first bioreactor (R1) removal efficiency (G_a=800 m^3/h and C_x=9mg/L)

Figure 2 shows that when the pH is within 7.6 and 7.9 the phenols removal efficiency are between 83 and 86%. Also, the biomass registers values up to 9 mg/L, can be considered an optimum for the unit running.

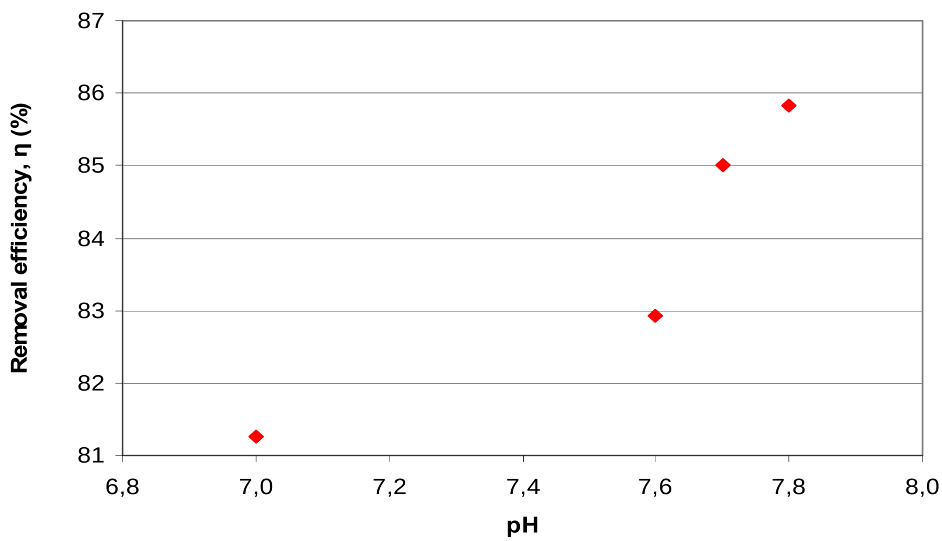

Fig. 2. PH effect on first bioreactor (R1) removal efficiency (G_a= 800 m^3/h, C_x= 9.5 mg/L)

The effect of pH changing on the second bioreactor removal efficiency (R2) is illustrated in figure 3.

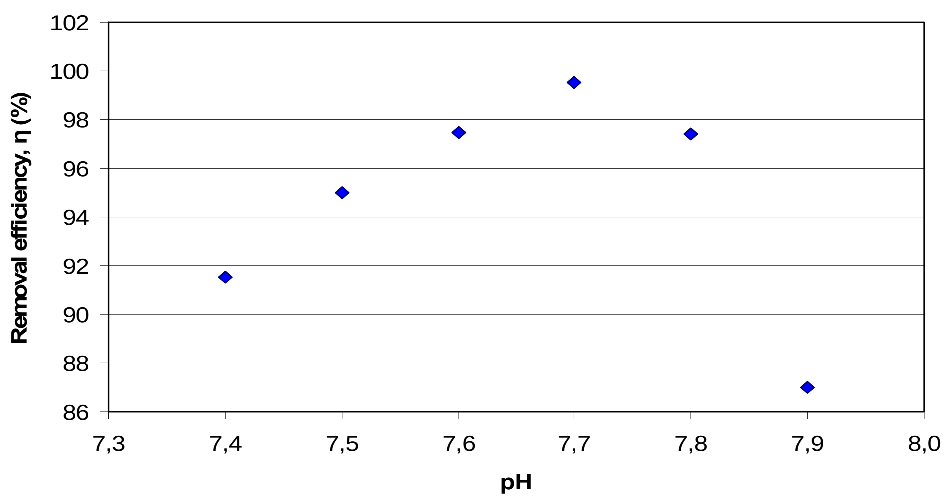

Fig.3. PH effect on second bioreactor (R2) Removal efficiency (G_a= 800 m^3/h and C_x= 8.5 mg/L)

Figure 3 shows that on the second bioreactor R2 the biomass removes better the phenols at values of the pH within 7.4-7.7. At values of the pH up to 7.7 the phenols removal efficiency starts to decrease.

