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Removal of ammonium for drinking water by biological treatment and by electrodialysis

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ABSTRACT

Ammonium constitutes a hampering element in the production of drinking water. It interferes with the chlorination to form chloramines so modifying the smell and the taste of the water. This paper presents the description and the optimization operations of the biggest biological treatment plant in Morocco for the elimination of ammonium in the presence of sulphides. The difficulties met and the steps taken to surmount them are described. These steps greatly improved performance but did not reach the planned and the contractual requirements. The paper also presents the preliminary results of ammonium removal by an electrodialysis pilot plant. The ED tests showed excellent performance and the water quality was significantly improved, especially the TDS.

Keywords: Ammonium; Biological plant; Performance, Electrodialysis, Conductivity

1. Introduction

Ammonium (NH_4^+) is found in ground water, primarily from the discharge of wastewater from sources such as septic systems and wastewater infiltration beds. There may be other sources of ammonium in underground and surface water such as fertilization by mineral and natural fertilizers [1]. The ammonium (NH_4^+) dissolved in ground water persisted for decades after it entered the subsurface, while other forms of nitrogen in the plume, such as nitrate (NO_3^-), have moved on with the ground water.

The presence of ammonium in water is an indicator of pollution. It constitutes a hampering element in the production of drinking water. It interferes with the chlorination to form chloramines so modifying the smell and the taste of the water. Ammonium also constitutes food for certain bacteria which can proliferate in waters. The Moroccan standard fixed the maximal acceptable value to 0.5 mg/l.

Several techniques were developed for the elimination of the ammonium, particularly chemical oxidation, ion exchange and biological filtration [2–4]. The choice of the most appropriate technique is generally dictated by the advantages and the limits of each one and especially the adaptation of the chosen technique to the specificity and the quality of raw water. Biological techniques remain the most used processes. Biological filtration sometimes presents several difficulties such as the necessity to add oxygen and food in good proportion and the vulnerability of the system toward the change in the running conditions of exploitation. This is generally translated by

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a blocking of the conversion of the ammonium and the appearance of important contents of nitrites in the outlet water. Moreover, the application of this process is complex in the case of the presence of other elements such as iron or H_2S. The reduction of these elements requires treatments in conflicting conditions to those of the treatment of the ammonium. To avoid these difficulties, more and more alternative techniques are tested such as membrane processes and particularly electrodialysis [5–8].

This paper presents the description and the optimization operations of the biggest biological treatment plant in Morocco for the elimination of ammonium in the presence of sulphides. The difficulties met and the actions to surmount them are described. The paper also presents the preliminary results of ammonium removal by an electrodialysis pilot plant.

2. Experimental

The biological treatment plant is described further. This part concerns the electrodialysis part and the analysis methods in particular.

The electrodialysis operation was carried out on a laboratory pilot plant already described [9]. This apparatus was a batch electrodialysis unit composed of ten compartments alternatively separated by cation and anion exchange membranes. The two electrode compartments are separated from the others to prevent a modification of the composition of the solution, which could be caused by electrode reactions. The circulation of water through the dilute, concentrate and electrode rinse compartments was assured by pumps. The used membranes were a conventional cationic exchange membrane CMX and an anionic exchange membrane AFN manufactured by Tokuyama Corp. The stack design characteristics of the electrodialysis pilot plant are given in Table 1.

To prevent scaling and fouling of the membranes, the polarity of the direct current was reversed at the end of each test and the stack was flushed periodically with an acidic solution in order to remove eventual precipitation of salts. During the tests, water samples are taken periodically and the ion concentrations were determined analytically. The content of ammonium was determined by colorimetric method (NFT 90-015). The other parameters were determined following Standard Methods [10].

Table 1
Stack design.

Membrane area cm^2	200
Cation exchange membrane	CMS Tokuyama Corp.
Anion exchange membrane	ACS Tokuyama Corp.
Number of cell pairs	10
Separator	PE + PP
Electrode	DSE
Flow of dilute and concentrate compartments l/h	180–200
Flow of electrode compartment l/h	150
Current max A	9
Voltage max V/Cell	1.5
Polarity reversal	Manual

Table 2
Characteristics of the feed water.

