Revista Română de Inginerie Civilă, Volumul 13 (2022), Numărul 4

Nitrates removal from water using ion exchange technologies

Eliminarea nitraților din apă folosind tehnologii de schimb ionic

Alexandru Matei[1], Elena Vulpaşu[2], Gabriel Racoviţeanu[3]

[1]Ph.D. Student, Technical University of Civil Engineering Bucharest, Faculty of Hydrotechnics, Romania
e-mail: *mateialexandru.ioan@yahoo.com*
[2]Conf.dr.chem.eng., Technical University of Civil Engineering Bucharest, Faculty of Hydrotechnics, Romania
e-mail: *vulpasu@utcb.ro*
[3]Prof.dr.eng., Technical University of Civil Engineering Bucharest, Faculty of Hydrotechnics, Romania
e-mail: *gabriel.racoviteanu@utcb.ro*

DOI: 10.37789/rjce.2022.13.4.2

Abstract. During the last decades, ion exchange materials technology has evolved from laboratory to industrial use with significant technical and commercial impact. The goal of this paper is to briefly review the ion exchange technologies used for nitrate removal from water intended for human consumption. The following information will be provided: a brief history of ion exchangers, design considerations, process considerations, advantages, disadvantages, process performance, costs and examples of water treatment plants across the Globe that use ion exchangers technology for nitrate reduction. Also, the experimental results regarding the influence of competitive ions on the nitrogen ion retention efficiency on a specialized ion exchange resin will be presented.

Keywords: Ion exchange, Nitrates, water treatment, Pollution

1. Introduction

Nitrogen compounds in natural waters (surface or groundwater) exist in several forms, depending on the level of pollution and depending on the presence or absence of oxygen.

The forms under which nitrogen compounds appear in water are molecular nitrogen, organic nitrogen, ammoniacal nitrogen, nitrates and nitrites.

High concentrations of nitrates in water can result from direct water pollution such as pollution from agriculture through intensive use of nitrogen-based fertilizers or indirectly through the release of organic substances that release nitrogen compounds in a lower state of oxidation by decomposition, which then, through bacterial oxidation, leads to the formation of nitrates.

Normally, the concentration of nitrogen compounds in surface waters is low, ranging from 0-18 mg/l, but can reach much higher values in the case of farms, industrial discharges or discharges of insufficiently treated wastewater. Also, the concentration of nitrates can fluctuate seasonally.

In most European countries, the concentration of nitrates in raw water has gradually increased in recent decades.

The concentration of nitrates present in groundwater is dependent on the geology of the aquifer. In the case of waters containing nitrates of natural origin, the recorded concentrations do not have values higher than 4-9 mg/l. In the case of aquifers located in areas where intensive agriculture is practiced, the nitrogen concentrations recorded can reach hundreds of milligrams per liter. For example, in agricultural areas in India, values of 1500 mg/l have been recorded [1].

Nitrogen compounds endanger human health. Nitrates ion is a less dangerous form for adults, but for newborn's, it can cause methemoglobinemia - "blue baby syndrome". Nitrates as such are not toxic, for becoming dangerous to the newborn's body, they must be converted into nitrites. Once in the blood, nitrites combine with hemoglobin, forming methemoglobin, which creates an oxygen deficiency in the body. Methaemoglobin is oxidized and cannot act as a carrier of oxygen in the blood.

Nitrites are formed by the reaction of nitrate with saliva in most cases. In infants under one year of age, however, the relatively alkaline conditions in the stomach allow bacteria to form nitrites. Up to 100% of ingested nitrate is reduced to nitrite, compared to 10% in adults and children over one year of age.

Nitrosamines and nitroamides are formed when nitrates or nitrites are administered with nitrosatable amines, such as amino acids in proteins. However, epidemiological studies, mainly on gastric cancer, have not yielded consistent results. Studies on the carcinogenic effect of nitrates are currently being reviewed.

A balanced diet, adequate in vitamin C, can partially protect against the effects of nitrate–nitrite intake [2].

In Romania, the maximum allowable limit for nitrates in drinking water is 50 mg/l, according to law 458/2002 [3], the same value that is recommended by the World Health Organization (WHO, 2011). Also, the 2184/2020/EU Directive impose a maximum allowable concentration of 50 mg/l for nitrates in water intended for human consumption. According to the EPA, the maximum allowable limit for nitrates in drinking water is 10 mg N/l.

