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Nitrates Removal from Ground Water in a Hybrid Process

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ABSTRACT. The research aimed at determining effectiveness of nitrates removal from ground water in a hybrid process of biological denitrification and microfiltration on ceramic membrane. The biological denitrification occurs with heterotrophic bacteria in an anaerobic reactor. The decrease of the ratio of dissolved oxygen in the water is necessary to start the biological denitrification. This condition is accelerated with the addition of iron metal to the water. At the end of this biological treatment, the potential bacterial contamination of treated water is so important that its disinfection becomes inevitable. The cross flow microfiltration is used as subsequent treatment to clarify the water and to remove and to retain all microorganisms. The optimum operational parameters of microfiltration on the selected membrane module were determined.

Keywords: *Bioreactor, Denitrification, Cross Flow Microfiltration.*

Introduction

Biological denitrification is the process by which the nitrate is converted to nitrogen and other gaseous end products. This process is highly selective for nitrate removal (Mateju *et al.*, 1992). There are two biological treatments to denitrify water. The first involves autrotrophic bacteria which use mineral substrate for development (Hiscock, 1991; Metcalf and Eddy, 1991; Mateju *et al.*, 1992; Montiel and Welté, 1994). These are the same as those active in certain processes of natural denitrification of water poor in organic matter (Landreau *et al.*, 1988; Mariotti, 1986; Korom, 1992). The second involves heterotrophic bacteria and requires an organic carbon source for respiration and growth (Hiscock *et al.*, 1991; Metcalf and Eddy, 1991; Mateju *et al.*, 1992). This biological denitrification is generally made in anerobic condition. Some studies have shown that adding iron to the water accelerate the reduction of the oxygen dissolved. This process brings into play first a physico-chemical process of iron corrosion followed by biological processes (Huang *et al.*, 1981; Montiel and Welté, 1994; Rahman and Agrawal, 1997; Till *et al.*, 1998). At the end of this treatment, the potential bacterial contamination of treated water is so important that subsequent treatment and disinfection of denitrified water becomes inevitable.

Literature shows that the subsequent treatment consisted generally of aeration, activated carbon filtration and chlorination (Mateju *et al.*, 1992). The results presented here reproduce the denitrification of water by metallic iron; however we use the biological treatment with heterotrophic bacteria by addition of ethanol as a source of carbon substrate; and we introduce the cross flow microfiltration as subsquent treatment, to retain all microorganisms and other particles present in the water.

Marerials and Methods

Principal Laboratory Equipments

The principal laboratory equipments used are: Biological equipment. It consists of bioreactor wih 20 L of capacity supplied by ground water rich in nitrates. It is a discontinuous process. To reduce the rate of dissolved oxygen in water we place iron in this reactor. Then we isolate it by plastic lid in order to constitute an anaerobic system. Through this lid we inject 50 ml of ethanol (Merck) by a syringe. Tbe temperature of the reactor is maintened at 25°C.

A pilot of cross flow microfiltration on ceramic membrane (Tech-Sep). It essentially consists of a feeding tank, a pump, a flow meter and a module of filtration in which is placed the membrane. The characteristics of used membrane are presented in the Table 1.

Table 1. Characteristics of membrane.

Parameters	**Membrane**
Name	Kerasep
Materials	Al_2O_3-TiO_2
Number of channels	7
Porosity	0.1 µm
Length	856 mm
Ontside Diameter	20 mm
Interior diameter of a channel	4.5 mm
Surface of exchange	0.08 m²

Iron

Iron is used as cast iron powder. It is analysed, by sweep electronic microscope (Philipps XL30). The spectra shows that iron and oxygen are the main present elements. A amount of 1100 g of iron at each experience is placed in the reactor.

Studied Ground Water

The studied ground water is taken from four forages selected for their excessive contents in nitrates as shown in Table 2.

Table 2. Concentration of nitrates in the waters of selected forages.

Forage	**Samples**	**NO_3^- (ppm)**
Ain bidha	1	100
Sfaya	2	165
Larbeus	3	170
Ain snan	4	80

Analytic Methods

Nitrates have been measured directly by UV spectrophotometer (HACH- DR4000) with a wave length of 220 nm (Benedetto, 1996). The dosage of anions (chloride, sulphate and bicarbonate) has been done by HPLC (Beckman). The dissolved oxygen has been measured by an oxymeter (Mettler). The measurement of the pH is done by pH-meter (Merk PM220).

The revelation of denitrifiant power has been detected by the reagent of Griess-Ilosways. It is a specific reagent to the nitrites, it shifts to the red color when the nitrates are reduced to the nitrites. The intensity of this coloration is proportional to the denitrifiant activity. The identification of bacteria has been nsed on galleries API. Some observations of bacteria are used by microscope of phase contrast (Olympus BX50).

