

Ammonia Removal using the Bed Filtration across the Abundantly Available Clinoptilolite-rich Tuff

Eva Chmielewská^{1*}

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Abstract

The objective of this study was to determine the feasibility at the laboratory and to evaluate the pilot potential in the field operation for ammonia removal out of the drinking water with enhanced ammonia concentration by applying Slovakian clinoptilolite-rich tuff deposited at the domestic municipality Nižný Hrabovec. Detailed technological parameters were determined for the inland clinoptilolite-rich tuff and compared with some other foreign samples including common water treatment adsorption materials like active coke and silica sand. The one zeolite column was able to treat 85 m³ of drinking water with enhanced ammonia concentration up to the limited value of 0.5 mg/L (the laboratory model only a volume of 675 L), what means that the 4 days operated zeolite filter removed from the whole treated volume of water 81 g of ammonia. Any heavy metal concentrations over the hygienic limitation occurred in water treated by clinoptilolite-rich tuff. The 2 h lasted regeneration was sufficient. The aqueous NaCl solution with pH = 9 was used for the zeolite bed regeneration. The increased pH and temperature of regenerant brines positively influenced the ammonia removal during the recovery of regenerant solution using the air stripping. The zeolite ion exchange pilot installation (ZIEPI) with a hydraulic loading rate of 900 L/h was situated than at the field experimental facility of Water Research Institute in Vajnory, the closed vicinity of Bratislava.

Keywords: Clinoptilolite rich tuff; Ammonia removal; Ion exchange; Regenerant recovery; Water purification; Air stripping; Recycling loop; Technological parameters

1. Introduction

Removal of ammonia from waters can be accomplished through the use of air stripping, breakpoint chlorination, ozonation, ion exchange or biological nitrification-denitrification (N-D). The first three physicochemical techniques are used rarely in practical application. Chemical ozonation is relatively expensive due to the high capital investment for the ozone generation. Moreover, some undesirable chemical precursors in treated water may appear after this and breakpoint

*Corresponding e-mail: chmielewska@fns.uniba.sk

^{1*} Comenius University, Faculty of Natural Sciences, Bratislava, Slovak Republic
Edgbaston, Birmingham, West Midlands, B15 2TT, United Kingdom

Note: The research was done at the author's previous employer Water Research Institute in Bratislava

chlorination methods, respectively. Today the most popular method for denitrification of wastewaters, on the basis of its environmental acceptability, remains the biological nitrification-denitrification. A significant majority of recent developments in wastewater treatment today relates specifically to biological processes and advanced treatment technologies such as adsorption and nanotechnology.

Removal efficiency of few of above methods is considerably dependent on the temperature, e.g. N-D and air stripping lose their high removal performance, especially during the winter time. From this point of view as well as on the base of its economic feasibility, the ion exchange on natural clinoptilolite seems a competitive solution for ammonia removal out of the polluted waters. However, one drawback of ion exchange may be mentioned, i.e. recovery of ion exchange ability needs to be done by permanent regeneration of zeolitic filters, what partially increases the ammonium removal cost by this method (Chmielewská, 2003; Directive 2000/60/EC of the European Parliament and of the Council, 2000; Hårleman et al., 2009; Horváthová, 1989; Inglezakis and Zorpas, 2012; Pepe et al., 2001).

Since the last decades, there have been constructed advanced media filters using one or more layers of sand, gravel, anthracite, natural zeolite, semiconductor grade mixed bed ion exchange resin or similar inert materials. Some water filters have used filter element having a limited service life, which required frequent replacement in order to remove unwanted solids with appropriate efficiency. Such systems have been proposed to use prior to filtration units to extend the service life of filter cartridges. Also there was developed a drinking water filter which removed major contaminants from tap water and adjust pH, respectively. The water filter contained a cylindrical cartridge with sponge filters, used as dividers between different layers of filtration material and along a length of the cartridge. The sponge filters removed suspended solids and the filter consisting from a layer of granulated zinc and copper alloy removed chlorine, heavy metals and bacteria, a fine mesh carbon black especially organic contaminants, pesticide, odor, color and trihalomethanes, a layer of granulated ion exchange resin removed dissolved solids and a layer of granulated activated calcite adjusted the pH of water. Some of another invention for water treatment relates to portable compact system with various components, all of which connect in an enclosure, so that there is no need for expensive piping (Tansel, 2008).

