Denitrification of Drinking Water by Hydrogenation over Pd Catalyst

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Hydrogenation of nitrates from water was performed on 0.5%Pd / granular activated carbon catalyst, using a fixed bed catalytic reactor, in continuous systems. The content of nitrate in water was established by analyzes of groundwater samples from seven drilling wells in Magurele-Lipanesti County agricultural area. The reaction mixture was analyzed spectrophotometric and by measuring of pH. The catalyst was characterized by determining the Langmuir isotherm and textural characteristics. Conversion of nitrate at 70 and 80ºC decrease with increasing of volume hourly space velocities of water with a similar slope. At a temperature of 55ºC nitrate reduction reaction does not occur. The pH of the nitrate solution processed at 70 and 80°C was basic.

Keywords : water denitrification, hydrogenation, catalyst, activated charcoal

In nature, in areas where man has not intervened, nitrates are found in soil in amounts between 0 - 2.5 mg/L - according to EPA (United States Environmental Protection Agency), WHO (World Health Organization), IARC (International Agency for Research on Cancer). When soil nitrate content exceeding 2.5 mg / L, then most likely is caused by pollution human factor.

EU Directive from 1991 about nitrates, shows that the major source of water pollution in Europe is   agricultural use of nitrates in organic fertilizers and chemical ones. Directive prescribes that the use of nitrates in organic fertilizers, especially chemical in intensive agriculture programs (started in the 60 and 70s), is the source of water pollution throughout Europe. This directive appeared need an EU legislative framework for the protection of water quality, the water sources are not restricted within national frontiers. In total of 300 Member States have developed action programs on across the EU. They recommend that water intended for infants and young children food preparation to be maximum 10 mg nitrate (NO_3) / L.

Determining the quality of groundwater deposits is a priority in environmental protection because of European legislation requiring Romanian Water Framework through Directive 60/2000 / EEC for groundwater to find solutions to improving water quality. Establishing water quality by authorities led to the identification of many areas vulnerable to nitrate pollution. Pollution quite high in some areas are agricultural works which were based on extensive uncontrolled application of organic and mineral fertilizers. Failure to report the amount of nitrogen required and the amount of nitrogen vegetable crops used as fertilizer led to groundwater pollution. The failure to comply with environmental regulations in handling and storage of manures represent another source of nitrate pollution [1].

Mohseni-Bandpi presented both heterotrophic and autotrophic processes for removing nitrate from drinking water. Carbon sources most commonly used for heterotrophic denitrification are methanol, ethanol and acetic acid. The autotrophic nitrate removal process has the advantage of not requiring an organic carbon source; The main disadvantages of this process are the slow growth rate of autotrophic bacteria and low rate of nitrate removal. The main disadvantage of ion exchange process is the obtaining of by-product, a brine rich in nitrate, chloride and sulphate, difficult to remove. Biological denitrification process has the advantage to have the final harmless Nitrates; thus it is promoted in the European Strategy process reference as opposed to alternative processes physico-chemical treatment [2].

A.I. Vasiliadou and collaborators studied hydro-genotrophic denitrification in packed-bed reactors with continuous operation. The maximum achieved at denitrification was 4.4g/L. [3] J. W. Lee presented a study at laboratory scale of hydrogenotrophic denitrification on a packed bed reactor [4].

Richard L. Smith et al performed a treatment by the bacteria that are easily found in the potable water aquifer. The bioreactor generates internal electron donor operates by gravity flow, remove the excess hydrogen dissolved in water while oxygenates this water. Much of microbial biomass was removed by sand filtration. The rate of production of hydrogen is relatively low (20 mL/min) and the total amount of hydrogen in the whole system is less than 500 ml, in order to avoid possible explosion. The bioreactor was effective in the treatment of drinking water, in particular when carbon dioxide has been added to the hydrogen input line [5].

Yan Liu et al. investigated denitrification efficiency in aqueous solutions in co-presence of synthesized zero valent nanometers iron and of previously isolated strain of YF1 (Paracoccus sp. strain). It is studied the action of various factors: oxygen, pH, temperature and corrosion products anaerobic (Fe^{2+}, Fe^{3+} and Fe_3O_4). Strain with slight toxicity increase efficiency by providing additional denitrification electron sources under aerobic conditions. Temperature and pH are the major factors affecting the removal of nitrates. Thus the removal of nitrate and cell growth took place in the pH range of 6.5-8.0, and a temperature of 25-35⁰C. Regarding anaerobic corrosion products compared to Fe^{2+} and Fe^{3+}, Fe_3O_4 promotes denitrification serving as an electron donor. The denitrification rate was increased in the range of pH 6.5-8.0 and 25-35⁰C [6]. Matthew R. et al. revealed that the addition of hydrogen gas (H_2) through gas-permeable membranes, have been shown to stimulate denitrification in a laboratory reactor [7].