The analysis of experiments shows that the phenols removal efficiency is depending on the system's pH. We can conclude that for the first bioreactor the optimum pH is around 7.5 when the removal efficiency of the phenols is within 95-99.5%. On the second bioreactor the optimum pH is between 7.4 and 7.7.

The optimum pH, from the removal efficiency point of view, is thus obtained around the value of 7.5. Important also is the phenols concentration at the water discharging in an industrial effluent. Taking into consideration this aspect it was analyzed the evolution of phenols concentrations with the pH. The below presented figures reveal the evolution of phenols output concentrations with the pH.

Figures 4 and 5 present the variation of phenols concentration with the pH on the first bioreactor R1.

Figure 6 contains the state of the phenols concentration as pH function for the second bioreactor R2.

Working at a pH below 6 (figure 4) and with a biomass concentration of 8.5 mg/L the phenols concentration at the output of the first bioreactor is enough high, between 0.1-0.35 mg/L.

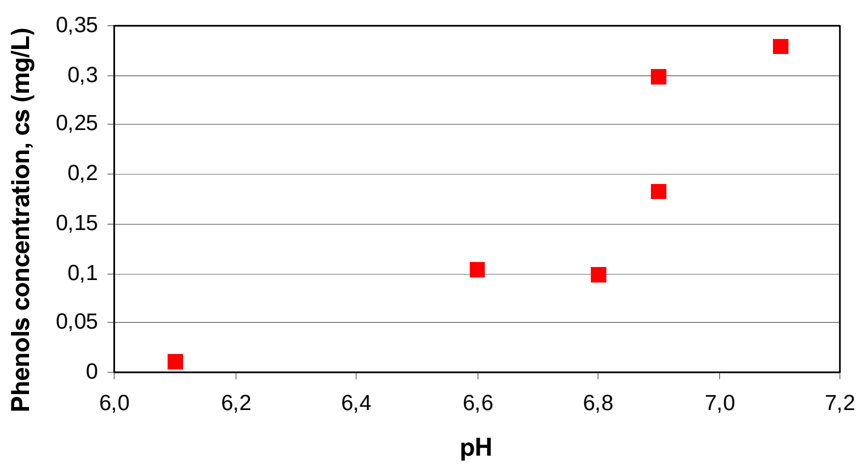

Fig.4. The evolution of the phenols concentration with pH for the first bioreactor (R1), G_a= 800 m^3/h and C_x= 8.5 mg/L

Figure 5 shows that working at a pH within 6.8 and 7.3 and with a biomass concentration of 9 mg/L results treated waters with phenols concentrations below 0.1. These waters could be sent directly into the effluent without a second treatment into the bioreactor R2.

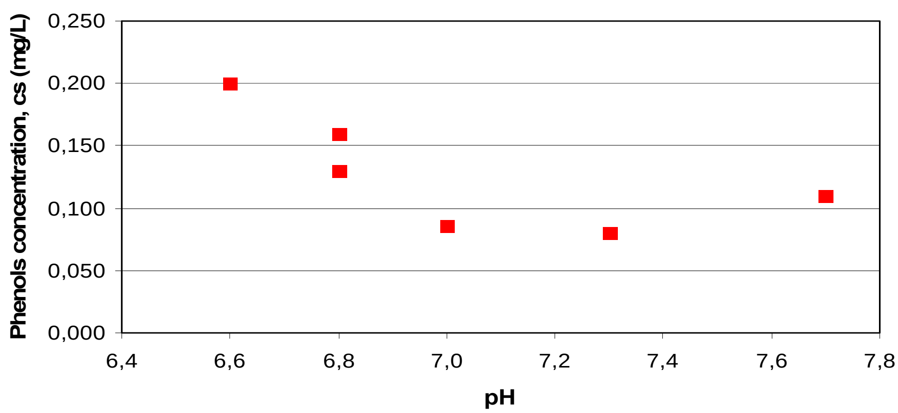

Fig. 5.The evolution of the phenols concentration with the pH on the first bioreactor (R1), G_a=800 m^3/h and C_x= 9 mg/L

At the second bioreactor (R2) the phenols concentration of the treated waters at a pH below 7 registers values of about 0.2 mg/L; at a pH between 7 and 7.5 registers values below 0.1 mg/L and increasing the pH up to 7.5 the phenols concentration also increases to values of 0.45 mg/L (figure 6).