Temperature (°C)	35.2
pH	7.35
Conductivity (at 20°C µS/cm)	2870
Turbidity (NTU)	0.24
TDS (at 105°C. mg/L)	2120
TAC (meq/L)	3.8
Ammonium (mg/L)	3.48
Nitrate (mg/L)	0.04
Nitrite (mg/L)	0.04

3. Description of the biological plant

Table 2 gives the characteristics of the feed water. The organoleptic properties of the water are altered by the presence of sulphides. Their content exceeds the standards. It varies from 0.8 to 1.1 mg/l. The ammonium concentration (NH^{4+}) reaches 5 ppm. The temperature is 35°C and the water is brackish. The salinity is of 2700 mg/l. An overtaking of the iron contents fluctuating between 0.13 and 0.60 mg / l and periodic ascents of sand in some drillings of the plant were also observed.

Figure 1 gives the schematic presentation of the Dakhla plant for elimination of sulphide and ammonium. The capacity of the plant is of 110 l/s. The water is pumped from wells towards two hydrocyclones to trap the ascent sand and to avoid itentering the plant.

The following stage is the reduction of sulphides. It is carried out by aeration in two parallel basins after injection of sulphuric acid. The acidification is obligatory to maintain the pH lower than 7 (around 6.3–6.5) to transform sulphides to H_2S form which is the only volatile form. Elimination of the ammonium is carried out in six biological filters arranged in two parallel lines, where autotrophic bacteria in aerobic conditions transform the ammonium in nitrites and then in nitrates according to the following known reactions:

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$$

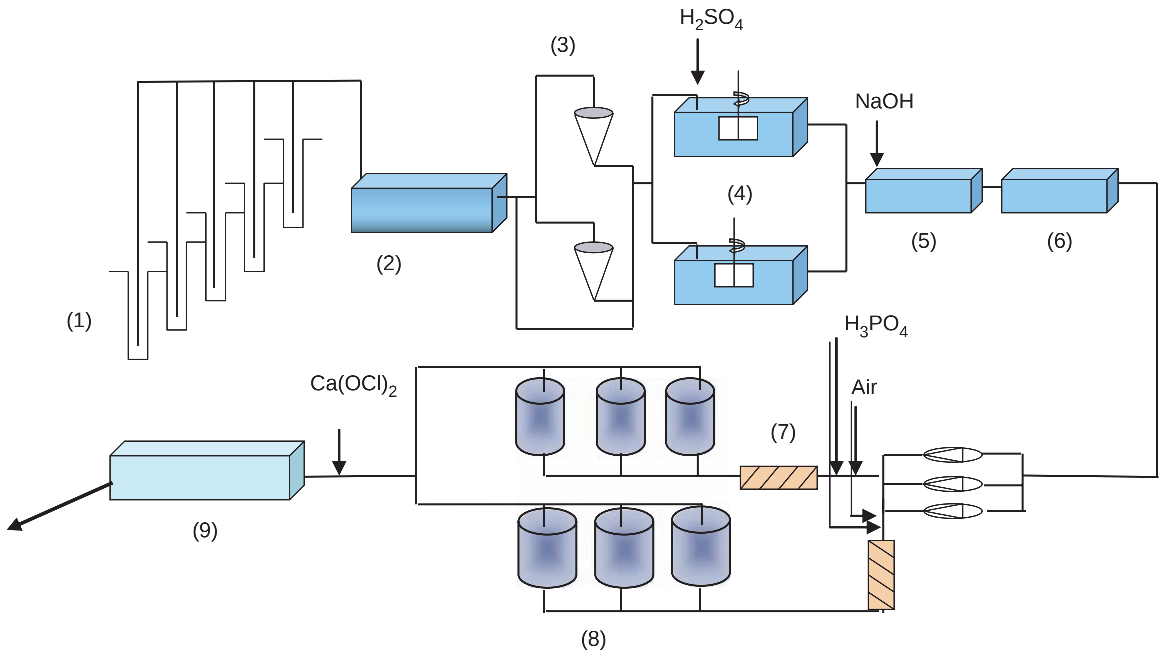

Fig. 1. Schematic presentation of the Dakhla plant for elimination of sulphide and ammonium. (1) Wells, (2) Collector of raw water, (3) Desanding pool, (4) Ventillator, (5) Baffle basins, (6) Basin plug, (7) Static mixer, (8) Biological filters and, (9) Tank of treated water.

The optimal biological activity requires an adapted temperature, a slightly alkaline pH, a sufficient nutrition for bacteria and a sufficient amount of oxygen for the elimination of ammonium. The temperature of the Dakhla water is around of 30°C. It is perfectly adapted to good biological activity. To regulate the pH at 8–8.5, NaOH is added at the exit of the basins. The nutriment and the necessary complement of oxygen for optimal bacterial activity are ensured by injection of H_3PO_4 and air upstream of the biological filters.