2. Nitrates removal technologies

As stated, an increase in nitrate concentrations of water is observed worldwide. Over time, several methods have been developed to reduce the concentration of nitrates in water for human consumption. The main treatment processes applicable to sources that exceed nitrates are:

- Biological processes – are based on the development of a specific biomass. For maintaining it, a food source must be added, usually methanol, increasing the concentration of total organic carbon and the risk of the formation of THM, in case of chlorine use for disinfection, which are susceptible of being carcinogenic. The process must be controlled rigorously, is very sensitive to inhibitory substances, the initiation of the process with biomass recovery takes about a month and if the biomass is lost, the process must be stopped during its regeneration [4];
- Reverse osmosis - is a physical process that involves forcing the water through a semipermeable membrane. The process takes place at high pressure levels, higher than the osmotic pressure, leading to a high energy consumption. From the process results ultrapure water (65% and 80%) and concentrate (20% -35%), regardless of the quality of raw water. The main problem is the concentrate, which must be treated, and managed properly [5.6];
- Electrodialysis - is suitable for low flows. Electrodes are inserted into the volume of water and a direct or alternating current is applied between the electrodes, thus leading to water electrodialysis [7, 8];
- Ion exchange - the process is relatively stable, but it can only work automated because the concentration of nitrates in the effluent is variable over a cycle, increasing progressively with the reduction of exchange capacity. For denitrification, masses of ion exchangers are especially dedicated to nitrate retention.

2.1 Ionic exchange

Ion exchange is a reversible reaction in which a target ion in the aqueous phase is transferred to a solid phase and exchanged with a like-charged ion that diffuses into solution [9].

Usually, the process is used for water softening, where calcium, magnesium and other polyvalent cations are exchanged for sodium [10]. The technology has high treatment capacity, high removal efficiency, fast kinetics and can be utilized for water reuse, which has a significant economic importance [11].

In water treatment plants, ion exchange is also used to remove specific contaminants such as nitrate, arsenic and radium [10].

2.1.1 Types of ion exchangers

In general, any water-soluble ionic compound has the property of ion exchange. Ion exchangers can be:

- Organic ion exchangers;
- Mineral ion exchangers.

Mineral ion exchangers were the first substances used for the ion exchange process. They are called zeolites and their general formula is:

$$Me_{2/x}O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O \text{ [7].} \qquad (1)$$

Although inorganic ion exchange materials were first to be recognized, they lost their utility after the discovery of organic resins due to their relatively low ion exchange capacity and chemical instability. Zeolites have been gradually replaced by synthetic resins due to their faster exchange rates, longer life and much higher treatment capacity. Currently, ion exchange resins are used. They consist of two main structural components: the resin support and the functional groups that participate in the ion exchange process.

The resin support has to maintain the mechanical and chemical stability. The functional groups have an acidic or basic character that can be strong or weak and ensure the electrostatic interaction with ions of opposite sign in the proximity. They react both with ionic species in their vicinity and with neutral molecular species, such as water, through ion-ion or ion-dipole interactions [6, 7, 10].

Ion exchange resins can be found in two forms, in the form of gel and macroporous or poorly crosslinked. Their structure is practically identical, in both cases, they are obtained by copolymerization, the difference between them is given by the porosity.

Gels have a natural porosity that results from the polymerization process and is limited to the distance between the molecules that make up the gel. Macroporous resins have a high porosity resulting from their artificial growth by using substances specially created for this purpose. These resins have larger channels called macropores that have a higher capacity to absorb organic substances [5]. An ion exchange resin consists of a three-dimensional, cross-linked polymer matrix of hydrocarbon chains carrying fixed ionic groups, the electric charge of which is compensated for by mobile ions of opposite charge (“counterions”). The usual matrix is polystyrene crosslinked with divinylbenzene of 3 to 8%, to provide structural stability.

Counter ions are free to diffuse. When the resin comes in contact with an electrolyte solution, the resin takes up the solvent and some additional mobile ions that have the same charge sign as the fixed ionic groups.

In the process, the counter ions present initially in the resin are replaced by another species of ions.