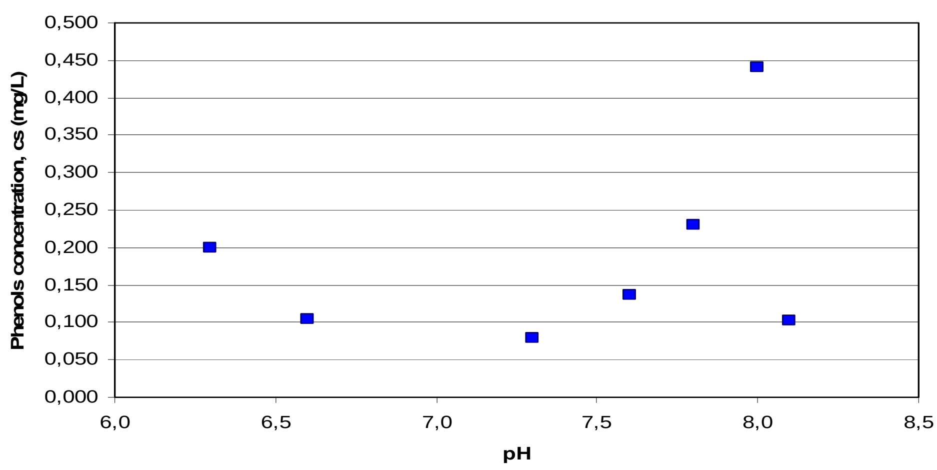

Fig. 6.The evolution of the phenols concentration with pH for the second bioreactor (R2), G_a= 800 m^3/h and C_x= 9 mg/L

By considering the all previously mentioned aspects, one can derive the following conclusions:

1. The maximum removal efficiencies of phenols are obtained when working at a pH of 7.5 on the first bioreactor, R1 and at a pH within 7.4-7.7 for the second bioreactor, R2.
2. The phenols concentration of treated waters registers values below 0.1 mg/L when working at a pH of about 7 on the first bioreactor and at a pH within 6.5 and 7.5 on the second bioreactor.

Under these conditions the unit should be run at a pH around 7.5, thus the treated waters will register phenols concentrations below 0.1 mg/L and could be discharged into the effluent.

The results from the literature reported working conditions of pH=6.8 when using simples cultures of microorganisms and at a pH of 7 for mixed cultures.

Thus, Monteiro and all [6] studied the phenol degradation with *Pseudomonas putida* DSM 458 and during the experiments used a pH of 6.8. Monteiro [6] reveals the fact that a slight reduction of the pH value was observed as biomass grew, but it was always less 10% of the initial pH value. After the exponential growth phase, the pH increases. Similar results have been reported by Lallai et all. [8]. PH increases when the input phenol concentration increases.

Sokol and Howell [9-11] also worked at a pH of 6.8 using for phenol biodegradation the same bacteria (*Pseudomonas putida)*.

Pawlowski and Howell [12] used for the phenol degradation mixed cultures and the pH was 6.6.

Tang [13] also used mixed cultures for the phenol biodegradation and the working pH was 7.

O'Fagain and all [14] studied the phenol biodegradation and 4-clorophenol using a combined method consisting in the water oxidation of phenol in presence of enzyme *Horseradish Peroxidase*. In this case the working pH was 9 for the removal of the phenol and 8 for the removal of the 4-clorphenol. The optimum results in the case of 4-clophenol were obtained by working at pH near to 4.

The second study aim was the analysis of biomass concentration effect on phenols biodegradation process. It was studied the phenols removal efficiency when was changed the biomass concentration in order to settle an optimum working concentration for which results best phenols removal efficiencies and final phenols concentrations below the limit admitted in the effluent.

The evolution of phenols removal efficiencies versus the biomass concentrations at constants flow rate and pH is presented in the figures 7-9.