4. Analysis of the plant functioning and actions undertaken

To analyse the plant performance some water parameters continuously or periodically were followed—temperature, turbidity, red-ox potential, oxydability, H_2S, dissolved oxygen, NH^{4+}, NO^{2-} and NO^{3-}.

Figure 2 gives the evolution of H_2S content along the stages of treatment. The H_2S content in the feed water was of 1 mg/l.

At the outlet of the aeration basins 70% were eliminated. The residual hydrogen sulphide content was of 0.3 mg/l. The 100% rate was not reached because the plant was dimensioned for an initial hydrogen sulphide concentration of 0.8 mg/l while the real concentration was 0.8 to 1.1 mg/l. Figure 2 shows that the elimination of the hydrogen sulphide continues at the level of the works, downstream to the ponds of aeration. The hydrogen sulphide content reaches 0.08 at the inlet of bioreactors.

Figure 3 shows the variation of the ammonium content at the inlet and the outlet of biological filters, during the first seven weeks of starting working of the plant. A significant decrease in ammonium was registered. However it presents fluctuation and remains far from the ammonium planned reduction 100%.

Figures 4 and 5 show the variation of the nitrite content at the outlet of the six biological filters during the plant start-up month of September. The elimination of the ammonium which should reach the ultimate phase

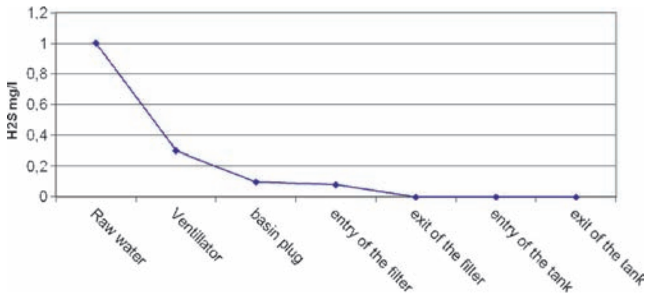

Fig. 2. Evolution of H_2S content along the stages of treatment.

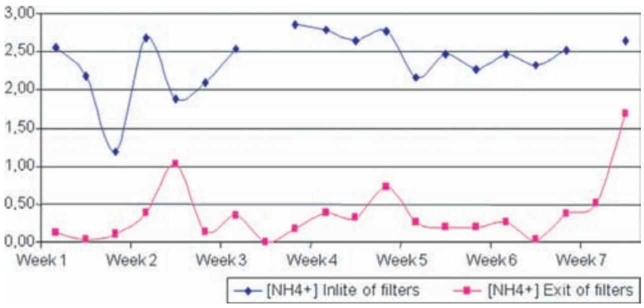

Fig. 3. Variation of ammonium content during plant start-up.

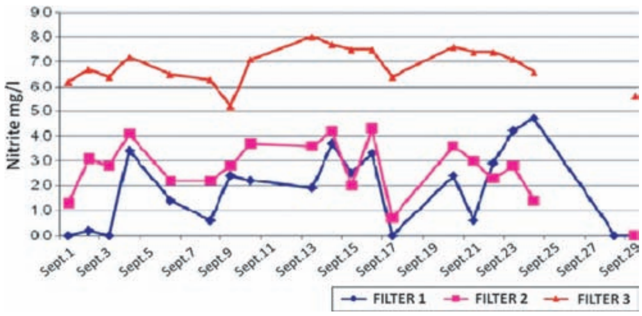

Fig. 4. Nitrite content at the outlet of the biological filters of line I.

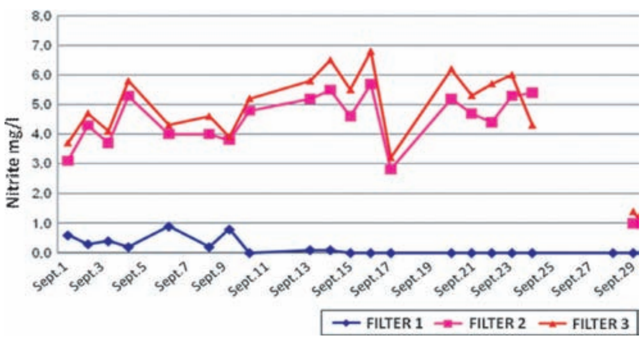

Fig. 5. Nitrite content at the outlet of the biological filters of line II.

which is the production of nitrate remained unfinished at the level of the nitrite phase. Higher values of nitrites were registered at the exit of filters reaching a maximum of 8 mg/l. Only filter 1 of line II seems to allow the total conversion of ammonium in nitrates.