2.1.2 Properties of Ion Exchange Resins

The most important properties of resins are exchange capacity, selectivity and structural stability.

Exchange capacity – the quantity of counterions that can be exchanged onto the resin is one of the major considerations when selecting an ion exchange resin [10].

The exchange capacity is a measure of how many ions the resin can capture per unit volume [7].

The exchange capacity can be reported as milliequivalents per gram of dry resin or milliequivalents per millilitre of wet resin. The typical dry-weight capacity of a strong resin is situated in the range of 3.6 to 5.5 meq/g [10].

Selectivity – Ion exchange resins have a variable affinity for the ions in solution. Selectivity can be expressed as a selectivity coefficient (Kji) where "I" represents the cation (or anion) and "j" represents the exchanged ion. The greater the selectivity coefficient is, the greater is the preference for the ion by the exchange resin. For process design considerations, usually, separation factors are used rather than selectivity coefficients. The separation factor is a measure of the preference of one ion for another ion and can be expressed as:

$$a_j^i = \frac{Y_i X_j}{X_i Y_j} \qquad (2)$$

Where:
a_j^i= separation factor;
Yi= resin phase equivalent fraction of counterions;
Xj= equivalent fraction of presaturant ion in aqueous phase;
Yj= resin phase equivalent fraction of saturated ions;
Xi= equivalent fraction of counterion in the aqueous phase. [10]

Structural stability and Service life – a lot of issues can occur in the operation of ion exchangers technology like resin bead compression that can lead to inadequate liquid distribution and reduced flow, swelling, shrinking, oxidation of the resin beads, etc.

Some of these issues can be avoided by selecting an appropriate resin, based on the quality of the raw water and selecting a proper pretreatment process [10].

2.1.3 Process operation

Commonly, the following steps are used in an ion exchange cycle:

1) Service – The raw water is passed through the ion exchange unit until the effluent is exceeding the designed limit of the pollutant intended for treatment. The unit is then taken out of service for the regeneration of the resin.

2) Backwash – water is introduced in the unit and it flows up through the bed until it is expanded by 50 percent. This step is used for removing any suspended solids that have accumulated through the cycle.

3) Regeneration - is a process that involves removing retrained ions from the in-service service from the fully loaded resin beads so the resins can be reused. It can be regenerated using a high concentration of salt or other regenerant chemical compound [12]. Depending on the flow direction of the regeneration solution, there are two methods:

- Co-current regeneration - the regenerating substance flows in the same direction as depletion;
- Counter current regeneration - the regeneration solution flows in the opposite direction to the depletion of the resin.

Co-current regeneration consists in bringing the concentrated solution with A ions in contact with the upper layers of the exchanger, saturated with B ions. They migrate into the lower layers of the resin (not yet exhausted) that can capture B ions. Total regeneration, the resin assumes a double ion exchange process. [5]. If the amount of regeneration solution is limited, the B ions will not be completely removed from the exchangers, and the lower layers will not be completely regenerated, leading to a shorter operating time than in the previous cycle and / or a quality weaker treated water than the previous cycle. The following figure schematically shows the co-current regeneration process of ion exchange resins.

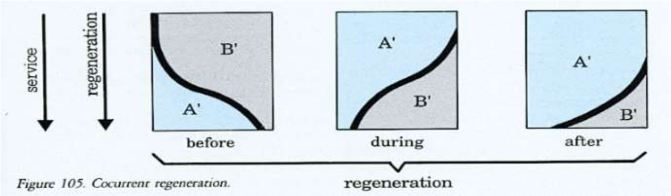

Figure 1. Co-current regeneration [5].

Counter current regeneration is different from co-current regeneration by the way of introducing the concentrated solution. Thus, counter current regeneration consists in bringing the concentrated solution with A ions in contact with the lower layers of the exchanger, unsaturated with B ions. In this case, B ions will be eliminated more easily because they cannot be regenerated in the already depleted layers and thus ensure a higher volume of regenerated resin that can be used in the next cycle, compared to current regeneration [5].

In conclusion, counter current regeneration confers a much higher efficiency in terms of the amount of resin regenerated compared to co-current regeneration [5].

