



Comparison between nitrate and pesticide removal from ground water using adsorbents and NF and RO membranes

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ABSTRACT

An investigation was carried out regarding the removal of pollutants such as nitrate and pesticides (atrazine, deethylatrazine and deisopropylatrazine) from actual ground water samples obtained in Slovenia, by the use of two new adsorption resins, one derived from styrenedivinylbenzene and one from polystyrene, and commercial nanofiltration and reverse osmosis membranes. Atrazine and deethylatrazine were also bound to the activated carbon. Despite the different technologies applied, the effort was directed towards simultaneous removal of the above-mentioned pollutants. According to the results, the first of the mentioned adsorption resins was successfully used for pesticides' removal among the tested adsorption media, whereas the removal of nitrates was unsuccessful. The reverse osmosis membrane displayed a high rejection of all compounds. All concentration values after treatment were below the maximum concentration allowed, while the nanofiltration membrane showed lower compound rejection, thus being suitable for atrazine removal.

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1. Introduction

Water pollution by pesticides and nitrate during routine agricultural practices is a common and growing problem in major agricultural areas of the world [1]. From among the triazine pesticides, atrazine and its metabolites, deethylatrazine and deisopropylatrazine, are still identified as major emerging contaminants in Slovenian drinking water supplies. Analyses in north-eastern Slovenia reveal that, even in the ground water, pesticide concentrations of individual pesticides and nitrate ions exceed the concentration limits of 0.1 µg/L and 50 mg/L, respectively. Nitrate concentrations are often high in regions where pesticide contamination is a problem [1].

Several techniques for the removal of nitrates and pesticides (atrazine and deethylatrazine) are known such as: various oxidation processes [2,3], membrane filtration [4–7], and adsorption onto different media [8–10]. Among these, the activated carbon adsorption process has been used as an effective method for removing the residual pesticides in raw water during drinking water treatment. Activated carbon is well-known among adsorption processes, e.g. adsorption on Calgon WPH and Norit HDB for atrazine, deethylatrazine, deisopropylatrazine, deethyldeisopropylatrazine,

simazine, and propazine removal has already been studied [8]. Lower adsorption capacities have been determined for deethylatrazine and deisopropylatrazine using activated carbon adsorption compared with atrazine [9]. Picabiol and WCM 106 activated carbons were used for atrazine removal too [10]. Once activated carbon is saturated or the treatment objective is reached, it has to be recycled by thermal reactivation in a high temperature reactivation furnace at over 800 °C, for reuse. Beds could be regenerated using organic or inorganic solvents (e.g. ethanol, NaCl). Adsorption of atrazine on zeolite [11] and other sorption media (Nyex) [12] are feasible procedures for atrazine and its derivatives' removal. Although the activated carbon adsorption process seems to be the most feasible process for removing trace pesticides, these physico-chemical treatment processes have poor selectivity for nitrate and are limited because they produce concentrated wastes [13].

In order to achieve adequate control of pesticides in drinking water, it is necessary to be aware of their behaviour, not only in water sources but also during the water purification process. Chlorination and ozonation, which are the principal processes of water purification, may produce by-products as a result of reaction between chlorine or ozone and pesticides in raw water, and it has been reported that, for some organophosphate pesticides, the degradation by-products have higher toxicity than the original pesticides themselves [2].

One emerging alternative treatment technology is membrane filtration such as reverse osmosis (RO) and nanofiltration (NF). In recent years, membranes have become fully or partly inte-

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Table 1
Physico-chemical analyses of the ground water sample.

Water parameters	
pH	7.58–7.60
γ_{TOC} (mg/L)	1.5
γ_{C} (mg/L)	58–66
γ_{NO_3} (mg/L)	78.2
γ_{Cl} (mg/L)	14.2
γ_{SO_4} (mg/L)	26.3
γ_{CIET} ($\mu\text{g/L}$)	0.18–0.19
γ_{CIAT} ($\mu\text{g/L}$)	0.20–0.23
γ_{CEAT} ($\mu\text{g/L}$)	<0.05

γ : Mass concentration.

grated into those facilities that produce drinking water [14]. Recently, membrane filtration by reverse osmosis (RO) and nanofiltration (NF) have been considered for the removal of organic compounds from water. However, wider use of RO membrane technology in the drinking water industry has been hampered greatly by membrane fouling [4]. The extent and rate of membrane fouling are largely affected by membrane surface characteristics [5,6].

It has been discovered [15], that rejection of the model solution by very tight RO membranes is dominantly affected by membrane porosity parameters (pore size distribution and effective number of pores in the membrane's skin), whilst, it can be expected that the rejection of organics by those membranes having larger surface pores would be influenced more by the physico-chemical parameters (charge, hydrophobicity) [7]. Therefore, retention properties are very important in NF: the possibility of retaining relatively small organic molecules and multivalent ions from aqueous solution is crucial for most applications.

Therefore, the aim of this work was to study the removal efficiency for atrazine and nitrate ions using two novel adsorption resins, Dowex Optipore L493 and Lewatit VP OC 1064 MD PH, and commercially-available NF and RO membranes; DK and SG, respectively. Significant effort was directed towards making a comparative assessment of the two systems based on pollutants' removal efficiency, despite using two technologically different systems. The results were compared in terms of simultaneous removal of the above-mentioned pollutants.