Analysis of this situation shows that these dysfunctions can be attributed to the following.

- The injected air is not sufficient to ensure the needed oxygen for the elimination of ammonium. The air boosters were thus undersized.
- The distances between the injection points of air in the raw water for both lines and filters are different, 1.7 m for the line I and 6 m for line II.

Other problems and disorders were observed during the plant exploitation:

- Precipitation of calcium carbonate at the level of the pumps, leading to frequent stops of the plant for maintenance. This is attributed to the adjustment of the pH at 8.5 by injection of soda, upstream to bioreactors to ameliorate the bacterial activity.
- Important algal proliferation in the aeration pond, attributed to the strong sunshine, which can affect the good functioning of the plant.

5. Undertaken actions for optimization

Some actions were undertaken to ameliorate the plant performances, aimed mainly to improve the transfer of oxygen in water and to assure identical operating conditions for all the filters. The actions taken allowed a considerable improvement in the performance of the various filters as it shown in Figures 6 and 7.

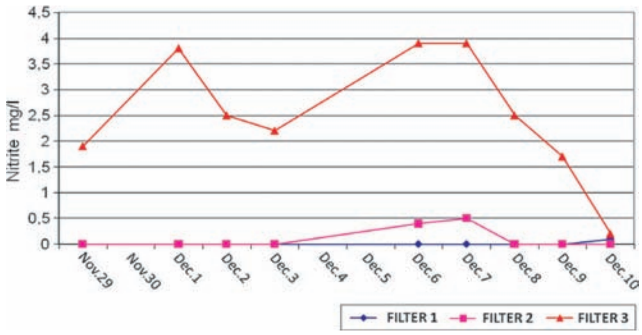

Fig. 6. Nitrite content at the outlet of the biological filters of line I.

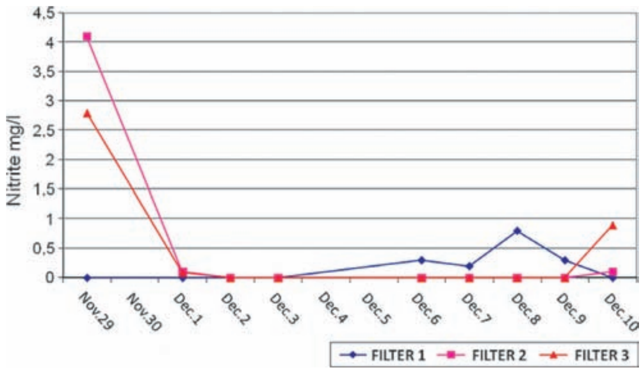

Fig. 7. Nitrite content at the outlet of the biological filters of line II.

Table 3
Variations with time of the ammonium content and of conductivity for the initial ammonium content of 3.5 ppm and for the two applied voltages.

T (min)	10 V		15 V	
	$[NH_4^+]$ (mg/L)	Conductivity (µS/cm)	$[NH_4^+]$ (mg/L)	Conductivity (µS/cm)
0	3.71	2180	3.66	2490
5	1.46	1750	1.24	1460
10	0.69	1390	0.18	760
15	0.26	1010	0.09	380
20	0.14	790	0.06	180
25	0.12	650	0.02	70

Table 4
Variations with time of ammonium content and of conductivity for the initial ammonium content of 6 ppm and for the two applied voltages.

T (min)	10 V		15 V	
	$[NH_4^+]$ (mg/L)	Conductivity (µS/cm)	$[NH_4^+]$ (mg/L)	Conductivity (µS/cm)
0	6.42	2230	5.65	2420
5	2.34	1860	1.21	1640
10	0.98	1390	0.47	1010
15	0.21	970	0.22	620
20	0.14	670	0.05	380
25	0.02	500	--------	--------

The concentration of nitrite was considerably reduced except for filter 3 of line I. However the presence of nitrites was periodically observed at the outlet of almost all the filters. At this step, it was decided to increase the dose of calcium hypochlorite as disinfection agent.

Other measures are necessary to avoid the appearance of nitrites totally and to correct the other dysfunctions:

- It is necessary to replace the current suppressors of air by others of stronger capacity. This will allow bringing enough dissolved oxygen to transform completely the ammonium to nitrates and at the same time ensure the production of saturated water by oxygen.
- Reduce the pH of adjustment below 8.5 at the outlet of aeration ponds to avoid precipitation of the calcium carbonates. However it is necessary to maintain the good conditions of bacterial development.
- Improve the elimination of H_2S by the use of the first basins of water collection from wells as the first pond of aeration.
- Set up roofs and operate regular cleanings to decrease the algal development in the aeration basins.