The main advantages of counter current regeneration are:

- high efficiency and low amounts of reagent;
- better quality of treated water because the lower layers are regenerated with a larger amount of regenerating solution.

The following figure schematically shows the counter current regeneration process of ion exchange resins.

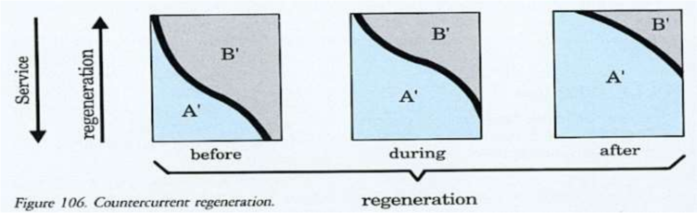

Figure 2. Counter current regeneration [5].

4) Slow rinse – Rinse water is passed through the unit using the same flow direction as the regenerating flow rate for pushing the regenerating chemicals through the bed.

5) Fast rinse – Final rinse step, consists of rinse water at the same flow as the service flow rate for removing any remaining regenerating solution.

6) Return to service.

The following figure presents a typical ion exchange unit.

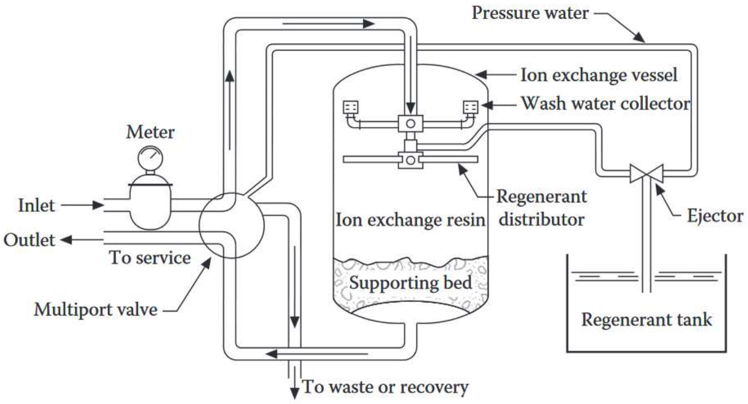

Figure 3. Typical ion exchange unit [13].

2.1.4 Brine disposal

The solution resulting from regeneration, which contains high concentrations of salt and ammonium, is a waste that can create complications in management because it is hardly accepted in a treatment plant. For small household units, it has an insignificant impact on the wastewater treatment plant but for larger municipal systems, the problem is much more significant.

The alternative solutions for the evacuation of brine resulting from regeneration are the evacuation in the seas and oceans, the injection in deep wells and their use as fertilizer (depending on the substances dissolved in the regeneration solution). The solution for brine disposal is site-specific and has to be considered very early in the design process because it can be very expensive.

2.1.5 Ion exchangers used for nitrate removal

Now, ion exchange is the most used method for the removal of nitrate in potable water treatment.

The process involves passage of nitrate loaded water through a resin bed that contains a strong base anion exchange resin on which nitrate ions are exchanged for chloride until the resin is exhausted [14].

The relative order of affinity for the three most common ions in drinking water compared to nitrates is Sulphate > Nitrate > Chloride > Bicarbonate [15]

2.1.6 Design consideration

There are various tools used for assisting ion exchange design, like CADIX and Ion Exchange calculator [7].

The key considerations in the application of ion exchange to nitrate removal, according to California's State Water Resources Control Board – Drinking water treatment for nitrate are presented in the next table:

Table 1.

Summary of design considerations for conventional ion exchange [7].

Applications	Main considerations
Resin Selection	• Generic SBA resins for maximum exchange capacity (for low sulfate) o Less expensive than nitrate selective resins o Less frequent regeneration due to higher capacity (in the absence of co-contaminants) o Nitrate dumping potential •Generic SBA resins for maximum exchange capacity (for low sulfate) o Less expensive than nitrate selective resins o Less frequent regeneration due to higher capacity (in the absence of co-contaminants) o Nitrate dumping potential •Nitrate selective resins to avoid nitrate dumping (for high sulfate) o More expensive than generic resins o Longer bed life o More nitrate removed per unit of waste brine
Pretreatment	•Filtration to remove iron, manganese, TSS, and organic matter to prevent resin fouling •Water softening (antiscalant, acid, or water softener) to prevent scaling •Dichlorinations to prevent resin oxidation
Post-Treatment	•Chloride: alkalinity ratio •Chloride: sulfate ratio and galvanic corrosion •Potential: pH adjustment and restoration of buffering capacity to avoid corrosion
Chemical Usage	• pH adjustment (caustic soda or soda ash) • Regenerant brine, salt consumption
O&M	•Frequency of regeneration depends on water quality and resin type •Fresh brine preparation and waste disposal •Resin loss and replacement: 3 – 8 years lifetime