2. Materials and methods

2.1. Adsorption experiments

Table 1 summarises the physico-chemical analyses of the ground water sample. It was taken directly from the water well V2.

2.1.1. Experiments in erlenmayer beaker

The amount of adsorbent necessary for a full scale operation depends on the contact time between the adsorbent and adsorbate. Contact time for the adsorption of atrazine to adsorbent was determined using the same amounts, 0.5 g of adsorption resin (Dowex Optipore L493, Lewatit VP OC 1064 MD PH) or activated carbon Filtrasorb 400 GAC exposed to the 1 L of atrazine and its metabolites in water. The water suspension was mixed for different time units (10, 30, 60 and 120 min). Atrazine was desorbed from Dowex Optipore L493 resin using pure ethanol (96% Merck, expressed as 100% ethanol solution) and other ethanol/water solutions (90%,

80%, 70%, 60% and 50%, v/v). The experiments were carried-out in four replicates. Spectroscopic measurement ($\lambda = 224 \text{ nm}$) was used for determination, only in this part of the experiments.

Freundlich isotherms were developed by exposing a given amount of adsorbate in a fixed volume of water (the initial concentration of atrazine was $0.19 \mu\text{g/L}$, and of deethylatrazine 0.23 g/L) to varying amounts of activated carbon, ranging from 0.01, 0.05, 0.1, 0.15, 0.2, 0.5, 1, 2 to 3 g of activated carbon Filtrasorb 400 (Chemviron Carbon), Dowex Optipore L493 resin (Dow Chemical Company), and Lewatit VP OC 1064 MD PH resin (Lanxess). The characteristics of the employed activated carbon and resin are presented in Table 2. For all the batch experiments, the 1 L well water sample and a defined amount of adsorbent were mixed on a shaking table for 24 h and, subsequently, filtered through Sartorius black filter paper. After filtration, the samples were analysed for atrazine, deethylatrazine, and deisopropylatrazine (Table 3). The activated carbon granules uniformly activate throughout the whole granule, not just the outside. This results in constant adsorption kinetics over a wide-range of applications. Whole granules of activated carbon were used. Regeneration of the saturated adsorbent bed was done using ethanol (96%, Merck).

Nitrate ions were not measured when using the adsorption resin or activated carbon. This is due to the fact that some preliminary tests either the used adsorption resin or activated carbon showed no binding affinities to nitrate anions in water.

2.1.2. Small-scale column tests

Small-scale column experiments were conducted to simulate the results obtained using full scale reactors. The laboratory tests were conducted using a vertical glass column of 200 mm height and 17 mm diameter. The column was filled with 10 g of activated carbon or adsorption resin. The water flow was 1 L/h. The initial concentration of atrazine was $0.19 \mu\text{g/L}$, and deethylatrazine $0.23 \mu\text{g/L}$. The initial concentration of deisopropylatrazine was below the quantification limit. After filtering through the column, the samples were analysed for atrazine, deethylatrazine and deisopropylatrazine).

2.2. Chemical analysis

The atrazine concentrations were determined using GC/MS on Agilent (Hewlett Packard) 6890/5972 and Varian 3900/Saturn 2100T chromatographs, equipped with HP-5MS type capillary columns. Atrazine and deethylatrazine were determined using SPE extraction on Varian cartridges, filled with 500 mg ENV (stirene-divinylbenzene), using a volume of 6 mL. It was conditioned by rinsing twice with ethylacetate, followed by rinsing twice with methanol, and then twice with deionised water. One litre of sample passed through the SPE at 1 L/h flow. Cartridges were eluted with 5 mL of ethylacetate and methanol solutions. The eluate was then evaporated up to 0.5 mL of volume using Supelco vacuum pumps. Separation was performed on a $30 \text{ m} \times 0.25 \text{ mm}$ DB-5MS (J&W scientific) column (Hewlett Packard 5890, type II instrument) using helium as the carrier gas. A split-splitless injection in the splitless mode was used and the temperature was programmed from 50°C (initial time, 2 min) to 170°C at a rate of $20^\circ\text{C}/\text{min}$, $170\text{--}195^\circ\text{C}$ at a rate of $1^\circ\text{C}/\text{min}$, $195\text{--}260^\circ\text{C}$ at a rate of $20^\circ\text{C}/\text{min}$ and held at 260°C for 5 min. The injector and mass spectrometer (Hewlett

Table 2
Characteristics of the activated carbon and resins employed.

Adsorption resins and activated carbon	Matrix	Colour, diameter
Dowex Optipore L493 (DOW)	Macro-porous styrene-divinylbenzene	Brown bead, 20–50 mesh
Lewatit WP OC 1064 MD PH (Lanxess)	Cross-linked polystyrene	White bead, 0.44–0.54 mm
Filtrasorb 400 (Chemviron Carbon)	Agglomerated coal based granular activated carbon	Black bead, 0.7 mm

Table 3
Chemical structures, names, abbreviations, and solubility of atrazine, deethylatrazine and deisopropylatrazine [17].