Figure 7 shows good phenols removal efficiencies obtained on the first bioreactor, when working at a pH of 7.5. The efficiencies record values of 80%.

The biomass concentration for these values is within 9 and 9.5 mg/L. The flow rate of 800 m^3/h was constant.

Figure 8 shows the phenols removal efficiencies on the first reactor, R1, at the same constant flow rate of 800 m^3/h, but at a pH 7. High efficiencies are obtained at a biomass concentration of 8.5 mg/L.

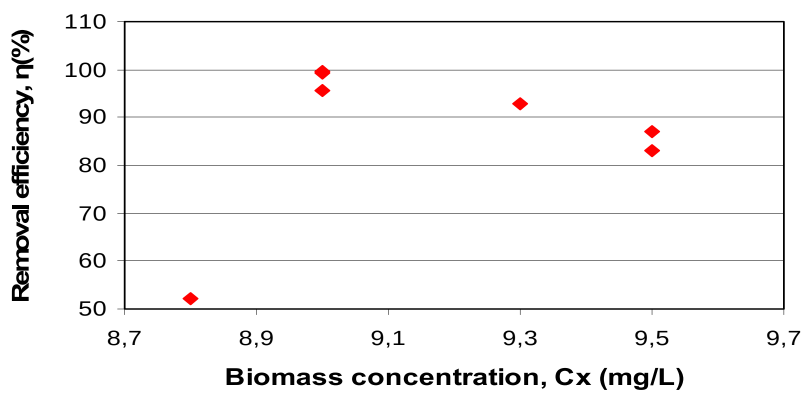

Fig. 7. The evolution of phenols removal efficiency with biomass concentration for the first bioreactor (R1), G_a= 800 m^3/h and pH= 7.5

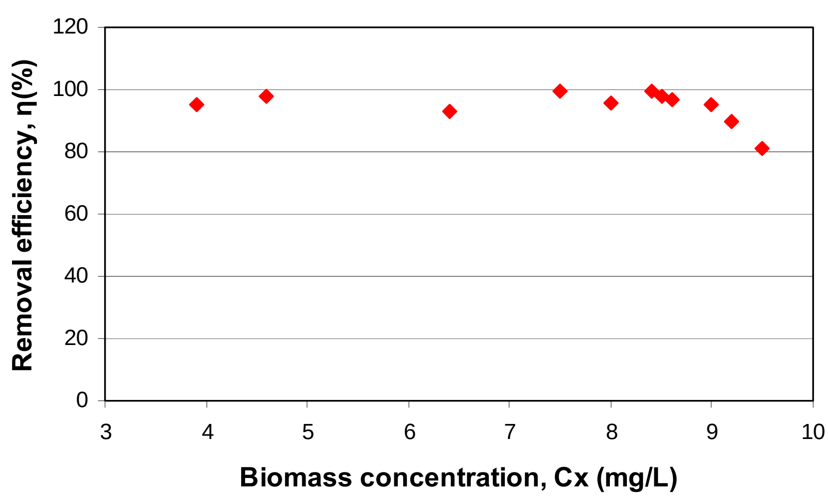

Fig. 8. The evolution of phenols removal efficiency with biomass concentration for the first bioreactor (R1), G_a= 800 m^3/h and pH= 7

Figure 9 shows the evolution of phenols removal efficiencies for the second bioreactor. As expected, the second bioreactor registers phenols removal efficiencies lower than the first bioreactor. However, efficiencies of 75% are obtained when working at a pH between 7.5 and 8. The biomass concentration is also lower on the second bioreactor, recording values between 5-6 mg/L.