Applications	Main considerations
	•Continuous or frequent monitoring of nitrate levels •Backwashing to dislodge solids
System Components	•Fixed bed versus continuous regeneration •Key system configuration parameters are system flow rate, bed swelling, bed depth, backwash flow rate, and rinse requirements o Vessels in parallel or in series o Co-current or counter-current regeneration
Waste Management and Disposal	•Significant cost of waste brine disposal is of greatest concern for inland systems •Close proximity to coastal waters is beneficial for brine disposal •Management options can include sewer or septic system, drying beds, trucking offsite, coastal pipeline, deep well injection, and advanced treatment •Disposal options can be limited by waste brine water quality (e.g., volume, salinity, metals, and radionuclides) •Optimization of recycling and treatment of waste brine is desirable.
Limitations	•Need to manage resin fouling o Hardness, iron, manganese, suspended solids, organic matter, and chlorine •Competing ions (especially sulfate) •Disposal of waste brine •Possible role of resin residuals in DBP formation

2.1.7 Treatment plants that use ion exchangers for nitrate reduction

The reduction of nitrate from water supply sources by means of ion exchangers began in France in 1985. Since 1989 there are 6 treatment plants with ion exchangers in operation with flow values ranging between 10 m^3/h and 600 m^3/h.

Technologies of ion exchange-based denitrification have been developed in France and include the AZURION, ECODENIT and NITRACYCLE systems [6].

The ECODENIT system

It was developed by OTV and is used for nitrate reduction at the treatment plant of Binic, a locality situated in the western region of France.

The treatment plant treats a flow of 160 m^3/h, the source being surface water with a concentration of nitrate ranging from 45 to 100 mg NO3-/ l, with a maximum value of 165 mg NO3-/l.

The plant consists of three beds with ion exchangers, each containing 2700 l of natural resin Dowex SRBP. Before entering in the ion exchange step, the water is pretreated using a unit of coagulation, decantation and filtration.

After the process, 75% of the nitrates are reduced, along with 90% of sulphate ions and 30% of bicarbonates.

The brine which results after regeneration is transported to the nearest wastewater treatment station that accepts it. The volume of brine is approximately 55 m^3/day and it contains 450 kg/day NO3- and 516 kg/day Cl- [6].

The same system is used in Pleven, another locality from France. The raw water has a concentration of 70 mg/l of nitrate. In the treatment process, only a part of the whole volume of raw water is treated by ion exchangers. The treated water is blended with raw water so that the resulting nitrate concentration is below 25 mg/l [6].

The NITRACYCLE system

It was developed by S.A.U.R. (Société d'Aménagement Urbain et Rural) – a French group operating in the water sector, whose main activity is the delegated management of services to local authorities and is a major player in the market of engineering and construction related to water treatment [16].

In this process, a macroporous resin is used to reduce nitrates in the water. The process consists of repeated operating cycles in the following order: treatment, prewash, regeneration and washing. Regeneration is performed counter current.

The used regenerant is usually discharged into the local sewer system. The brine generally contains sodium (15 g/l), chloride (13 g/l), nitrate (12 g/l) and sulphate (5 g/l). Since 1990, eight NITRACYCLE systems have been in operation; 6 for drinking water sources and 2 for the treatment of water used in the food industry. Drinking water treatment plants are located in France. Their characteristics are presented in the following table.

Table 2.

Nitracycle treatment plants [6].

Treatment plant	**Capacity (m^3/h)**	**Nitrate (mg/l)**		**Efficiency**
		Raw water	**Effluent**	
Plounevez – Lochrist	50	120	25	79%
Grez en Bouere	60	70	35	50%
Souppes sur Loing	120	60	25	58%
Ballee	60	80	25	69%

The Azurion system

It was developed by Degremont and it is used in Ormes-sur-Voulzie, near Paris and Plouenan, Brittany. Both were commissioned in 1987.