Results

Characterization of Water

Table 3 presents the middle anionic composition of the ground water treated. These analyses permit to deduce that samples come from sites greatly contaminated by nitrates since the anionic mineralization is relatively important.

Isolation, Selection and Identification of Bacteria

The isolation of bacteria has been done from the ground water and from sewage collected at the exit of the station of treatment of the urban waste water. About twenty bacteria species were isolated on nitrate gelose and on cetrimide gelose. All were submitted at the test of nitrate reduction by the reagent of Griess-Ilosways. Only two bacteria species revealed intense and fast coloration. Short stick and Gram (-) were shaped. The biochemical character exam was done by technique of the galleries API which permitted us to identify these two stumps of bacteria: one is *Xanthomonas maltophilia* and the other is *Pseudomonas aeruginosa*. They belong to the same family of *Pseudomonadaceae*. This family is the frequently freestanding for its important denitrify activities (Jorgensen and Tiedje, 1993).

Table 3. The used analyses of the groundwater.

Anions	**Mean concentration (mg/l)**			
Samples	1	2	3	4
pH	7.6	7.8	7.9	8
Nitrates	100	165	170	80
Chlorides	335	400	-	50
Bicarbonates	360	265	275	-
Sulphates	450	265	240	210

Biological Treatment

Table 4 and Fig. 1 show the results obtained with biological treatment of sample N°2. We note that the nitrate content in the water drops progressively. After ten days, a very important reduction of nitrate is obtained.

Table 4. Reduction of nitrates of the sample N°2 with time.

Time (day)	1	2	3	4	5	6	7	8	9	10
NO_3 (ppm)	147	126	111	99	72	60	41	23	9.5	7
pH	8.0	8.1	8.4	8.3	8.2	7.9	8.4	8.6	8.5	-
E_H (mv)	-49	-58	-71	-68	-58	-64	-73	-84	-87	-

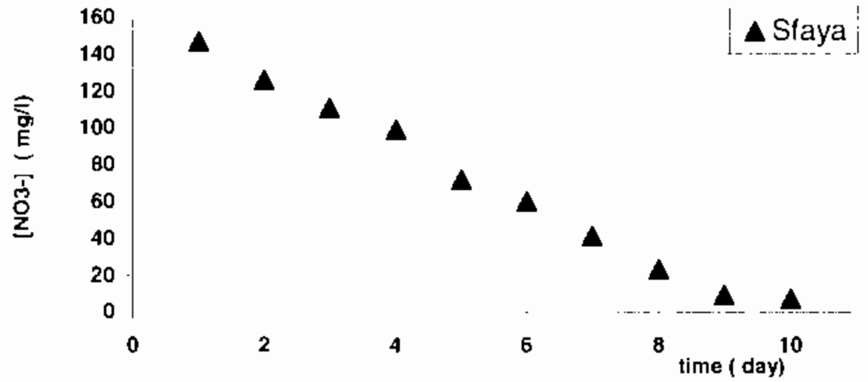

Fig. 1. Reduction of nitrates of the sample N°2 in function of time.

Similar results are obtained with the other samples (Table 5 and Fig. 2). All experiences are accompanied by an intense fizzy clearing in the reactor. These results are confirmed by analysis of the treated water by HPLC. The spectra obtained show a very strong attenuation of the peak corresponding to the nitrate.

Table 5. Reduction of nitrates of the sample N°1, 3 and 4 with time.

	$[NO_3^-]$ (mg/l)									
Time (day)	0	1	2	3	4	5	6	7	8	9
Sample 1 (Ain Bidha)	100	95	60	86	79	60	35	17	8	5
Sample 3 (Larbeus)	170	158	150	146	140	105	52	33.5	12	3
Sample 4 (Aïn snan)	80	-	-	13	-	-	-	-	-	4.8

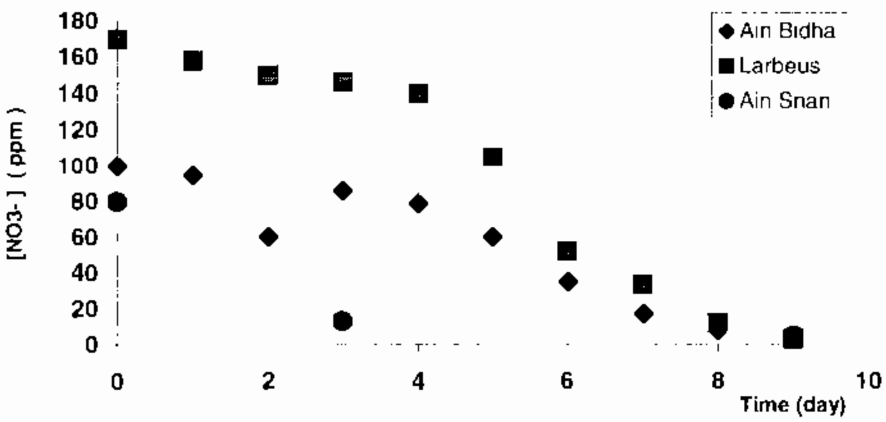

Fig. 2. Reduction of nitrate of samples 1,3 and 4 in function of time.

