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Nitrate Removal from Drinking Water by Point of Use Ion Exchange

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ABSTRACT

Background: A laboratory study was conducted to investigate the ability of a special type of strongly basic resin MP500WS for the removal of nitrate from different waters.

Methods: Two different types of Point-of-Use (POU) devices containing an identical resin were used. MP500WS known as macro porous was used in POU devices for removal of high concentrations of nitrate and sulfate ions from water. Sulfate and chloride ions are considered the most important interferences in the treatment process of nitrate by most anion exchange resins.

Results: The results obtained by treatment of water samples having different ranges of nitrate (20 to150 mg/L), sulfate (50, 100 and 800 mg/L) and chloride (50 and 500 mg/L) have shown that the method was suitable for delivering water with NO_3 concentrations in less than its maximum contaminant level (MCL=45 mg/L) as long as the initial NO_3, SO_4 and Cl concentration has remained in less than 150, 100 and 500 mg/L, respectively.

Conclusion: For this purpose, POU systems that utilize a suitable tested resin may be considered as an economical and effective alternative to conventional systems. This study shows this strategy very effective for nitrate reduction to acceptable levels when macro porous type strongly basic resin is used as the resin.

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Introduction

Nitrate is one of the most important pollutants in water resources especially groundwater and is considered as a growing water pollution problem. The use of nitrogen fertilizers and irrigation with domestic wastewater are the main sources of nitrate pollution [1, 2]. Besides, discharge of wastes rich in ammonia is another source of soil and water pollution to nitrate. Therefore, nitrate contamination is diffused in both developed and developing countries [1].

Nitrate and nitrite have some hazards for human. The primary health hazard from drinking water with nitrate-nitrogen occurs when nitrate is transformed to nitrite in the digestive system [3]. While nitrate is considered relatively non-toxic to adults, concentrations greater than 50 mg/L can be fatal to infants under six months of age since nitrate combine with hemoglobin in the blood and result in blue baby syndromes. Other adverse health effects such as hypertension even for adults are also

reported [2-5]. The content of nitrates in polluted water sometimes reaches the level of 200-270 mg/L, which greatly exceeds the threshold of 45 mg/L fixed by the standards of the World Health Organization (WHO) for drinking water [3].

Nitrate is a highly soluble and stable ion that makes it difficult to remove by using conventional water treatment plant [3, 4]. The common technologies can be used to remove nitrate from drinking water are chemical reduction, ion-exchange, reverse osmosis, electrodialysis, catalytic hydrogenation and biological denitrification [2, 4, 6, 7].

The ion exchange process is simple, effective, selective, recoverable, and relatively low cost and seems to be the most suitable for small water suppliers contaminated by nitrate [3, 7, 8]. In the recent years, several selective resins have been developed for nitrate removal [3, 7-12]. Resins commonly used are Duolite A-101D and A-104, Dowex SAR, Ionic A-550, and Amberlite IRA-900 as well as IRA-910. These resin types can be regenerated using sodium chloride brine. In this process, the polluted water passage through a resin bed containing strong base anion exchange resins on which nitrate ions are exchanged for chloride until the resin's exchange capacity is exhausted [2].

The most important interference in the treatment process of nitrate by resin is sulfate ion which reduces the resin capacity due to sulphate ion displacement of nitrate [2-4, 9, 11].

It is often possible to establish point-of-use (POU) and point-of-entry (POE) treatment devices to achieve compliance with some of the maximum contaminant levels (MCLs) [6]. POU or POE treatment devices may be an option for small public water systems where central treatment is not affordable. Additionally, the health risks of the drinking water in the end-point still exist due to the limited capacity of treatment processes and the secondary pollution in the distribution system [13].