The Ormes-sur-Voulzie treatment plant has a capacity of 27 m^3/h. The average concentration of nitrates in raw water is 60 mg/l. After the treatment process, the amount of nitrates in effluent doesn’t exceed 25 mg/l.

The Plouenan treatment plant has a capacity of 600 m^3/h. Raw water comes from a surface source. The average concentration of nitrates is 80 mg/l. During the treatment process, only a part of the volume is treated by ion exchange. The treated water is then blended with raw water (that by-passed the ion exchange unit), resulting in a concentration below 25 mg/l nitrates in distributed water. The solution resulting from regeneration is discharged in the sea.

For both treatment plants, the countercurrent regeneration is used for regeneration [6].

In the USA, there are 12 treatment plants in which ion exchange is used for denitrification. The flow values are ranging between 7.4 m^3/h (Ellsworth, Minnesota) to 1,577 m^3/h (Des Moines, Iowa) [7].

The city of Ohio treatment plant

The City of Ohio public works operates a groundwater source impacted by nitrate pollution. The amount of nitrate in raw water is ranging between 40 and 100 mg/l. The water also contains perchlorate. The capacity of the treatment plant is 1,135 m^3/h.

Ion exchange and blending are used to address high nitrate and perchlorate levels. Treated water from the Metropolitan Water District of Southern California (3 parts) and treated water from the Chino Basin Desalter Authority (1 part) is used for blending, for achieving a maximum nitrate concentration of 36.3 mg/l in drinking water. The system was commissioned in 2006.

Waste brine is sent to the LA County Sanitation District, with a total disposal cost of 50,000$ per year [7].

Indian Hills

The Indian Hills Water District operates a groundwater well which has a capacity of 12 m^3/h. Because the well has historical nitrate concentrations ranging from 12 mg/l to 16 mg/l as N, the District has implemented a countercurrent ion exchange that uses a Magnetic Ion Exchange resin in a series of fluidized beds which reduce the brine generation.

The magnetized resin encourages agglomeration of loaded resin particles and a faster settling. The loaded resin is removed from the bottom of the Ion exchange unit and it is passed to regeneration. Regenerated resin is continuously added to the top of the unit. Using this configuration, the risk of nitrate spiking is reduced. Also, the competing ions, like sulphate can be removed early on the resin vessel. Regeneration is performed continuously in small batches, the number of regenerations per day depends on the system's flow rate.

The waste brine is stored in an underground storage tank. Periodically, the brine is pumped from the tank and it is land applied [7].

3. Materials and methods

The experimental trials were performed on two samples of synthetic water prepared from distilled water in which NO3-, SO42-, HCO3- ions were added, using different concentrations so the influence of ions that compete with the nitrate ion in the ion exchange process can be highlighted.

Table 4.

Characteristics of synthetic water.

No.	Item	U.M.	Sample 1	Sample 2
1	NO_3^-	mg/l	100	100
2	KNO_3	mg/l	163	163
3	SO_4^{2-}	mg/l	130	165
4	K_2SO_4	mg/l	181	271
5	HCO_3^-	mg/l	103.7	201.3
6	$NaHCO_3$	mg/l	138	276
7	pH	mg/l	9.1	8.6

The A520 E Purolite ion exchange resin was used to perform the experiment. This is a macroporous resin, strongly basic, which is specially designed to retain nitrates from water.

An installation consisting of glass mini-columns with porous glass drainage was used. 25 ml of resin was introduced into it. The flow rate through the columns was adjusted to 26 ml/min.

The experimental setup is shown in the following figure.

Figure 4. Experimental setup.

After the following volumes of water passed through the column, samples were collected:

- 250 ml (10 BV);
- 1250 ml (50 BV);
- 2500ml (100 BV);
- 5000 ml (200 BV);
- 7500 ml (300 BV).

For every sample, the following ion concentrations were determined: nitrates, bicarbonates, sulphates and chlorides.

The concentration of nitrates and sulphates was measured using a spectrophotometer, HACH DR3900 and the bicarbonates concentration was determined using the volumetric method, according to SR EN 9963-1/2002.