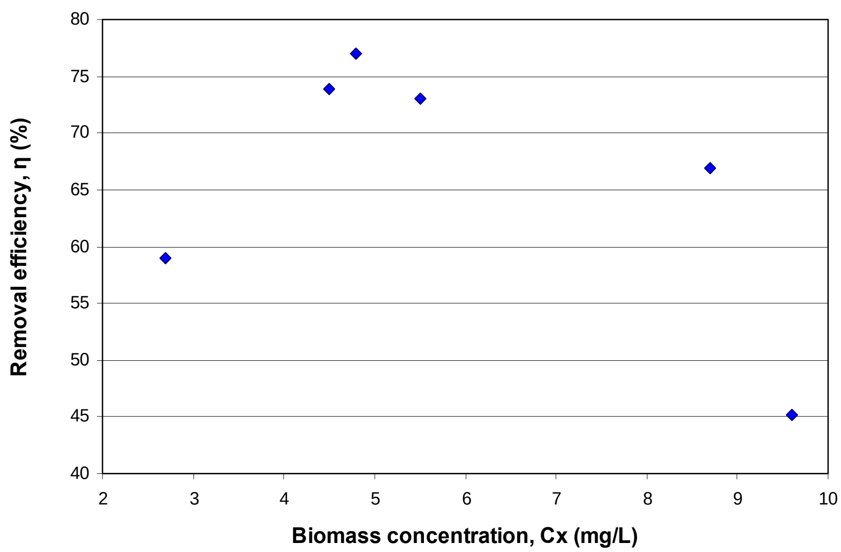

Fig. 9. The evolution of phenols removal efficiency with biomass concentration for the second bioreactor (R2), G_a= 800 m^3/h and pH = 7.5-8.2.

The evolution of final phenols concentration (before sending the treated waters in effluent) was analyzed versus the biomass concentration in order to find an optimum point of working taking into consideration both conditions of high efficiencies and lower phenols concentrations.

Figures 10 and 11 present the evolution of phenols concentrations for the 2 reactors, R1 and R2. The phenols concentrations are enough high on the first bioreactor when working at a pH of 7.5 (figure 10). This level could be explained by the fact that wastewaters have to pass trough the second bioreactor before to be discharged in effluent. The biomass concentration on the first bioreactor in these conditions varies between 8.8 and 9.5 mg/L. On the second bioreactor (R2) we obtain phenols concentrations enough low, thus the treated waters could be sent to the effluent for a pH of 6.9. The biomass concentration varies within the interval 2.0-5.5 mg/L (figure 11).

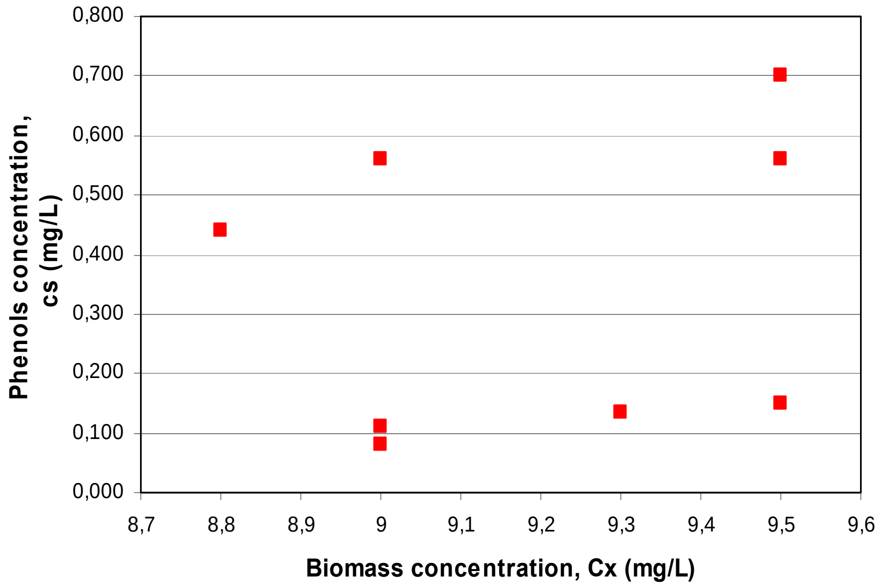

Fig. 10. The evolution of phenols concentration with biomass concentration for the first bioreactor (R1), G_a= 800 m^3/h and pH=7.5