POU and POE treatment devices are designed to treat only a portion of the total flow. POU devices treat only the water intended for direct consumption (drinking and cooking), typically at a single tap or limited number of taps, while POE treatment devices are typically installed to treat all water entering a single home, business, school, or facility [14]. It seems as though that utilizing POU water treatment systems that use proven methods is an effective alternative for the reduction of difficult to treatment contaminants such as nitrate to acceptable levels [5, 15].

In this paper, MP500WS (a special type of strong-base-anion exchange resin) known as macro porous was used in POE devices for removal of high concentrations of nitrate and sulfate ions from water. Sulfate ion is considered the most important interference in the treatment process of nitrate by most anion exchange resins.

Table 1: Physico-chemical properties of resin MP500WS

Skeleton	Polystyrene cross-linked, macro porous type
Functional groupings	Quaternary ammonium
Physical aspect	Opaque balls, beige color
Ionic form	Cl
Granulometry (mm)	0.4–1.25
Effective size (mm)	0.55 (± 0.5)
Uniform coefficient	1.6
Total exchange capacity (eq/L)	1.1
Limits of pH	0–14
Limit of temperature (^{0}C)	20-100
Real density	1.06

Materials and Methods

A special type of strongly basic resin (SBA) with high porosity was used. This anion exchange specialised as MP500WS macro porous was a product of Bayer Co. with chloride as the negative ion exchange site (Table 1).

All chemical reagents used in this study were obtained from Merck (Germany). One M HCl or NaOH was used to adjustment of pH=7.0 and controlled by pH meter (Suntex model sp-701). Water was purified with a water distiller (Fater Electronic model 2104). For all experiments, glassware and bottles were washed and rinsed before use with HNO_3 and distilled water respectively.

Two types of POU water treatment made of Plexi glass were established both suitable for counter top and/or facet mounted placement. The first was a thick cylinder with 17 cm effective height enjoyed both an upward and downward flows for water treatment and the second unit was a simple column with total and effective heights of 52 and 26 cm operated in down flow regime (Figure 1 a and b). The diameters of these units were 15 and 5 cm, so the volume of resin used was 3 litters for the first unit and 0.5 litters for the other.

Synthetic water samples were prepared by adding various amounts of $NaNO_3$, Na_2SO_4 and NaCl to distilled water. In this way, the samples with concentration ranges of 20 to 150 mg/L nitrate, 100 to 800 mg/L sulphate and up to 500 mg/L of chloride had been prepared. The temperature of reactors was controlled at 20 ^oC. Treatment of these samples had been performed in the first unit (cylinder type) by adjusting two separate flow rates of 150 and 79 litters per hour, and for the second unit (column type) the treatment was accomplished for flow rate of 22 litters per hour. Empty Bed Contact Time (EBCT) and Bed Volume per hour are two significant parameters on run length. Selection of the operating EBCT represents a compromise between the improve nitrate removal versus the additional cost for a longer EBCT. The efficiency removal of sulfate and nitrate from the cylinders and column was evaluated for influents with two different reactors. The systems were operated with a feed rate of 2.5, 1.32 and 0.37 L/min, corresponding to an empty bed contact time (EBCT) of 1.2, 2.29 and 1.35 min and bed volume per hour (BV/hr) 50, 26 and 44 [11].

Determination of nitrate, sulphate and chloride concentrations was performed according to the procedures outlined in Standard Methods [16]. Method of NO_3 analysis was based on UV spectrophotometer (Spectronic-21D) at two wavelengths (in 220 and 270 nm) and the average between the two-adsorption measurements was used to determine nitrate concentration.