Structure	Common name	Chemical name	M (g/L)	Solubility in water (mg/L), $\vartheta = 25^\circ\text{C}$
	Atrazine	2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine	215.7	33
	Deethylatrazine	2-amino-4-chloro-6-(isopropylamino)-s-triazine	187.6	380
	Deisopropyl-atrazine	2-amino-4-chloro-6-(ethylamino)-s-triazine	173.6	210

Packard 5972) temperatures were held at 280°C , respectively. The initial concentration of deisopropylatrazine in the ground water sample was below the quantification limit of $0.05\ \mu\text{g/L}$. According to European legislation it is necessary to control the concentration of atrazine, and its metabolites deethylatrazine and deisopropylatrazine in drinking water sources.

The nitrate was determined by IC Dionex DX-100, carried out on an IonPac AG12A analytical column, following ISO 10304-1. The guard column Ion Pac AG12A, $4 \times 50\ \text{mm}$, Dionex, was used, followed by a IonPac AS12A column $4 \times 200\ \text{mm}$, Dionex. The detector cell used the principles of conductivity measurement. Na_2CO_3 ($c = 0.0027\ \text{mol/L}$) and NaHCO_3 ($c = 0.0003\ \text{mol/L}$) were used as effluent solution. The test sample was prepared by suitable dilution with deionised water, when necessary. The Carry 50, Varian, $\lambda = 224\ \text{nm}$ spectrophotometer was used for the measurement of high mass concentration of atrazine during the desorption experiment.

The chemical structure, molecular weight and solubility of common and chemical names for atrazine, deethylatrazine and deisopropylatrazine are presented in Table 3.

2.3. Membranes and pilot plant operation

The detailed characteristics of the membranes used in the experiment are shown in Table 4 [18].

The streaming current measurements were done using an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria) equipped with a clamping cell, where two pieces of membrane were mounted on the measuring cell. The membranes were separated by a spacer that introduces a streaming channel with dimensions of $25\ \text{mm} \times 5\ \text{mm}$. The height of the channel was determined from the measurements of flow-rate and differential pressure. The elec-

Table 4
Manufacturer's specification for DK and SG membranes.

Manufacturer data	DK	SG
Manufacturer	GE Osmonics Desal	GE Osmonics Desal
MgSO_4 rejection (%)	96	99.5
Pressure (bar)	0.5–28	1–41
pH range	2–11	2–11
Water permeability ($\text{L m}^{-2}\ \text{h}^{-1}\ \text{bar}^{-1}$)	4.57	1.95
Contact angle ($^\circ$)	58.3	60.9

trolyte was circulated through the measuring cell alternatively from both sides, thus creating differential pressures and the corresponding streaming potential/streaming current signal. A 1 mM KCl solution was used as the background electrolyte and, prior to measurement, the given sample was rinsed with this aqueous solution. The pH dependence of the zeta potential within the range pH 2–9 was determined using 0.1 M NaOH as the titration liquid. The zeta potential was calculated from the measured streaming current using the Helmholtz–Smoluchowski equation, which takes into account any surface conductivity. Variation of the zeta potential as a function of pH for the two membranes under study is plotted in Fig. 1. The hydrophobicity of the membrane was determined using contact angle measurements taken from a goniometer and data taken from the literature [14].

The experiments were carried out in a modified NF/RO unit (purchased from Tehnobiuro, Slovenia) in which membranes were installed in series; the system was operated in batch mode. The membrane areas for each membrane sheet were $0.01108\ \text{m}^2$. For performance evaluation, experiments were carried out in a total recycle mode of filtration (TRMF) in which both the retentate and permeate are recycled into the feed tank. The first step, before the start of the experiments, was the flushing-out of each membrane with deionised water for 24 h under a feed pressure of 15 bar, in order to remove any remaining preservation liquids, and to ensure compaction of the membranes.

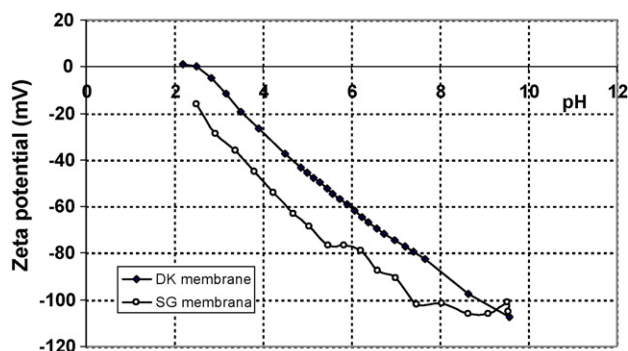


Fig. 1. Zeta potential versus pH for DK and SG membrane (background electrolyte solution 1 mM KCl).

