

The Study of N- NO₃ Restraint on Soil

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Abstract: The aim of this paper was to study the restraint kinetic of N-NO₃ on a sandy soil sampled from Caracal-Olt area. The kinetic study aimed to establish the interdependences between ion exchange-sorption global process and the main factors that influence the retention process on sandy soil granule level, N- NO₃ concentration and N- NO₃ soil load.

Theoretical studies present in the speciality literature lead to various kinetic models able to give a satisfactory answer for samples regarding dependence between rate determinative stage of ion exchange process and process parameters. The problem becomes complicate when it is necessary to describe mathematically mutual influence of different elementary stages, solving this kind of problems being impossible with the existing models. In this paper it was presented a methodology by which ion exchange process rate is expressed only based on experimental results, that aren't influenced by changes of ion exchange mechanism during process. The present paper initiates a new perspective in problem approach by offering a new graphical presentation of the experimental data (kinetical maps), after achieving a proper experiments time table.

Keywords: nitrate removal, sandy soil, mathematical interpretation, restraint kinetic, retention

INTRODUCTION

Nitrogen is the most important element in the plant nutrition being the determinative factor in crops development. Nitrogen is the component present in nature and in all living organisms, the semnificative quantity 97.82% from total quantity (16.25·10¹⁰ t) being under gaseous form at primary rocks level, with the smallest recycling possibility [Korom, S.F., 1992]. Nitrate contamination of drinking water occurs throughout the United States and is most frequently associated with shallow wells in agricultural areas with well drained soils (Nolan, 2002).

In the actual context, the nitrates reduction concept, refers to the processes that transform NO₃²⁻ in other nitrogen forms that are not relevant for processes in stream. In his study, Sparrow realized an approach to the problem of nitrates dilution without transformation separately. Because nitrate ion is leaching beyond roots area, denitrification is the only transformation process which offers a permanent equilibrium between gaseous nitrogen transformation and nitrogen oxides. (Korom, S.F., 2005). Mediated microbial denitrification is a process that requires anaerobic conditions, which can be classified in two types : organic electrons donor (heterotrophic bacteria) or anorganic (autotrophic bacteria). Frequently was reported that Fe²⁺ containing groundwaters have low concentration of nitrates. (Korom, S.F., 2005). The main processes present involved in nitrogen cycle: [V. Davidescu, 1976]

<i>Mineralization</i>	The process throught which an organic matter is decomposited by microbial biomass in N-ammonium.
<i>Nitrification</i>	The process that consists in the biological oxidation of ammonia to nitrate. Ammonium-N, that is not nitrificated will be aborbed by the soil.

<i>Immobilization</i>	Nitrates are absorbed and immobilized by bacteria.
<i>Leaching</i>	The process of descendent circulation of nitrates through soil profile.
<i>Ammonium volatilization</i>	Represents an ammonia gas loss. Organic fertilizers are the main sources for ammonia loss by volatilization.
<i>Denitrification</i>	Denitrification is a microbially facilitated process of dissimilatory nitrate reduction that may ultimately produce molecular nitrogen (N ₂) through a series of intermediate gaseous nitrogen oxide products. This respiratory process reduces oxidized forms of nitrogen in response to the oxidation of an electron donor such as organic matter. The process needs soil temperature raising and anarobic conditions.

Nitrates pollution is mainly due to the land cultivation. The increased use of artificial fertilizers and land cultivation lead to higher levels of nitrates that are washed from the soil into rivers, lakes, and aquifers. There they cause an excessive enrichment of the water (eutrophication), leading to a rapid growth of algae, which in turn darkens the water and reduces its oxygen content. The water purification is expensive and many plants and animals die. The high levels are now found in drinking water in arable areas. These may be harmful to newborn babies, and it is possible that they contribute to stomach cancer, although the evidence for this is unproven.