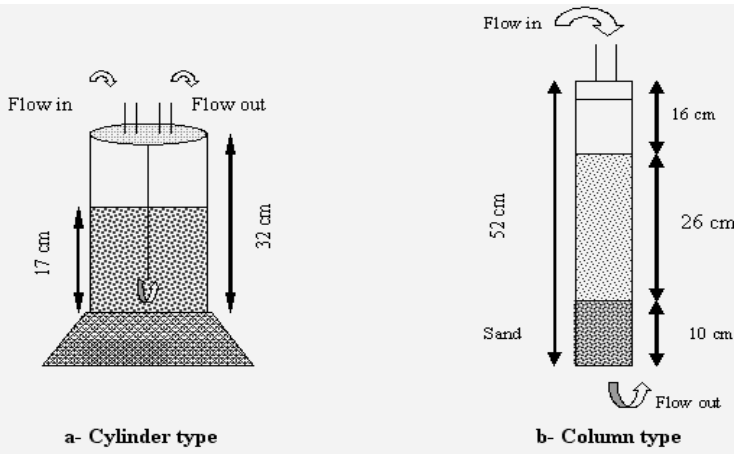

Figure 1: Schematic of designed reactors for Point of Use Ion Exchanger

Results

The effectiveness of POU devices in removing nitrate from various samples with normal concentrations of sulfate and chloride (both in less than 50 mg/L) versus initial nitrate concentration can be seen in Figure 2. As can be seen, the efficiency is high for both cylinder and column types. However, for treating samples with sulfate concentrations of 100 and 800 mg/L, the efficiencies have decreased to about 99 and 96 percent (Figure 3 and 4). On the other hand, for water samples with interference of 500 mg/L chloride, the efficiency for NO_3 removal

has reduced (Figure 5). The results of NO_3 removal for samples with both SO_4 and Cl in high concentration can be seen in Figure 6.

Discussion

Nitrates are being detected with increasing frequency in drinking water supplies of our country and in some cities; the concentration of nitrate in groundwater aquifers has reached to about five times the MCL, for example, in Isfahan region [17]; Zanjan [18]; and Bahar [19]. Thus, utilizing a process for NO_3 reduction seems to be an essential task. For this purpose, POU systems that utilize a suitable tested resin may be considered as an economical and effective alternative to conventional systems. This study shows this strategy to be very effective for nitrate reduction to acceptable levels when macro porous type SBA is used as the resin.

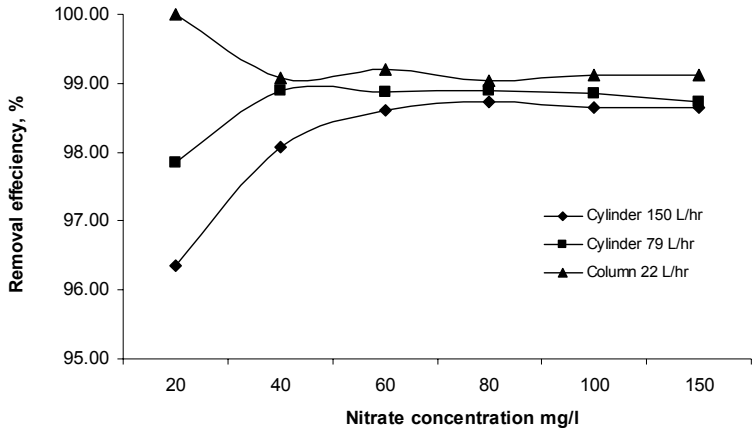

Figure 2: Removal efficiency of nitrate versus reactor types: SO_4^{2-} and Cl<50 mg/L

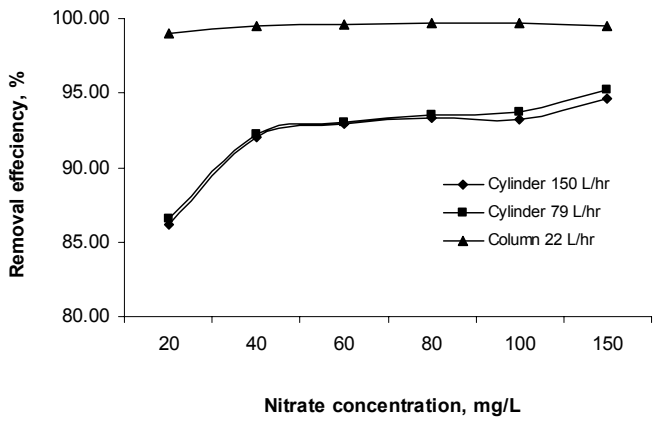

Figure 3: Removal efficiency of nitrate versus reactor types: SO_4^{2-} 100 mg/L and Cl<50 mg/L