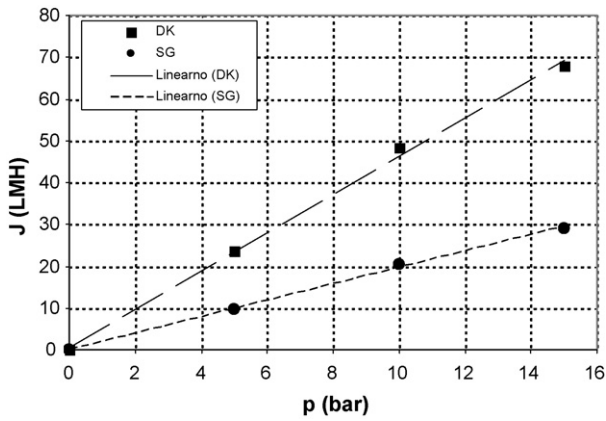


Fig. 2. Pure water flux versus applied pressure for the NFT-50 and SG membranes.

Thus, the feed quality was assumed to be constant since the feed volume would be kept constant throughout the experiment. The TMP was set at 2 bar and stabilized flux was obtained after 10 min. The pressure was then raised to 5, 10, and 15 bar every 30 min to permit flux stabilization, until the flux became pressure-independent. The variations in permeate flux using step increment of trans-membrane pressure (TMP) were studied at cross-flow velocities of 0.6 m/s. Before completing the tests, the permeate was sampled for further analysis, after reaching the steady state. A single pump was employed to provide both cross-flow flush and operational pressure for permeate production. The general details of the set-up and the experiment were the same as described in literature [16].

Fig. 2 shows permeate flux versus applied pressure for both membranes. The slopes of the straight lines give the water permeability values for each membrane. The slope is a measurement of the resistance exerted by the membranes as a diffusion medium, when a given force (pressure) is acting on a component [16]. Table 4 lists the water permeability values in $L m^{-2} h^{-1}$ or LMH.

3. Results and discussion

3.1. Removal of nitrate and pesticide using adsorption resins

3.1.1. Contact time of pesticides and resin regeneration

It can be seen from Fig. 3 that the mass concentration of atrazine (γ , $\mu g/L$) lowered to below the limit of quantification after 120 min of contact time with either of the adsorbents used. Fig. 4 shows the removal of deethylatrazine below the limit of quantification after 120 min of contact time with Dowex Optipore L493 and Filtrasorb 400 GAC. The fastest adsorption over time was reached

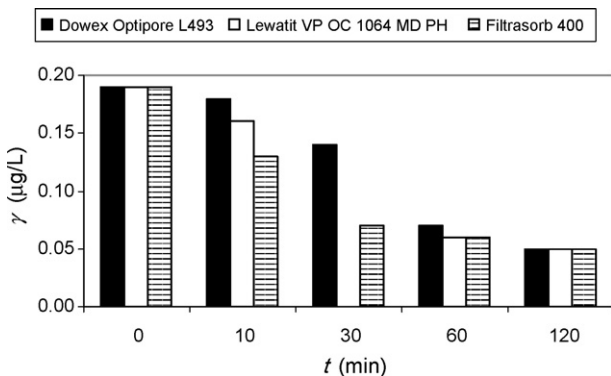


Fig. 3. Mass concentrations of atrazine (γ) in the water samples for three adsorbents during the adsorption time. There was no measurement for 30 min for Lewatit VP OC 1064 MD pH.

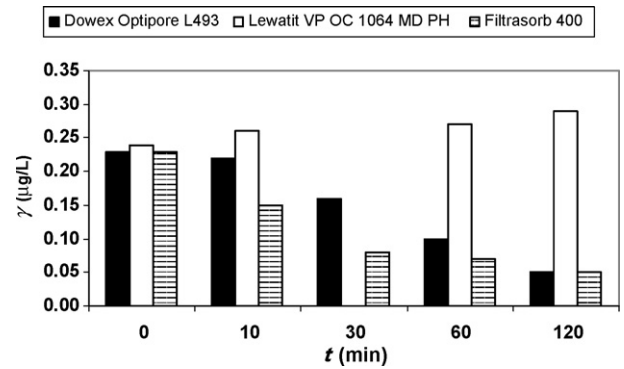


Fig. 4. Mass concentration of deethylatrazine (γ) in the water samples for three adsorbent during the adsorption time. There was no measurement for 30 min for Lewatit VP OC 1064 MD pH.

with Filtrasorb 400, and the slowest with Dowex Optipore L493. After 1 h, the achieved atrazine concentration was below $0.1 \mu g/L$ for both resins and activated carbon. The concentration of deethylatrazine dropped below $0.1 \mu g/L$ with the usage of Filtrasorb 400 and Dowex optipore L 493. However, when using Lewatit VP OC 1064 MD PH resin, the concentration of deethylatrazine rose over time, as seen in Fig. 4. The reason for the increase in deethylatrazine concentration could be the unknown compound which appears at the same retention time as deethylatrazine, on the GC column. Unfortunately, it was impossible to confirm this assumption by determining this unknown substance. It might be assumed that this unknown compound was most likely eluted from the resin.

Desorption of atrazine and deethylatrazine was also investigated. The solution of NaCl did not affect atrazine and deethylatrazine desorption. Methanol and acetone showed desorption affinity, but their peaks obtained during spectroscopic measurement ($\lambda = 224 \text{ nm}$) were unresolved. Any desorption of atrazine was not seen, but this was not the case with ethanol. Because of this ethanol was chosen for further work.