Many dispersed point sources can appear to come from one single source of diffuse pollution. Ford and Tellam (1994), for example, suggest that a general increase in nitrogen levels in the Birmingham aquifer may partly arise from ground discharges of nitric acid and nitrate compounds from metalworking industries. Small nitrate plumes from individual septic soakaways can be dispersed in the aquifer to form one observed plume. Similarly, Fukada *et al.* (2004) suggest that sewer leakage beneath UK towns tends to appear as one diffuse source. Lerner *et al.* (1999) estimated that the total annual loading of N to groundwater from the Nottingham urban area is 21 kg N/ha, comprised of leaking mains (37%), leaking sewers (13%), soil leaching (9%) and other sources such as contaminated land and industry (41%).

Nitrates effects on human health and environment

Macrophites and phytoplants growth is mainly stimulated by nutrients like nitrogen and phosphorus. Nutrients stimulate primary production and are recovered in lakes and estuaries which should be stimulated by physical factors such as: light penetration, time and available substrate and not by nutrients. Aquatic ecosystem perturbation can lead to following results:

- an habitat that becomes improper for fish species and invertebrate, leads to reduction of aquatic habitates, biodiversity and presence of some species in feed link;
- the oxygen quantity reduction that affects a series of species like fish and crustaceans;
- the high value wild fauna conservation value deterioration;
- the contribution to appearance and development of some toxic algae which are responsible for fish and crustaceans poisoning, making them improper to use for human meals and harmful in fishing industry. But it is not yet well established the relation that exist between nutrient enrichment and toxicity incidence about crustaceans from sea waters;

Vegetation production is so high that pleasure navigation or water usage becomes impossible, consequently is observed a serious impact on tourism and entertainment industry.[Rojanschi, 1997] Numerous studies have shown that the soil zone can act both as a source of nitrate and a zone of active denitrification (Parkin, 1987; Goulding *et al.*, 1993; Bakar *et al.*, 1994).

The nitrate contamination of drinking water sources is the result of the land use activities that allow nitrate and other nitrogen-based compounds to enter in the water supplies.

These land use activities include the use of synthetic fertilizers, land application of manure, and septic systems. A good management of fertilizers and manure can minimize nitrate leaching into the groundwater. Long-term source protection activities are recommended regardless of other actions taken by the purveyor, since improved source protection may eliminate the need for treatment in the future. And for that reason, was studied the retention process of nitrate ion on a sandy soil. The kinetic study aimed to establish the interdependences between ion exchange-sorption global process and the main factors that influence the retention process at sandy soil granule level, N- NO₃ concentration and N- NO₃ soil load.

The theoretical studies present in the speciality literature lead to various kinetic models able to give a satisfactory answer for samples regarding dependence between speed determinative stage of ion exchange process and process parameters. The problem becomes complicate when it is necessary to describe mathematically mutual influence of different elementary stages, solving this kind of problems being impossible with the existing models. In this paper it was presented a methodology by which ion exchange process rate is expressed based only on the experimental results that aren't influenced by changes of ion exchange mechanism during process. Present paper initiates a new perspective in problem approach by offering a new graphical presentation of the experimental data (kinetical maps), after achievieng a proper experiments time table.

MATERIALS AND METHODS

The aim of this paper was to study the restraint of N-NO₃ on a sandy soil. Experimental set-up was made on sandy soil samples drawn on following depth profiles: 0-10, 11-20, 21-30, 31-40 si 41-50 cm. The soil was sampled from Caracal-Olt area. The substances used (KNO₃) for the experiments were p.a.

The mutual influence of all factors expression by mathematical relations involves seriously complications and that's why it is necessary a high precission and accuracy experimental data, consequently the graphical solutions can reveal visibly advantages and can be used as basis for subsequent analytical processing.