Among the areas targeted with a high content of nitrates are those Buzau-Ialomita basin. Inside this basin the Magurele-Lipanesti area shows an important farmland and

livestock farms. This paper aims to study the possibility of eliminating nitrates from groundwater by finding an optimal technical and economical solution.

Experimental part
Groundwater quality monitoring
Experimental study took as its starting point the analysis of groundwater quality. Their monitoring should consider both qualitative and quantitative analysis of the water supply.

For this purpose has been taken a total of seven samples from drilling wells Magurele-Lipanesti County agricultural area. Drilling points were selected on criteria that took into account more accessible locations, optimal structural-geological and hydrogeological conditions. The drillings had maximum depth of 15 meters, crossing an alternation of clay, silty clay or sandy gravel with elements of gravel and intercalations of gravel and boulders with clay matrix.

The main directions of flowing of the aquifer currents in the feed area are from North to South, and then gradually will be NW-SE direction, according to allure of alluvial cone. Establishment of sampling sites depending on the direction of flow was performed using M3TDMS model [8]. The equation that led to the mathematical model is:

$$\frac{\partial(\omega C^k)}{\partial t} = \frac{\partial}{\partial x_i}\left(\omega D_{ij}\frac{\partial C^k}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(\omega v_i C^k) + q_s C_s^k + \sum R_n$$

where:

w is the underground porosity, dimensionless;
C^k- the concentration of nitrates in groundwater, g / L
t- time, days;
xi, j - the distance from the axis x, m;
Dij - diffusion coefficient, m^2 / s;
Vi - linear component of water infiltration rate, which includes hydraulic conductivity, m/s;
C_s^k- nitrate levels at source, mg/L;
$\sum R_n$ - chemical reaction term, $kg/m^3 s$.

The drillings monitored had an average concentration of NO3 more than 10 mg /L (monitoring criteria required by law).

Laboratory testing of catalytic hydrogenation process for obtaining drinking water
The raw materials used in experiments were granular activated carbon (Merck), electrolytic hydrogen purity from Linde company, sodium nitrate ACS reagent, ≥ 99.0% and palladium(II) chloride (Sigma-Aldrich).

The experimental program was performed in a continuous fixed bed catalytic reactor. The temperature was automaticaly regulated and the process was carried out in isothermal conditions. The measure of the reaction temperature was achieved with two thermocouples fixed, placed in the reactor jacket and with a mobile thermocouple placed in a metallic jacket in the axis of the reactor.

Reaction conditions for catalysts were:
-pressure: 5 atm;
-temperature: 55 -80^{0}C ;
-volume hourly space velocities of water (VHSV): 1.5 – 3.0 h^{-1};
-molar ratio hydrogen/ water: 2/1.

Table 1
CODIFICATION SAMPLES DEPENDING ON WORKING CONDITION

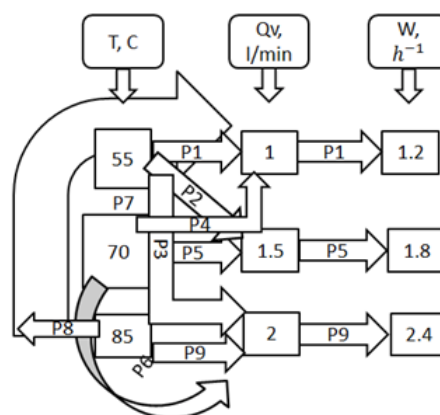| Nr. Crt.	Sample	T, °C	Qv, L/min
1	P1	55	1
2	P2	55	1.5
3	P3	55	2
4	P4	70	1
5	P5	70	1.5
6	P6	70	2
7	P7	80	1
8	P8	80	1.5
9	P9	80	2

Fig.1. Codification samples depending on working condition

The catalyst used, 0.5% Pd / granular activated carbon, was prepared by incipient wetness impregnation method. Catalyst activation occurred at 150°C for four hours in a hydrogen atmosphere.

Samples received from the reactor have received indicative of 1 to 9 according to figure 1.

The conversion was calculated by reporting the difference between the initial and final concentration of nitrates reported on their initial concentration.

The methods of analysis used to determine the physico-chemical of samples are conform to standards [9-11] (table 1).

Results and discussions
The composition of the groundwater samples collected, corresponding to the seven drillings analyzed, is presented in table 3.

According the analysis performed it is found that changes in concentrations of pollutants recorded in all the studied area shows no significant differences. This is confirmed by the migration of pollutant front on the model NW-SE direction according of the model M3TDMS.