The study of the nitrate removal of water by MP500WS macro porous resin has been used in POE devices while varying the speed of raw water through the rectors, the initial contents of sulphate, nitrates and chlorides in raw water. The variation of these parameters was taken in order to reveal their impacts on the service output of the resin and the ionic leakage of nitrates (NO_3) in the treated water. These resins will remove a number of anions in addition to nitrate, including sulfate, nitrate, chloride, and bicarbonate. The order of affinity for these anions is [2, 20]:

Sulfate>Nitrate>Chloride>Bicarbonate

Because sulfate ions are preferentially removed over nitrate ions, and nitrate ions are preferentially removed over chloride, and bicarbonate ions, as the resin becomes exhausted, bicarbonate breaks through first, followed by chloride, then nitrate. The sulfate ion is the most strongly adsorbed, and hence will display previously removed nitrate ions at

the end of the service cycle. This is an undesirable situation, and can be resulted to a higher nitrate concentration in the exchanger product water than in the exchanger feed water. The service cycle must be terminated before this point [20].

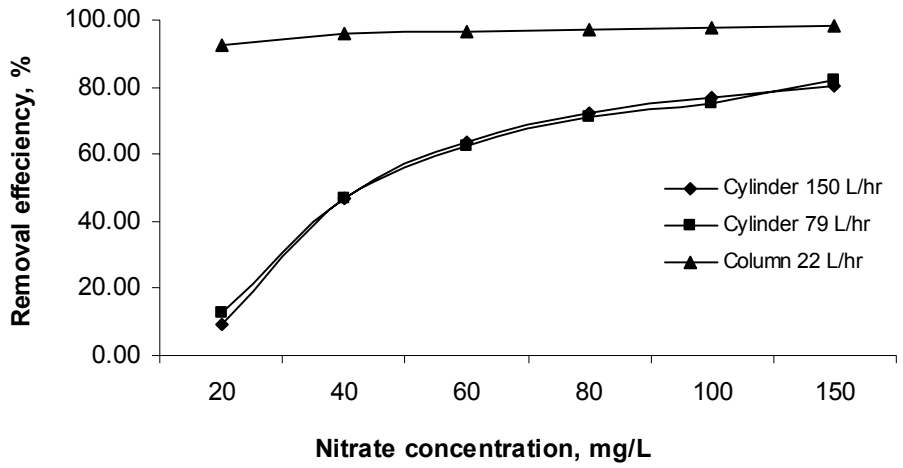

Figure 4: Removal efficiency of nitrate versus reactor types: SO_4^{2-} = 800 mg/L and Cl<50 mg/L

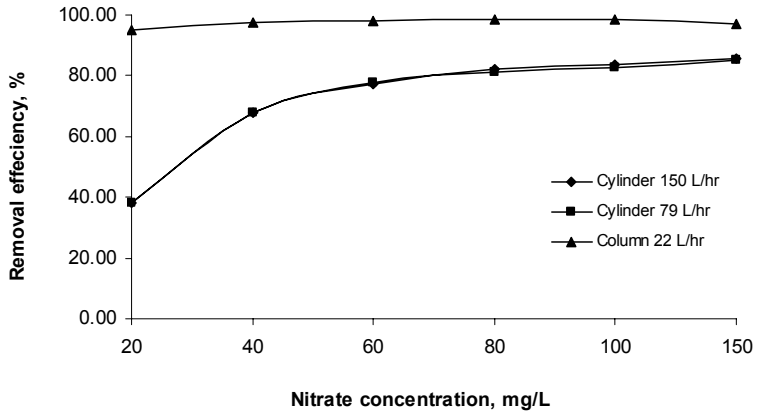

Figure 5: Removal efficiency of nitrate versus reactor types: SO_4^{2}<50 mg/L and Cl=500 mg/L