Fig. 5. shows the ratio between the atrazine mass concentration and initial atrazine mass concentration depending on the concentration of ethanol used for regenerating the saturated Dowex Optipore L493 resin. Atrazine was spiked in deionized water in order to gain an almost saturated solution. This initial atrazine concentration in the water sample was determined at 1.377 mg/L by a spectrophotometer. When using pure ethanol solution for resin regeneration (pure solution of 96% ethanol, expressed in the text as 100% ethanol solution), the concentration of atrazine in the regeneration eluent solution was determined at 84–81% (as mass

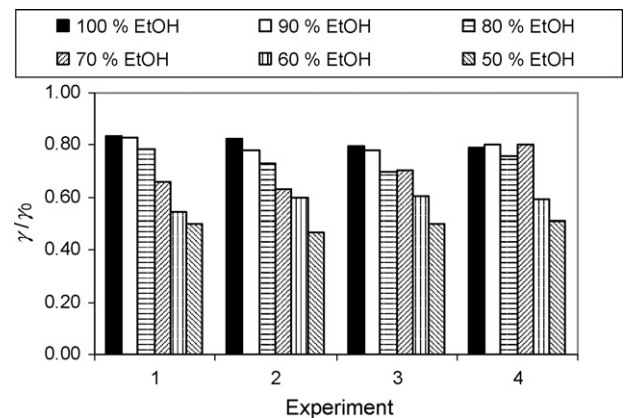


Fig. 5. Atrazine in spent bed eluent solutions of Dowex Optipore L493 with regard to its initial concentration (γ/γ_0) using different ethanol solutions.

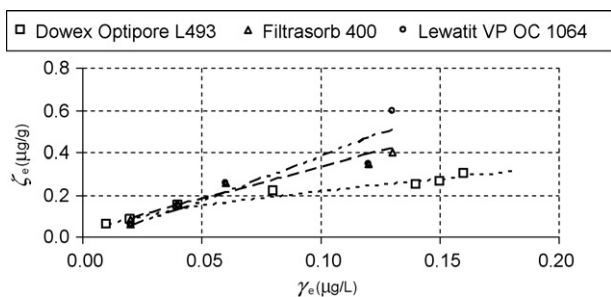


Fig. 6. Freundlich isotherms of atrazine in the water sample after 24 h of equilibria (mass ratio of adsorbens ζ_e versus mass concentration of adsorbate γ_e).

ratio with regard to atrazine). Dowex Optipore L493 resin could be regenerated by using ethanol/water solutions. The concentration of atrazine in the regeneration eluent solution rose with any decreasing volume percent (%v/v) of ethanol used. Also, the concentration of atrazine varied during the tests if the same ethanol concentration is taken into consideration, and differences between the replicates (or standard deviation s) using the same diluted ethanol solution were observed within 3%. However, results using other diluted ethanol solutions for regeneration showed that the mass concentrations of atrazine in the spent regeneration eluent were lower than when using 100 (%v/v) ethanol solution. A higher standard deviation of atrazine concentration in the experiments using 50% up to 90 (%v/v) ethanol solutions was obtained than for that obtained using 100% ethanol solution ($s \approx 2, 4, 7, 3, 2$ for 90%, 80%, 70%, 60% and 50%, v/v). It is assumed, that the regeneration process is slower in diluted ethanol solutions.

3.1.2. Adsorption isotherms

Formula (1) was used for calculating Freundlich adsorption isotherm, because adsorption isotherm data fitted the Freundlich isotherm model [19]. Langmuir model does not fit at all. The adsorption capacity represents the ratio of the amount of solute adsorbed per unit mass of sorbent. The parameter, k_f , primarily relates to the capacity of the adsorbent, while n relates to the adsorption strength.

$$\zeta_e = k_f \gamma_e^{1/n} \quad (1)$$

- ζ_e – mass of adsorbate adsorbed per unit mass of adsorbent (mg/g),
- k_f – Freundlich capacity factor (mg/g) (L/mg) $^{1/n}$,
- γ_e – equilibrium concentration of adsorbate in solution after adsorption (mg/L),
- $1/n$ – Freundlich intensity parameter.

Adsorption isotherms were determined using Filtrasorb 400 activated carbon, Dowex Optipore L493 and Lewatit VP OC 1064 MD PH resins. Figs. 6 and 7 show the Freundlich isotherms of atrazine

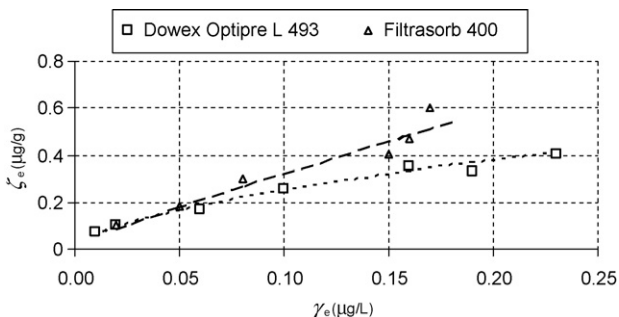


Fig. 7. Freundlich isotherms of deethylatrazine in the water sample after 24 h of equilibria (mass ratio of adsorbens ζ_e versus mass concentration of adsorbate γ_e).