4. Results and discussions

The results showed that in the first phase of the process nitrates and sulphates are retained with great efficiency, reaching concentrations of 2-3 mg/l after passing a volume of water equal to 50 times the volume of resin (50 BV), regardless of their initial concentration. After this threshold, the concentration of nitrates begins to increase slightly, which indicates a decrease in the exchange capacity of the resin. After passing a volume of water equal to 300 BV, the concentration of nitrates in the effluent reaches close to the limit imposed for drinking water (50 mg/l).

The sulphate concentration increases relatively rapidly after the threshold of 50 BV, reaching the initial concentration after 300 BV for the first sample, respectively after 200 BV for the second sample. For the second sample, it is found not only that there is no exchange of the sulphate ion in the water with the chloride ion grafted on the resin but also an elution of it (ratio C/C0> 1).

For the bicarbonates, it was found that there is a retention of them up to half of the initial concentration, followed by a sudden increase in the effluent concentration so that after 100 BV the bicarbonate concentration in the effluent becomes equal to the concentration of the influent.

The following figures show the variations of the concentrations depending on the volume of water passed through the column and the variation of the C/C0 ratio of the volume of water passed through the column expressed in BV.

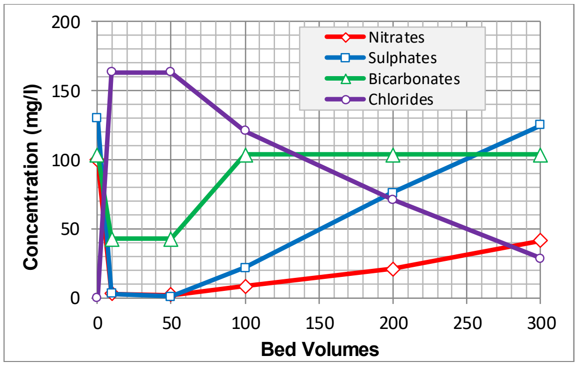

Figure 5. Concentration of indicators depending on the volume of water passed through the column - SAMPLE 1.

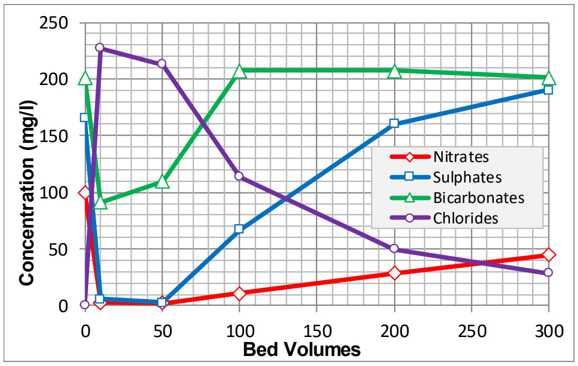

Figure 6. Concentration of indicators depending on the volume of water passed through the column – SAMPLE 2.

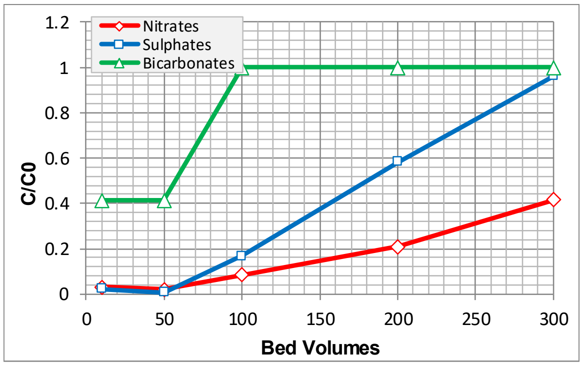

Figure 7. C/C0 variation depending on the volume of water passed through the column - SAMPLE 1.

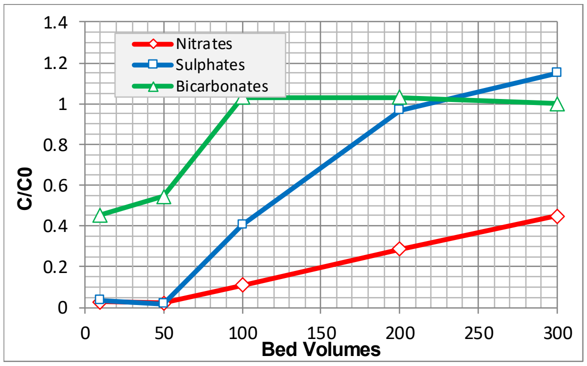

Figure 8. C/C0 variation depending on the volume of water passed through the column - SAMPLE 2.