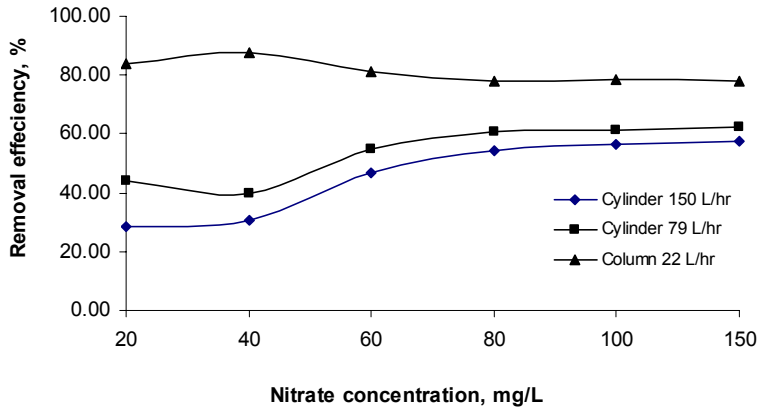

Figure 6: Removal efficiency of nitrate versus reactor types: SO_4^{2}=800 mg/L and Cl=500 mg/L

The ionic leakage of nitrates in treated water became weaker as the speed of water percolation through the column decreased. In addition, the increase in the concentrations of nitrates in raw water treated led to an increase in the service output of the resin passing. Our results show that the column type reactor is better than cylinder type reactor in nitrate

removal. Therefore, the results show that the increase in SO_4 and Cl concentration led to decreased in nitrate removal efficiency. Samatya et al. as well as Boumediene and Achour showed that the existence of chloride and sulfate ions influenced the breakthrough capacity of the resin (Purolite A 520E) for nitrate [2, 3]. In the current study, the selectivity of the resin for nitrate over sulfate decreased significantly when the ionic strength of the solution increased due to addition of chloride, although the SO_4/NO_3 separation factor decreased, to the point where NO_3 was the preferred adsorbate at the highest ionic strength investigated [11]. Therefore, the test results by Amberlite IRN-78 were shown that the presence of other competitive anions in solution, specifically chloride, sulphate, and bicarbonate were affected on nitrate removal efficiency [4]. However, and with regard to contamination of water by nitrates, the underground waters are often charged by sulphate. These latter, whose valence is higher than nitrates, have the property to be fixed preferentially by the resins, consequently reducing the cycle of production of the exchanger [3]. For this reason, we have used the specific resin MP500WS in the framework of this study whose selectivity is better for nitrates than for sulphate.

Conclusion

The MP500WS macro porous resin for adsorption nitrates was examined. The following conclusions can be deduced from experimental data:

- Initially, the rate of adsorption of nitrates onto MP500WS macro porous resin was very high, followed by decreasing rates, until an almost constant value.
- Based on the results, the column type reactor was better fitted that cylinder type reactor for nitrate removal under the considered conditions.
- The results indicated that the method is suitable for delivering water with NO_3 concentrations in less than its MCL (45 mg/L) as long as the initial NO_3, SO_4 and Cl concentration has remained in less than 150, 100 and 500 mg/L, respectively.
- The present work studies the removal of nitrate by a strong anionic ion-exchanger resin, MP500WS macro porous resin in POU systems. It has been shown that in simple reactors can be used to simulate ion exchange when using a macroporous resin.
- It confirms that the nitrate removal of underground waters by specific resins (MP500WS macro porous resin) leads to the nitrate concentrations that are much lower than the permissible maximum concentration for drinking water.

Conflict of interest statement

The authors declare that they have no conflicts of interest.

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