The objective of this study was to determine the feasibility at the laboratory and to evaluate the pilot potential in the field operation for ammonia removal out of the drinking water with enhanced ammonia concentration by applying filter beds consisting from the Slovakian clinoptilolite-rich tuff deposited at the domestic municipality Nižný Hrabovec.

2. Materials and Methods

Following equipment was installed at the laboratory, before the pilot examination started to be realized in the field. Each of two vertical glass columns of the height 150 cm, with a diameter of 3.2 cm were filled with 700 g (equaled to 0.8 L of Bed Volume – 1 BV) of zeolite clinoptilolite, which chemical and mineralogical composition reports the literature (www.zeocem.sk, 2008).

The used clinoptilolite-rich tuff had the grain size 0.3 – 1 mm. The zeolite columns were operated down flow mode with the loading rate 9 L/h (11 BV/h) using two peristaltic pumps (PP-2-15 Zalimp, Poland). Tap water enriched with ammonium chloride (p.a.) to the initial concentration of 3.2 mg/L was pumped on the top of the column and regularly monitored using the sampling ports at the bottom of these columns. To increase the number of bed volumes (BV) throughput across the laboratory columns, while maintaining a low ammonia concentration in effluents, a semicountercurrent operation with two zeolite beds in series was proposed. By this way, the zeolite filters operated at the laboratory uninterrupted for several months.

After a successful laboratory operation, the zeolite ion exchange pilot installation (ZIEPI) with a hydraulic loading rate of 900 L/h (~ 13 Bed Volumes BV/h) was situated at the field experimental facility of Water Research Institute in Vajnory, the closed vicinity of Bratislava. This pilot facility treated the tap water which was enriched by ammonium chloride to the initial concentration of 1 mg/L.

Two pressure steel columns operating in series, each one filled with 70 L or 56 kg of clinoptilolite rich tuff of size-granulation 0.4 – 1 mm, as the part of above described pilot facility, provided the drinking water purification with the high efficiency for several weeks. Bottom of each column was filled with 14 L of about 3 mm grain-sized sand as the drainage support layer.

The zeolite filters were operated in downflow mode during the common working service and upflow mode during the chemical regeneration. For the chemical regeneration of the loaded zeolite filter 2% NaCl solution of pH ~ 9 was used. Two hours lasted chemical regeneration required approximately 25 BV of 2% NaCl solution. To regenerate a zeolite filter by 85% or to eluate the ammonia out of the loaded zeolite bed by this effectivity was satisfactorily for the maintaining a solid time schedule and the required water quality. To provide a permanent running of the whole facility (ZIEPI) and the uninterrupted water purification, ammonia exhausted regenerants needed to get recover using the air stripping. HDPP plastic tower of the total height 6.5 meter, assembled from 6 modules of the ground-plane measures 980 x 650 mm, was applied for ammonia stripping. To strip ammonia out of the regenerant brine a large quantity of air through the tower was necessary, therefore the design of stripping tower was improved by installation of two lateral air blowers at its bottom module (each one with the blowing capacity of 450 L/s). Stripping ammonia out of the exhausted regenerant solutions was then processed in countercurrent configuration, by which the entire air flow entered the bottom, while the treated regenerant was pumped to the top (with the same hydraulic loading rate as into the ZB, i.e. 900 L/h) and fell across the vertical waves-like shaped laminated slats to the bottom of the tower. The whole regenerant volume was air stripped without the mass closed loop operation, because the ZIEPI with the rather low operation capacity did not affect the surrounded air quality at that time significantly. While, the stripped ammonia was at that pilot facility discharged into atmosphere, for the higher-grade facility was necessary to plan ammonia recycling. The entire volume of regenerants (1800 L) was recycled through the tower during 150 minutes to decrease the initial ammonia concentration of 50 mg/L to less than 10 mg/L. In the first stripping cycle 47% of ammonia was stripped out, therefore the second stripping cycle was necessary.