Table 5

Freundlich parameters for atrazine and deethylatrazine in the ground water.

Adsorbent	1/n	k_f /(mg/g)(L/mg) $^{1/n}$	R^2	ζ_e /(μ g/g)
Atrazine				
Dowex Optipore L493	0.5633	0.04	0.921	0.32
Filtrasorb 400	0.8446	0.81	0.982	0.59
Lewatit VP OC 1064 MD PH	1.1196	11.58	0.949	0.79
Deethylatrazine				
Dowex Optipore L493	0.5825	0.05	0.979	0.41
Filtrasorb 400	0.8387	0.75	0.964	0.67

and deethylatrazine, respectively, in the water sample after 24 h of equilibria, depending on the mass concentration of adsorbent.

The Freundlich coefficients are shown in Table 5 for atrazine and deethylatrazine adsorption. The adsorption capacity of atrazine is the highest using Lewatit VP OC 1064 MD PH resin, followed by Filtrasorb 400 and Dowex Optipore L493 resin which have half the capacity determined for Lewatit VP OC 1064 MD PH. Deethylatrazine adsorption on Lewatit VP OC 1064 MD PH was very low, therefore, adsorption isotherms were determined only for Filtrasorb 400 and Dowex Optipore L493. It was calculated that the capacity was 33% higher using Filtrasorb 400, compared with Dowex Optipore L493.

In literature, there is no available data in regard to the adsorption isotherm of atrazine, deethylatrazine or any other kind of pesticide, for any of the above-mentioned resins. However, data regarding differently activated carbon are available [8,9,18] where the k_f values are much higher than those obtained during our experiments. Data from literature shows, that the results depend on the model or real samples used, and the initial concentrations of atrazine in each sample. The solubility of atrazine is approximately 33 mg/L while deethylatrazine is significantly more soluble, 380 mg/L at 25 °C (Table 2). The Lundelius rule predicts that the extent of a solute's adsorption is inversely proportional to its solubility in the solvent [9]. The metabolites had lower capacities, in general, than the parent compounds which is due to the loss of alkyl group imparting greater hydrophobicity for atrazine, as compared with metabolites. This is expected due to lesser hydrophobicity of the degradates than that of the parents due to the loss of hydrophobic alkyl moieties [8]. We expect lower capacities of degradates (deethylatrazine) than those of the parent (atrazine). Therefore, more atrazine should be adsorbed. From our results it follows that the adsorption of atrazine is lower than that of deethylatrazine. Freundlich isotherms are known from literature to have the initial concentrations of atrazine from 5 to 50 μ g/L. In our experiments 0.19 μ g/L of atrazine and 0.23 μ g/L of deethylatrazine, respectively were the initial concentrations, which are up to 250 times lower. However, the results showed that atrazine and deethylatrazine can be adsorbed well in very low concentrations. There is still competition for available adsorption sites regarding granular carbon [20], and steric effects also influence the attachment of adsorbate to adsorbent. The reason for the higher adsorption capacity of deethylatrazine is possibly due to the higher initial concentration of deethylatrazine.

It can be concluded that optimum results were obtained using Filtrasorb 400, due to the fact that we are unable to analyse deethylatrazine when using Lewatit VP OC 1064 MD PH. Two unresolved peaks were observed during GC-MS analyses of Lewatit VP OC 1064 MD PH eluate. We were unable to measure concentrations of deethylatrazine accurately, and therefore, the cause of high deethylatrazine concentration Lewatit VP OC 1064 MD PH eluate could not be explained.

$1/n$ relates to the strength of adsorption, and the smaller the value of $1/n$, the stronger the adsorption bond [8]. Using Lewatit VP OC 1064 MD PH $1/n$ for atrazine was higher than that obtained when using Dowex Optipore L493 and Filtrasorb 400. The adsorption of

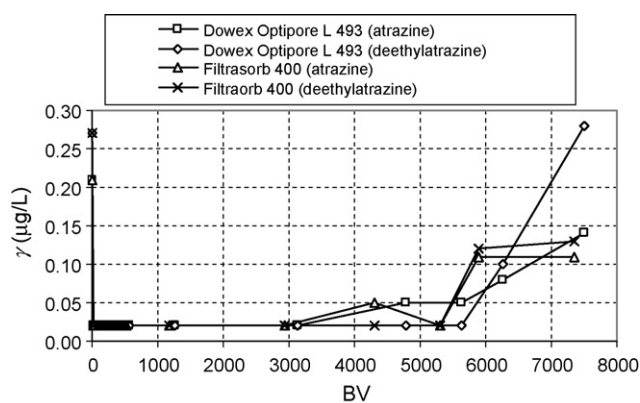


Fig. 8. Atrazine and deethylatrazine mass concentrations (γ) versus BV.

atrazine to Lewatit VP OC 1064 MD PH is weaker than that of the other resin and activated carbon. Lewatit is a macroporous adsorber resin without functional groups and beads are uniform particle size. Optipore is copolymer of styrene and divinylbenzene, while activated carbon surface structure depend on activation process.