The mean value obtained after of analyzes of groundwater samples was used to prepare a synthetic

Table 2
ANALYSIS METHODS AND APPARATUS USED FOR DETERMINING THE CONCENTRATION OF PHYSICO-CHEMICAL PARAMETER

Parameter	Methods	Equipment used
pH	SR ISO 10523 -2009	pH-meter TOLEDO
Nitrates	SR ISO7890-3:2000	spectrometer UV-VIS JENWAY

THE COMPOSITION OF THE GROUNDWATER SAMPLES TAKEN
FROM THE AREA STUDIED

Parameter	pH, mg/L	Nitrates, mg/L
1	5.80	72.8
2	5.81	61.5
3	5.76	71.5
4	5.79	70.8
5	5.8	73.2
6	5.79	72.1
7	5.72	70.9
AVERAGE	5.78	70.41

adsorption and desorption, the low hysteresis effect highlighting the microporous structure of the catalyst.

Textural characteristics of the catalyst were determined by the BET method:
- Surface area: 106.818 m² / g;
- Pore volume: 0.107 cm³ / g
- Average pore diameter: 3.294 nm.

Pore size distribution of the catalyst 0.5% Pd / C was determined by the BJH desorption method.

This figure shows a higher concentration of pore with diameter of approx. 3.3 nm. Influence of volume hourly space velocities of water charged with nitrates on the conversion of nitrates and on pH is shown in figures 4 and 5.

It shows a decrease in conversion of nitrate with increasing of volume hourly space velocities of water. The slope of temperature variation is similar for 70 and 80°C. At a temperature of 55°C nitrate reduction reaction does not occur.

The variation of the pH of the nitrate solution with volume hourly space velocities of water is reduced, the pH of the nitrate solution processed at 70 and 80 °C being basic. The pH values are similar for the two temperatures.

samples used to the achievement of the nitrate removal by catalytic hydrogenation.

Langmuir isotherm for 0.5% Pd / C catalyst is shown in figure 2. It is noted a little difference between the curve of
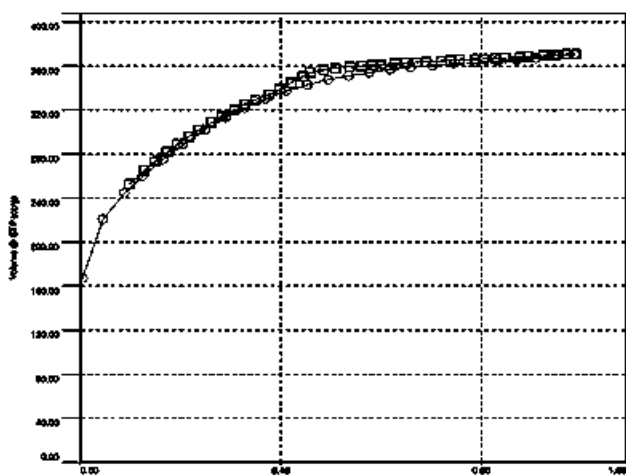
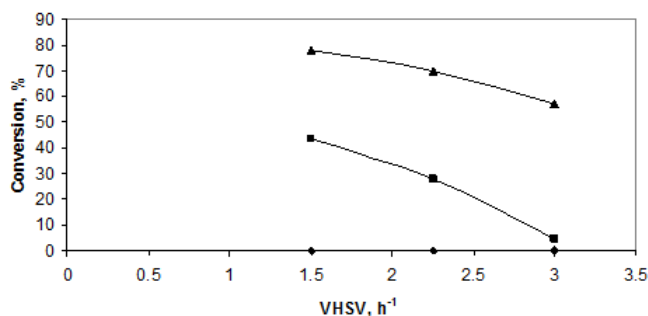Fig. 2. Langmuir isotherm for 0.5% Pd / C catalyst

Fig. 3. The pore size distribution of the 0.5% Pd / C catalyst

Fig. 4. The variation of the conversion of nitrate with volume hourly space velocities of water at different temperatures
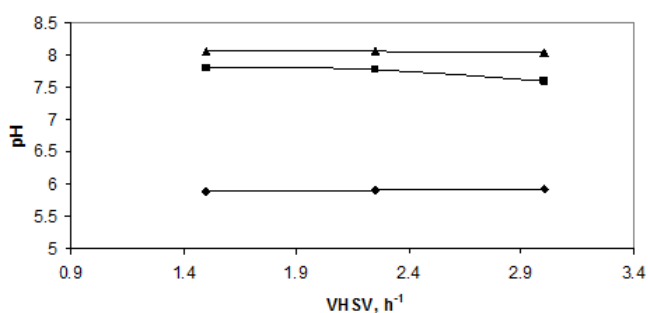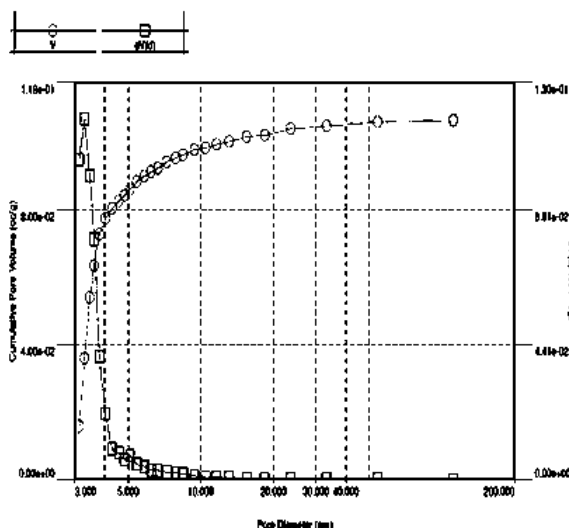