6. Results and discussion of the electrodialysis operation

The ED operations to remove ammonium were carried out on synthetic water having practically the same composition as that of Dakhla city. The conductivity was 2870 µS/cm and the ammonium content was 3.5, 6 and 8.5 mg/l. The tests were conducted for two applied voltages 10 and 15 volts.

Table 3 gives the variations with time of ammonium content and of conductivity for the initial ammonium

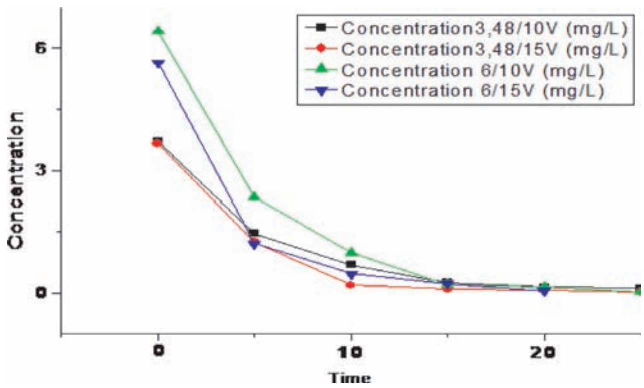

Fig. 8. Variation with time of ammonium content of the treated water.

Table 5
Final compositions of two types of treated water by electrodialysis.

	Treated water initial $[NH_4^+]$: 3.8 mg/l	Treated water initial $[NH_4^+]$: 3.8 mg/l	Treated water initial $[NH_4^+]$: 8.5 mg/l	Treated water initial $[NH_4^+]$: 8.5 mg/l
Ammonium, mg/l	0.39	0.22	0.044	0.037
pH	8.12	7.85	8.08	7.76
T, °C	19	19	19	19
Cond., µs/cm	1074	847	604	543
TA, meq/l	0.25	0.26	0	0
TAC, meq/l	0.39	0.28	0.6	0.4
Oxydab, mgO2/l	0.79	0.88	0.3	0.46
CO_3^{2-}, mg/l	0	0	0	0
HCO_3^{2-}, mg/l	0	0	36.6	24.4
OH^-, mg/l	1.87	4.42	0	0
Cl^-, mg/l	170.4	99.4	46.15	46.15
TH, meq/l	19.4	15.4	15.6	12.7
Ca^{2+}, mg/l	96.24	79.2	72	58.4
Mg^{2+}, mg/l	35.87	33.26	29.23	27.21
SiO_3^{2-}, mg/l	0.33	0.09	0.099	0.50
SO_4^{2-}, mg/l	296.53	289.81	232.15	226.52

content of 3.5 ppm and for the two applied voltages. Table 4 gives the same variations for the initial ammonium content of 6 ppm.

For the lower initial ammonium content, the standard of ammonium was reached after 11 min for 10 V and 3 min for 15 V. For the higher value, the standard was reached after 13 minutes for 10 volts and 08 minutes for 15 volts. Figure 8 shows these variations.

In both cases, the water quality was significantly improved because the removal of ammonium was accompanied with an impoverishment in salt.

Table 5 gives the final compositions of two types of treated water by ED and having an initial ammonium content of 3.5 and 8 mg/l. The four waters obtained meet the requirements of drinking water. This table shows that it is relatively easy to obtain by ED desired water with a good ionic balance corresponding to the standards of drinkability from ammonium-rich brackish water.

7. Conclusion

Studies on ammonium removal by biological treatment and by electrodialysis are conducted on underground water of the south of Morocco (Dakhla) and on synthetic water having the same composition.

Ammonium removal by a biological plant showed considerable problems attributed essentially to the underdesigned of some works of the plant. The undertaken actions to surmount these difficulties, allowed to sharply improve the plant performances. The plant performances are satisfactory but do not reach the planned and contractual requirements.

Several costly actions must be conducted to reach the planned performances. The preliminary tests of ammonium removal by electrodialysis showed encouraging excellent performance. Apart from the ammonium reduction, water quality was significantly improved especially the TDS. ED allows the obtaining of various waters having different qualities meeting the requirements for potable water.

A detailed study is in progress to complete the ED part and to test other biological solutions.

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