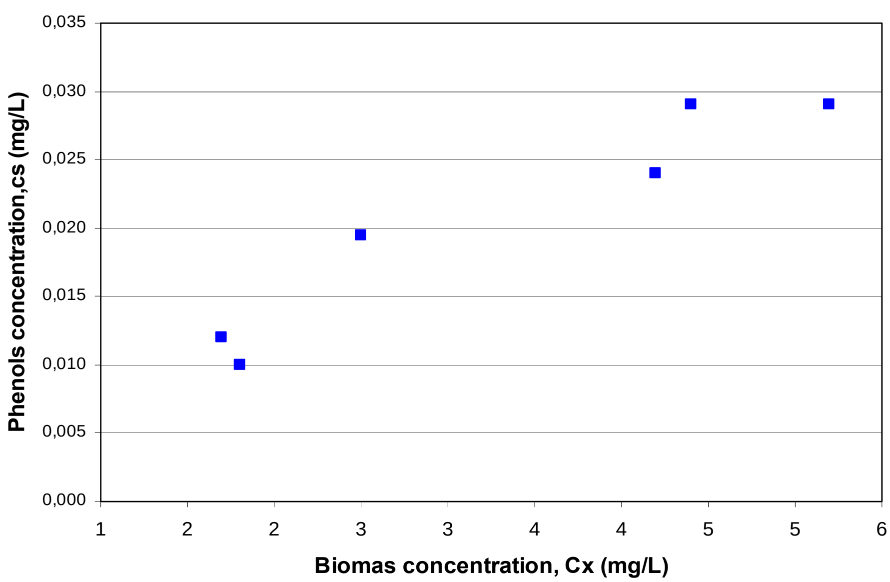

Fig. 11. The evolution of phenols concentration with biomass concentration for the second bioreactor (R2), G_a= 800 m^3/h and pH=6.9

Taking into account all above mentioned regarding the evolution of biomass concentration we can conclude the followings:

- for the first bioreactor we obtain bigger phenols removal efficiencies and lower phenols concentrations when working at a biomass concentration of 8-9 mg/L;
- for the second bioreactor we obtain bigger removal efficiencies and lower phenols concentrations when working at a biomass concentration of 2-5 mg/L.

The third and the last parameter analyzed was the nutrient concentration. During the experiments was monitored and recorded the evolution of ammonium concentration and the system answer at constants pH, flow rate and biomass concentration.

Figures 12 and 13 present the evolution of phenols removal efficiencies versus the nutrient concentration for the first bioreactor.

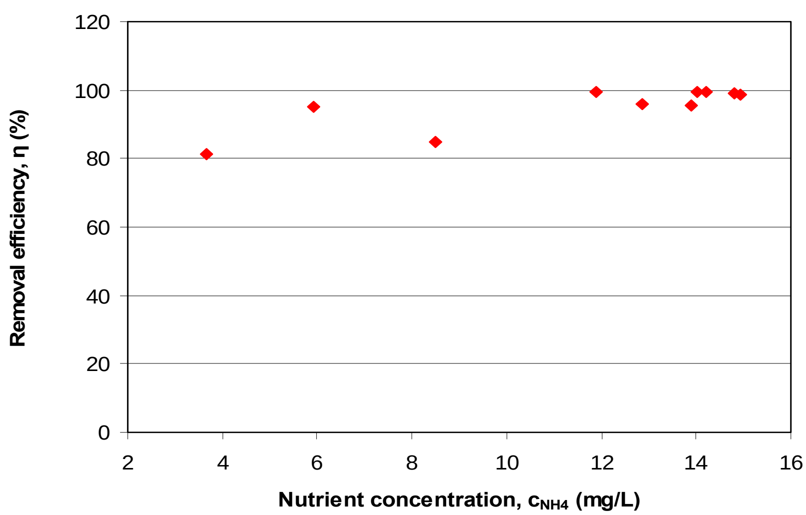

Fig. 12. The evolution of phenols removal efficiency with nutrient concentration for the first bioreactor (R1), G_a= 800 m^3/h, pH=7.5 and C_x= 9 mg/L

Figure 12 shows very high efficiency values when working at constant values of pH, flow rate and biomass concentration. The corresponding nutrient concentration is up to 10 mg/L ammonium, taking values between 12-15 mg/L.