Fig. 5. Variation of the pH with volume hourly space velocities of water at different temperatures
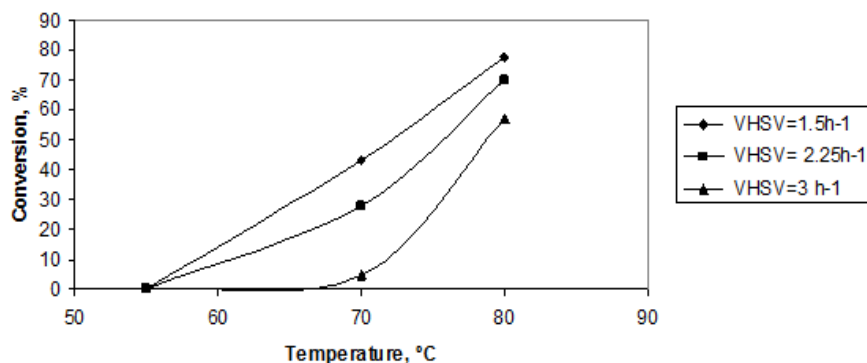
Fig. 6. Variation of nitrates conversion with temperature at different volume hourly space velocities
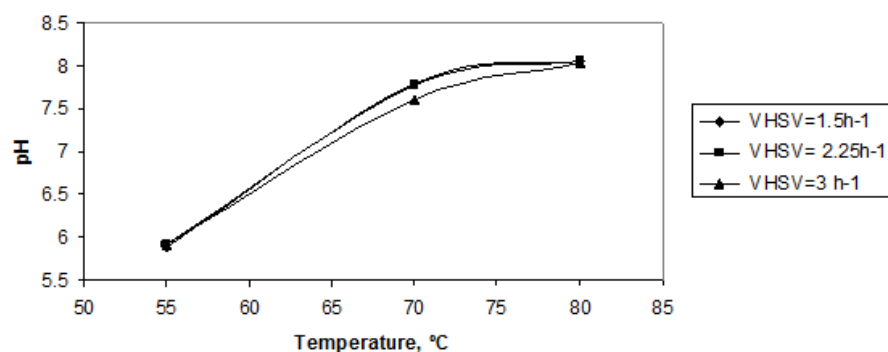

Fig. 7. Variation of pH with temperature at different volume hourly space velocities

The influence of reduction temperature of water loaded with nitrate on the conversion of nitrates and on the pH is shown in figures 6 and 7.

Observe in Figure 6 an increasing of nitrates conversion with temperature, the increased being nearly linear at low levels of volume hourly space velocities or by an exponential curve at higher values of volume hourly space velocities.

pH variation of nitrate solution with temperature arises after a slope that decreases with increasing of temperature. Differences between pH of nitrate solution after reduction for the three values of volume hourly space velocities are low.

Conclusions

Hydrogenation of nitrates from water was performed on 0.5%Pd / granular activated carbon catalyst, using a fixed bed catalytic reactor in continuous systems.

The content of nitrate in water was was established by analyzes of groundwater samples from seven drilling wells in Magurele-Lipanesti County agricultural area.

The reaction mixture was analyzed spectrophotometric and by measuring of pH.

The catalyst was characterized by determining the Langmuir isotherm and textural characteristics.

Pore size distribution of the catalyst 0.5% Pd / C was determined by the BJH desorption method.

At a temperature of 55°C nitrate reduction reaction does not occur.

Conversion of nitrate decrease with increasing of volume hourly space velocities of water with a similar slope at 70 and 80°C.

The variation of the pH of the nitrate solution with volume hourly space velocities of water is reduced, the pH of the nitrate solution processed at 70 and 80 ° C being basic.

Conversion of nitrates increase with temperature, the increased being nearly linear at low levels of volume hourly space velocities.

The experimental values determined in this study is not definitive data in determining groundwater quality in the area studied and implicitly characterize the natural background. For case studies are necessary correlations and extended areas and durations.

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