Ayranci and Hoda [21] stated that the more heterogenous the surface, the closer $1/n$ value is to 0. In case of Lewatit, $1/n$ is higher than 1 due to very homogenous surface. Other two resins have more heterogenous surface.

Lewatit VP OC 1064 MD PH has higher k_f which corresponds to higher capacity in comparison with the other two resins [8].

3.1.3. Small-scale column tests

10 g of Dowex Optipore L493 and Filtrasorb 400 were placed into the small column regarding atrazine removal from the ground water sample. Fig. 8 shows that atrazine and deethylatrazine were removed below $0.1 \mu\text{g/L}$. The breakthrough point was observed at 5800 bed volume (BV) when using Filtrasorb 400, and 6200 BV when using Dowex Optipore L493. It can be concluded that approximately 6000 BV of water could be treated using 10 g of adsorbent. The breakthrough points using Filtrasorb 400 and Dowex Optipore L493 was observed at lower BV values.

Comparison between Freundlich isotherms and small-scale column tests showed that more ground water can be treated in column than was calculated from Freundlich isotherms. As observed, the model did not match the experimental column data, besides, Freundlich isotherms are limited by the fact that only surface adsorption takes place because of low initial pesticide concentrations. Our small-scale column test beds were saturated with pesticides, thus diffusion in the pores of the sorbent was probably a rate-controlling step during the isotherm experiments.

3.2. Removal of nitrate and pesticide using NF and RO membranes

For a charged membrane, an ionic compound is retained through a combination of steric and Donnan effects. The values of the initial concentrations, the compound's concentration in permeate after membrane treatment using different pressures, as well as the maximum allowed concentrations (MAC), are shown in Table 6 [22].

Table 6
Compound concentrations versus pressure.

DK membrane	SG membrane					SG membrane					MAC
	Initial	2	5	10	15	2	5	10	15		
NO_3^- (mg/L)	67.42	56.20	55	49.1	48.6	3.75	2.21	1.85	1.69	50	
Atrazine ($\mu\text{g/L}$)	0.18	0.07	0.07	0.08	0.09	0.01	0.01	0.01	0.01	0.1	
Deethylatrazine ($\mu\text{g/L}$)	0.2	0.19	0.18	0.19	0.2	0.01	0.01	0.01	0.01	0.1	

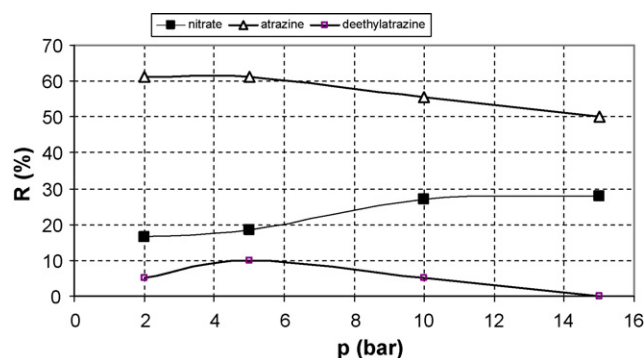


Fig. 9. The compound's rejection obtained under different pressures and DK membrane.

Rejection of the ionic components in NF is mostly based on Donnan exclusion: ions are rejected as a result of charge interaction between the membrane surface and the ions. This is valid for "loose" NF membranes which have negatively charged functional group. One possible way of determining whether the membrane is loose and exhibiting Donnan exclusion, is by conducting the test with NaCl , Na_2SO_4 and CaCl_2 . If the order of rejection is $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{CaCl}_2$, then the membrane rejection is based on classical Donnan exclusion [23]. Unfortunately, it was impossible to perform such tests in our case, because the membrane equipment is now unavailable. Yet, in the literature [24] it was stated that the rejection order for DK membrane is $\text{Na}_2\text{SO}_4 > \text{MgCl}_2 > \text{NaCl}$. The high retention of Na_2SO_4 and MgCl_2 can not be explained by Donnan exclusion, but rather by differences in diffusion coefficient. In the experiments, low nitrate removal was achieved and, therefore, the steric effect is predominant in the case of DK membrane. The NO_3^- ions rejection was low to a certain extent (16.6–27.0%), where the concentrations were above (MAC). The highest removal was achieved for atrazine (61–50%), followed by deethylatrazine (5–0%), by increasing pressure (Fig. 9). There is a significant difference between atrazine and deethylatrazine removal efficiencies. The achieved removal of atrazine was around 50%, which is sufficient to set a MAC value of $0.1 \mu\text{g/L}$. The rejection obtained with deethylatrazine was very low. Different rejections are connected to octanol–water partition coefficient K_{ow} values. Atrazine is more hydrophobic as deethylatrazine indicated by high $\log K_{ow} = 2.6$ compared to relatively low $\log K_{ow}$ of deethylatrazine ($\log K_{ow} = 1$) [25]. Rejection of more hydrophilic solutes ($\log K_{ow} < 1$) appeared to be mainly determined by steric interactions with the membrane, whereas for hydrophobic solutes ($\log K_{ow} > 3$) the solute–membrane interactions resulted in lower rejection values as expected, purely based on steric interactions [26]. Due to steric hindrance, the rejection of atrazine should be higher, but is decreasing due to hydrophobic interaction between the solute and membrane, while the rejection of deethylatrazine is low, mainly determined by steric hindrance. Other authors [27,28] also confirm that molecular size plays an important role. Physical sieving by pores is believed to be one of the main driving factors in rejection of organic solutes with a molecular weight (MW) larger than the MWCO of NF membranes. DK membrane MWCO was determined at 195 Da [29]. As can be seen from Table 3 the molecular weight of atrazine is 215 g/mol and