The soil was dried in drying stove at 40°C for 30 minutes. The kinetic study consists in contacting 1g of soil with 500 cm³ KNO₃ of same concentration at different contact times. The same analysis was made for following concentrations: 400, 600, 800, 1000 mgN/l. Those concentration were choosen in order to observe nitrate ions retention process on soil, because nitrate ion it is well restraint on soil at low concentrations. The bottles were covered with thin sheet in order to prevent evaporation and were agitated at different times (0 minutes, 5 minutes, 10 minutes, 15 minutes, 20 minutes, 30 minutes) at 10°C and room temperature. The stirring was made with a Heidolph Unimax shaker at 300 rotation/minute. At the end of the stirring the sample were filtered and bring 50 ml. From the liquid were drawn samples in order to determine nitrate concentration [ISO 7890]. From each balon were taken 10 ml, placed in evaporation vessels and then is realised dry evaporation on water bath.

Over the residue left after the evaporation, were added 0,5 ml fenoldisulphonic acid, and then were left in repose about 15 min for sample cooling. Ammonia is added in parts of 1 ml until the colour is developed and then are analysed spectrophotometrically at $\lambda = 410$ nm in order to determine nitrates concentration in samples.

RESULTS AND DISCUSSIONS

In order to establish soil load was used the following balance relation:

$$a = \frac{V(c_0 - c)}{m_R}$$

where:

V= nitrate solution volume (500 ml)

c₀= initial concentration in mg/l

c = concentration measured at time t (mg/l)

a = soil load in mg N-NO₃/kg soil

For retention rate calculus we tried to obtain a = f(t) mathematical function type. For this reason, was used the following relation:

$$a_0 = \frac{m + nt}{p + qt}$$

For which a condition at limit is represented by initial moment: at t = 0, a = 0 → m = 0, condition considered as being acceptable because in soil were not identified NO₃ mobile or changeable forms.

Consequently, the upper relation can be written also under the following form:

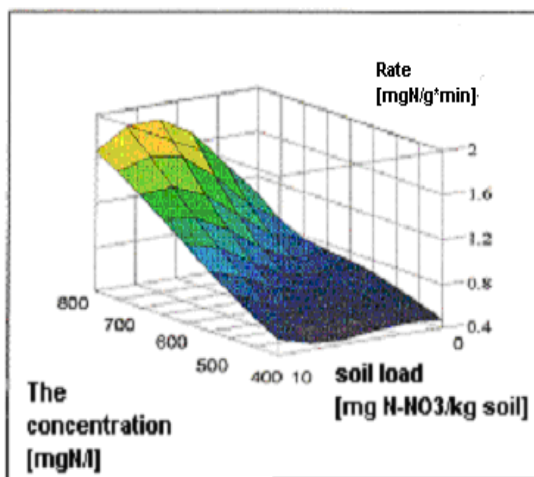
$$a = \frac{t}{At + B}$$

A and B coefficients were determined by linear regression, on the smallest square basis concordant to which the value of residual S, the square deviation sum must be minimum.

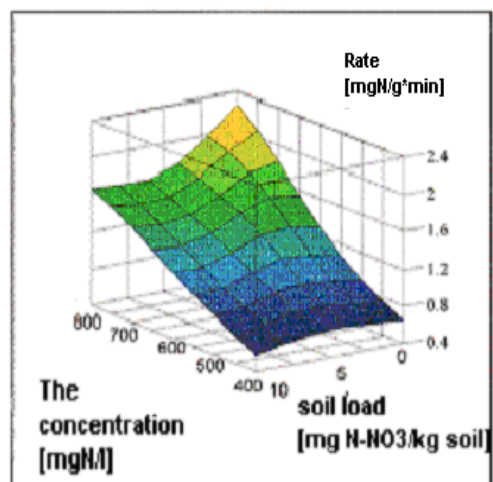
$$S = \sum_{i=1}^n (Y_i^{calc} - Y_i^{exp})^2 = \sum_{i=1}^n (A + B \cdot x_i - Y_i^{exp}) = \min im$$

which involves:

$$\begin{cases} \frac{\partial S}{\partial A} = 0 \\ \frac{\partial S}{\partial B} = 0 \end{cases} \Leftrightarrow \begin{cases} nA + B \sum_{i=1}^n t_i - \sum_{i=1}^n Y_i^{exp} = 0 \\ A \sum_{i=1}^n t_i + B \sum_{i=1}^n t_i^2 - \sum_{i=1}^n (t_i \cdot Y_i^{exp}) = 0 \end{cases}$$



a



a

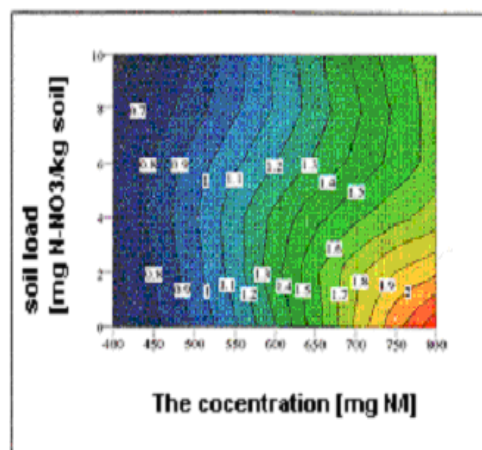
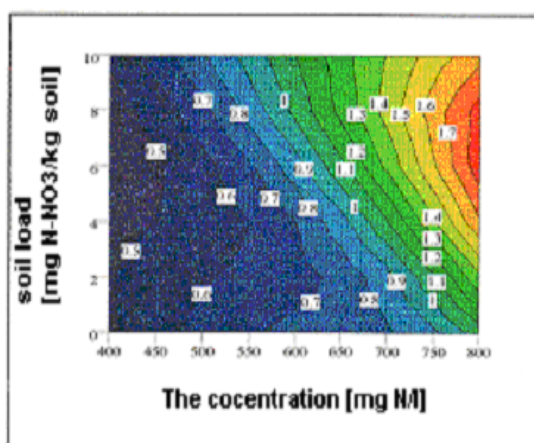
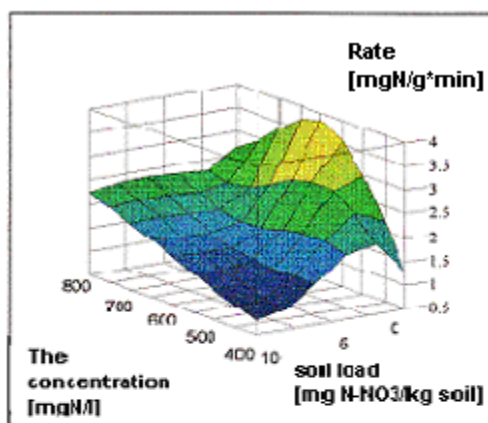
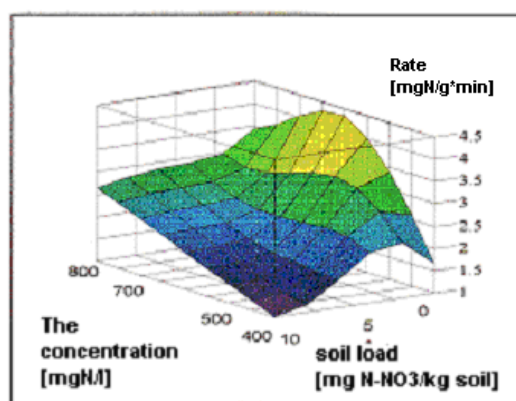


Fig. 1 Kinetic map of NNO_3 restraint on soil with depth 0-10 cm
a. Spatial representation
b. Base plane projection

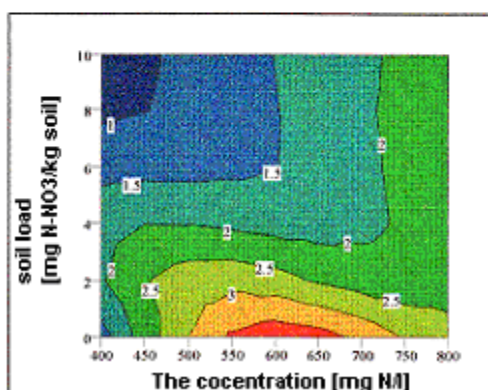
Fig. 2 Kinetic map a of NNO_3 restraint on soil with depth: 11-20 cm
a. Spatial representation
b. Base plane projection