Figure 13 shows the inefficiency of the system when working at pH up to 8, biomass concentration of 9 mg/L and flow rate of 800 m^3/h, due to the fact that are obtained very low removal efficiencies that decrease even if nutrient concentration will be increased from 2 to 10 mg/L.

The variation of the efficiency for the second bioreactor (R2) is presented in the figure 14. Good efficiencies are obtained when working at pH 8, biomass concentration of 9 mg/L and flow rate of 800 m^3/h. The efficiency registers increasing values from 40-60% to 90-99.5% when the nutrient concentration is increasing from 3 to 12 mg/L. The highest values of the efficiency are obtained at nutrient concentrations between 11 and 13 mg/L.

Based on these results, the evolution of phenols concentrations with the variation of nutrient concentration is presented for both bioreactors.

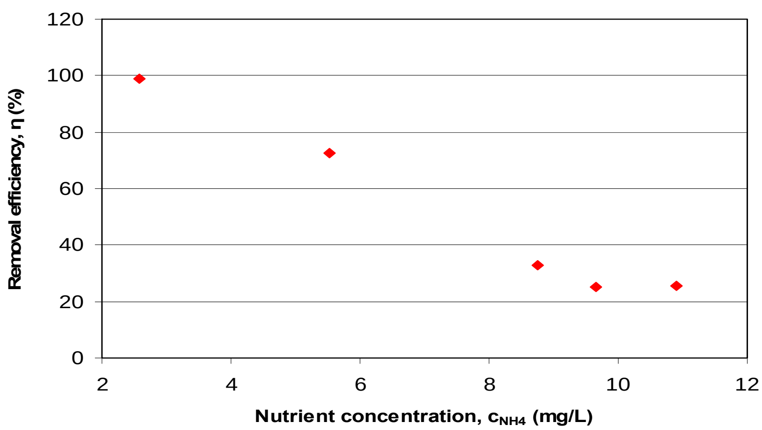

Fig. 13. The evolution of phenols removal efficiency with nutrient concentration for the first bioreactor (R1), G_a=800 m^3/h, pH= 8.1-8.5 and C_x=9 mg/L

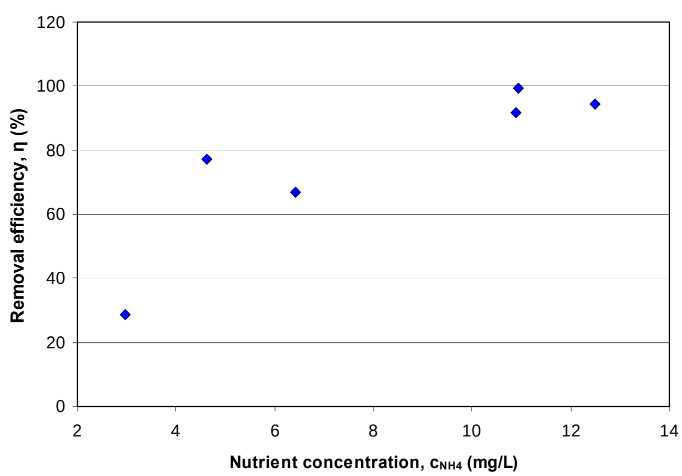

Fig. 14. The evolution of phenols removal efficiency with nutrient concentration for the second bioreactor (R2), G_a=800 m^3/h, pH 8 and C_x=9 mg/L

Figure 15 shows lower values of phenols concentration, below to 0.2 mg/L when working with ammonium concentration at values between 11 and 15 mg/L. The other parameters were kept constant; flow rate of 800 m^3/h, pH 7.5 and the biomass concentration of 9.5 mg/L.