Cross Flow Microfiltration Treatment

The treatment of denitrified water is done with cross flow microfiltration at ambient temperature, pressure of 2 bars and speed of 2.5 m/s. The variation of the permeat flux according to time is studied with samples 1, 3 and 4 (Fig. 3). This figure shows a progressive fall of the permeat flux, followed by stabilised value at 150 L/h.m^2 obtained after about ten minutes of filtration. This fall is owed to the clog of the membrane which constitute a gate to the bacterium passage and to all other particles which have high dimension in relation to the porosity of the chosen membrane. A microscopic exam of permeat confirms the absence of bacteria or other particles of the same order of size.

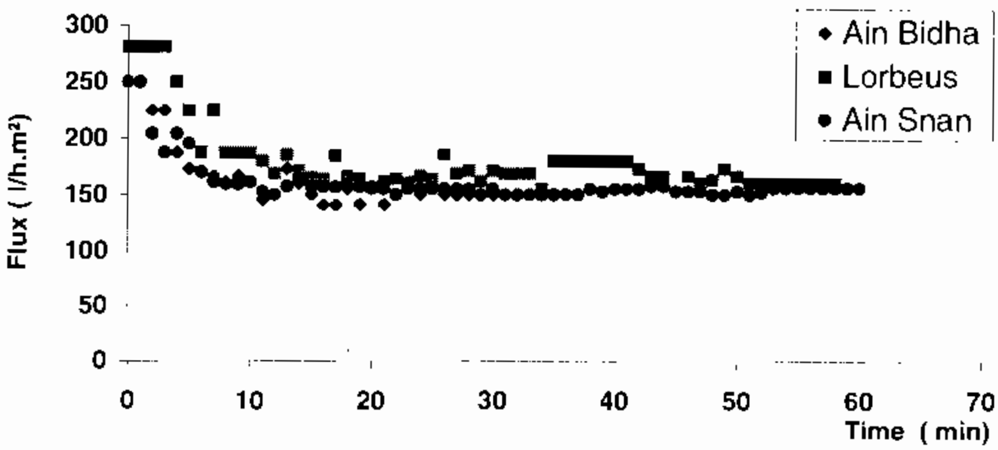

Fig. 3. Variation of the permeat flux according to time for samples 1, 3 and 4.

The analysis show that the microfiltration of samples is without meaningful consequence on the miniralisation of water, but leads to a very clear flux (Table 6).

Table 6. Mean composition of denitrified samples treated by micro filtration.

Sample	Unit	1		3		4	
		Raw	Filtrate	Raw	Filtrate	Raw	Filtrate
pH		8.2	7.7	8.2	8.1	8.2	7.8
Turbidity	NTU	88	2	76	3	90	2
Nitrates	ppm	3	2	2.5	2	4	3
Nitrites	ppm	ND*	ND*	ND*	ND*	ND*	ND*
Sulphates	ppm	458	475	246	230	203	182
Chlorides	ppm	366	328	396	356	79	91
Ammonium	ppm	2.8	3.7	10.2	22.3	4.6	7.4
Iron	ppm	0.35	ND	0.3	ND	0.22	ND

*ND No Detected.

Conclusion

This experimental study carried out the coupling of biological denitrification by heterotrophic bacteria with cross flow microfiltration. This hybrid process satisfies curent standards of disinfection and nitrate level in water. It is simple and constitute a possible alternative to the other processes since it represents an economical solution and integrates into the environnmental policy of zero reject.

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إزالة النترات من المياه الجوفية باستخدام عملية مختلطة

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المستخلص. يهدف هذا البحث لدراسة فاعلية نزع النترات الموجودة في الماء بالاعتماد على إقران عملية بيولوجية مع الترشيح الدقيق عبر غشاء سراميكي. الأجهزة المستخدمة تحتوي على مفاعل حيوي ومرشح دقيق للتيارات العابرة.

تحدث عملية إزالة النترات بيولوجيا بمفاعل لاهوائي. للإسراع في خفض نسبة الأكسجين المنحل وفي الماء تضاف مادة الحديد.

استخدمت عملية الترشيح الدقيقة لإزالة اللون وسحب المادة البيولوجية التي توجد في الماء جراء العملية الأولى.