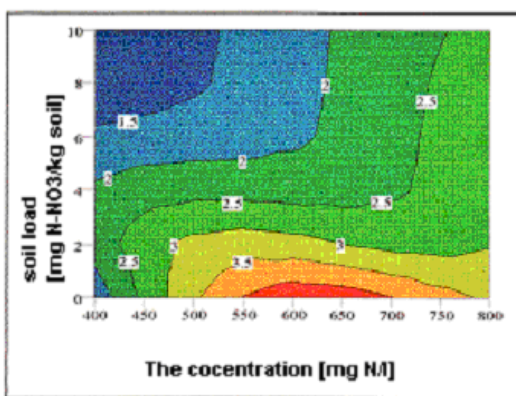
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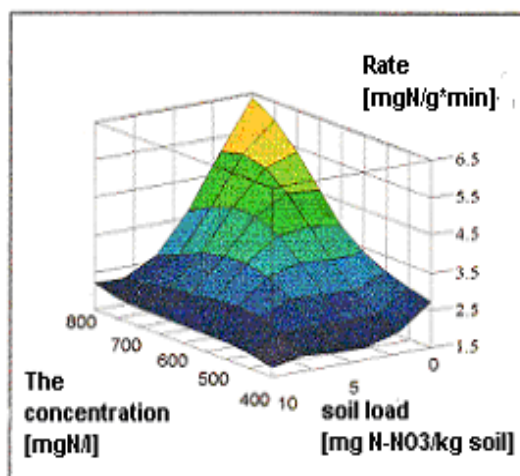
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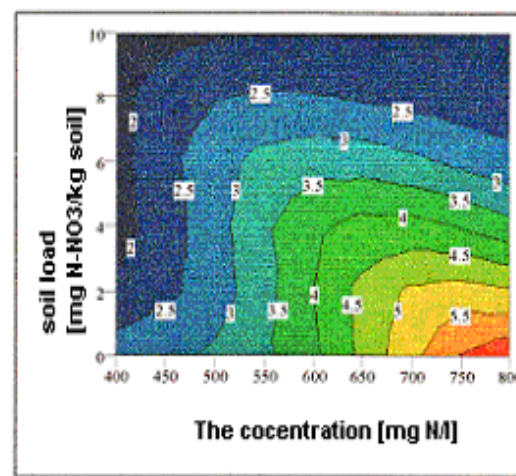
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Fig. 3 Kinetic map of NNO_3 restraint on soil with depth 21-30 cm
a. Spatial representation
b. Base plane projection

Fig. 4 Kinetic map of NNO_3 restraint on soil with depth 31-40 cm
a. Spatial representation
b. Base plane projection



a



b

Fig. 5 Kinetic map of NNO_3 restraint on soil with depth 41-50 cm
a. Spatial representation
b. Base plane projection

CONCLUSIONS

From N-NO₃ restraint on sandy soil kinetic study resulted five kinetic maps which offer informations regarding studied kinetic. In order to simultaneously watch some independent parameters influence (loading and concentration) about process rate, plane sections were represented at constant rate, resulting isokinetics curves adequate to ion exchange from hole parameter variation domain. Analyzing every kinetic map it may conclude:

- for constant load once with the concentration increase, the N-NO₃ soil load process increases
- for constant concentrations, the increase of soil load determines generally a certain variation of N-NO₃ soil load rate;
- for relative high concentrations (600* 800 mg N/1), and soils with depths (31-40 and 41-50 cm), N-NO₃ soil load rate remains appreciatively constant.

In order to prevent and stop nitrate ions into the aquifer it must install reactive barriers capable to restraint those ions, and consequently a good protection for groundwaters against pollution. is offered

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