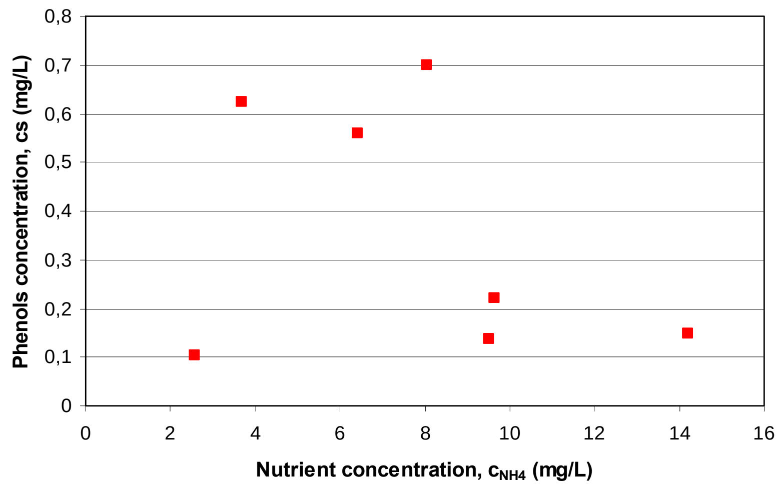

Fig. 15. The evolution of phenols concentration with nutrient concentration for the first bioreactor (R1), G_a=800 m^3/h, pH=7.5 and C_x=9.5 mg/L

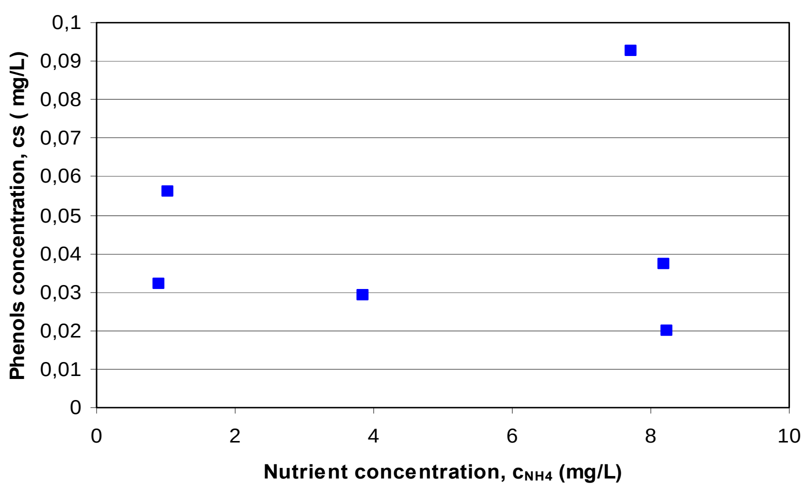

Fig. 16. The evolution of phenols concentration with nutrient concentration for the second bioreactor (R2), G_a=800 m^3/h, pH=7 and C_x=1.3 mg/L

Figure 16 shows values of phenols concentration below the limit when working at pH 7, flow rate of 800 m^3/h and biomass concentration of 1.3 mg/L. The corresponding nutrient concentration is between 1 and 8 mg/L.

Taking into account the above presented results we can conclude that for the first bioreactor is optimum working at pH 7.5, biomass concentration of 9 mg/L and nutrient concentration between 11 and 15 mg/L in order to obtain good efficiencies and lower phenols concentrations at the discharging in effluent.

For the second bioreactor, the optimum nutrient concentration is 8 mg/L when working at pH 7 and a lower biomass concentration between 1.3 and 1.5 mg/L.

4. Conclusions

By simultaneous analysing the three parameters studied we can obtain the finals optimum points of working for the two bioreactors, R1 and R2 studied.

1. The optimum working conditions for the first bioreactor are as follows: a constant flow rate of 800 m^3/h, a pH within the interval 7-7.5, a biomass concentration of 9 mg/L and a nutrient concentration within 11 and 15 mg/L ammonium.
2. The optimum working conditions for the second bioreactor are as follows: a constant flow rate of 800 m^3/h, a pH 7.5, a biomass concentration of 1.3-5 mg/L and a nutrient concentration of 8 mg/L.

Nomenclature

G_a – feed flow-rate (m^3/h)
C_S – phenols concentration (mg/L)
C_{S0} – initial phenols concentration (mg/L)
C_x – biomass concentration (mg/L)
C_{NH4} – nutrient concentration (mg/L)
T – temperature (°C)
η – phenols removal efficiency (%)

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