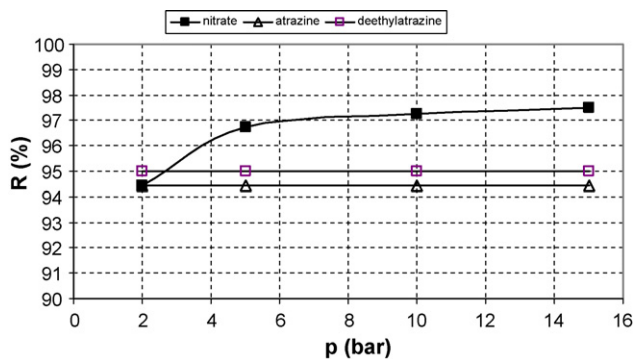


Fig. 10. The compound's rejection obtained at different pressures and SG membrane.

that of deethylatrazine is 187 g/mol, which is smaller than membrane MWCO, therefore, the rejection of deethylatrazine is very low.

With any increase in pressure, flux can be expected to increase accordingly (solution-diffusion model). A highly diffusive transport of ions through the membrane, compared to convective transport, is the reason for lower retention being found at low flux (lower pressure). With increasing flux, the contribution of convective transport becomes more important and rejection increases, which was confirmed by NO_3^- rejection results. The optimal pressure obtained was 10 bar. In literature [30] it states an optimal pressure of 8 bar where atrazine removal was satisfactory, whereas only a small fraction of nitrate was removed for most membranes, except for NF70 where a 76% removal of nitrate was obtained.

Fig. 10 shows the removal results for RO membrane (y axis shows the removal from 90%, above which it is different when compared to Fig. 9). Better removal values were achieved using RO membrane, which was also expected due to the tighter membrane structure, where all compounds are highly rejected. Also, the water permeability constant was lower when compared with DK membrane, indicating a tighter structure.

The highest removal was achieved for nitrate (94.4–97.5%), followed by deethylatrazine (95.0%), and atrazine (94.4%) with increasing pressure. This small difference is due to a slightly lower initial concentration of atrazine: the initial concentration was 0.19 $\mu\text{g/L}$ while for deethylatrazine it was 0.23 $\mu\text{g/L}$. Braeken et al. [31] stated that hydrophobic compounds adsorb to the membrane surface whereas the retention of hydrophilic compounds can not be influenced by adsorption. However, we can not prove that the rejection of atrazine is not influenced by adsorption. For deethylatrazine, atrazine, and nitrate, no clear effect of increasing pressure was noticed (solution-diffusion model). The optimal pressure where the maximal compound efficiency was obtained is 10 bar.

Once the optimal pressure had been determined, comparisons between both membrane efficiencies were analyzed. The much greater drop for the DK membrane compared to the SG membrane is due to the substantially smaller average pore radius of SG, which is in agreement with Nghiem et al. [32].

4. Conclusion

The removal efficiencies for atrazine and nitrate were studied using different adsorption media and membrane. Adsorption isotherms were determined using Filtrasorb 400 and two resins: Dowex Optipore L493 and Lewatit VP OC 1064 MD PH. The Freundlich equation was employed. Lewatit VP OC 1064 MD PH was the best adsorbent for atrazine, followed by Filtrasorb 400, and Dowex Optipore L493 resin with only half the Lewatit VP OC 1064 MD PH capacity. Filtrasorb 400 was determined to be the better solution

for deethylatrazine removal with a third higher adsorption capacity than Dowex Optipore L493. The results showed that approximately 6000 BV can be treated using 10 g of Dowex Optipore L493 resin or Filtrasorb 400, in order to remove atrazine and deethylatrazine from water, the initial concentration being around 0.2 $\mu\text{g/L}$ for each pesticide individually.

The research focused on RO and NF nitrate and pesticide rejection by pointing-out any significant differences between these membranes. The difference in nitrate rejection is not due to the influence of feed-water but rather to the intrinsic difference in nitrate rejection of the RO and NF membranes, with the NF membrane being "looser" than the RO membrane. The predominant mechanism of nitrate rejection for the RO membrane is size exclusion, while size exclusion and hydrophobic interactions are important for the NF membrane. The RO membrane displayed a high rejection of all compounds and also all the values were below the MAC value, while NF membrane showed lower compound rejection, only suitable for atrazine.

The removal efficiencies for atrazine were the same as obtained for membrane and adsorption tests. However, only the membrane allowed simultaneous removal of atrazine, deethylatrazine, and nitrate. Thus, in those cases where atrazine and nitrate removal is required, membrane separation has once again proved to be more appropriate.

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