5. Conclusions

As stated, an increase in nitrate concentrations of groundwater is observed worldwide. The main treatment processes applicable to sources that exceed concentration of nitrates are:

- Biological processes;
- Reverse osmosis;
- Electrodialysis;
- Ion exchangers.

Reverse osmosis and Electrodialysis have good automation possibilities and no need for extensive post treatment but the utility of these processes is limited due to big OPEX costs and the concentrated waste brine which is hard to treat and store [2,17].

The ion exchange process seems to be one of the most suitable treatment technologies for small water systems in terms of nitrate removal because of its effectiveness, simple use, selectivity and relatively low cost [18, 19].

However, the process has several limitations due to the concentration of chlorides in the water because the nitrogen ion in the water is exchanged with the chloride ion grafted onto the anion exchanger. There may be situations in which concentrations of nitrates are reduced but exceedances of chlorides may occur. Also, although anionites have been designed to be selective, there is still a competitive action given by sulphate and bicarbonate ions. Groundwater generally has high concentrations of bicarbonate that, when competing with the nitrogen ion, lead to premature depletion of the anionite's exchange capacity.

When the exchange capacity is exhausted, the anionite mass must be regenerated with significant consumption of regeneration brine and significant quantities of waste brine with high nitrogen content, which represents a difficult waste to be managed.

The process is relatively stable, but one of the drawbacks is that it can only work fully automated because the concentration of nitrates in the effluent is not constant over a cycle, but increases progressively with the reduction of anionite exchange capacity. The process requires permanently qualified operating personnel.

The efficiency of the processes in reducing the amount of nitrates in the water varies in the range of 30-96%.

The main advantages of ion exchange technologies are:

- easy to automate;
- the process can be started in minutes and ensures stable operation, regardless of temperature;
- can treat the whole flow or just a part of it, depending on the flow rate and the concentration of nitrates in it.

The main disadvantages of this technology are:

- waste brine is hard to be managed;
- the corrosivity and the aggressiveness of the water may increase due to the replacement of the bicarbonate and sulphate ions in the water;
- expensive technology if it is used to treat the entire flow in the treatment plant.

In terms of costs, they vary depending on the concentration of nitrogen and other pollutants in the raw water. An estimate of the costs involved in using this technology is presented in the following table.

Table 3.

Costs of ion-exchange technologies [6].

Investment cost ($/m³)	**Operation cost ($/m³)**	**Waste storage ($/m³)**	**Total ($/m³)**
0.06-0.31	0.12-0.2	0.01-0.08	0.18-0.57

The experimental results highlighted the following:

- the nitrate ion can be retained with high efficiency (higher than 95%);
- although the resin used is specially designed for nitrate retention, high efficiency retention of sulfates and bicarbonates has been recorded, which leads to a premature depletion of the resin's exchange capacity;
- the chloride ion is released in solution proportional to the amount of ions retained. In the first phase of the ion exchange process, when the exchange efficiency is very high, if the salt concentration of the water is high, the chloride concentration may increase and exceed the allowed limit for drinking water (250 mg / l according to Law 458/2002);

- It was found that the effluent of the ion exchange columns does not have a constant quality. Careful monitoring of the process is required for all ions involved. This can be a disadvantage if only a part of the raw water is treated using ion exchange technology;

The main conclusion of the experiment is that the ion exchange process for nitrate retention is efficient and can be applied in water treatment for drinking, especially in the case of water with low concentrations of sulfate ions and low alkalinity. Another indicator that limits the application of the process is the concentration of chlorides that will increase proportionally with the amount of nitrate, sulfate and bicarbonate ions retained.

In conclusion, due to the fact that biological denitrification processes are strongly influenced by temperature and reverse osmosis and electrodialysis processes involve high energy consumption, ion exchange is a feasible process for treating water with nitrogen concentrations above the allowable limit for drinking water.

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