All water as well as various technology stage samples were determined according to Slovak Technical Norm (EN ISO 25 667-2) harmonized with EU Norm (Council Directive 98/83/EC) by means of Diode Array Spectrometer Hewlett Packard 8452A (colorimetric determination of nitrite, iron, ammonia and manganese) and by means of Isotachophoresis (nitrate) on the Analyser ZKI 02 (Villa Labeco). The measured data were processed by ITP PRO 32 program (Kas Comp, Ltd. Bratislava). Atomic Emission Spectrometry (ICP OES, Jobin Yvon 70 Plus, France) was used for most of metallic species determination. Chemical oxygen demand (COD) was analyzed permanganometric and bacteriological analyses by plate method at the specialized Department of Water Research Institute.

3. Results and Discussion

To support the application of the examined clinoptilolite-rich tuff of Slovakian origin for water purification processes, some important technological properties comparable with adsorption materials common for water treatment, like silica sand and active coke incl. some foreign clinoptilolite-rich tuff samples, were measured (Table 1). To compare all the materials to each other, the grain-size of the adsorbents were kept more or less similar. Based upon the results obtained, the specific weights for silica sand reached the highest and for the active coke the lowest values. These data correlated well to their shipping weights, too. It was expected that with the enhanced porosity of the material, the surface areas (S_{BET}) proportionally arise. As generally known, very porous active coke use to reach the surface area even more than 1000 m^2/g . On the other hand, the attrition of this soft material was high (39.08%), in regard to the Slovakian clinoptilolite-rich tuff, who's attrition was about 5-times lower (8.2%). Depending upon the grain-size, the S_{BET} for Slovakian clinoptilolite-rich tuff was determined in the range of 36 to 59.2 m^2/g for its powdered form (Chmielewská, 2014; Chmielewská and Zeolite; 2012; Inan and Alaydin, 2014; Jorgensen and Weatherley, 2003; Li et al., 2012).

Table 1 Detailed technological parameters (specific and shipping weights, porosity, sphericity, attrition, surface area) determined for the Slovakian clinoptilolite-rich tuff and compared with some other foreign samples incl. common water treatment adsorption materials like active coke and silica sand

Species	Grain size [mm]	Specific Weight [$g \cdot cm^{-3}$]	Shipping Weight [$g \cdot cm^{-3}$]	Porosity ε [%]	Sphericity ϕ [-]	Attrition [%]	Surface area S_{BET} [$m^2 \cdot g^{-1}$]
Clinoptilolite (Nižný Hrabovec)	0.3-0.8 <0.125 mm	2.39	0.84	34.8	0.47-0.49	8.2	36 59.2
Clinoptilolite (Solárnica - Ukraine)	0.3-0.8	2.36	0.94	30.1	0.49-0.51	-	16.5
Clinoptilolite (Hector - USA)	0.3-0.8	2.31	0.84	33.6	0.54-0.59	-	31
Silica sand	0.3-1.0	2.66	1.55	11.7	0.83-1.1	0.57	<5
Active coke (Slovakian origin)	0.3-1.5	2.19	0.40	51.7	0.27-0.28	39.08	849

Tables 2 and 3 illustrate a representative example of chemical and bacteriological composition of water treated by means of above laboratory equipment during the current 5 – days operating cycle. In tap water, as can be seen in Table 2, the content of Ca and Mg cations fluctuates, especially in case of Mg²⁺, while the ammonia concentration is about three times lower regarding the Ca ion concentration. The K⁺ ions were removed from water simultaneously with ammonia and oppositively, the Na⁺ ions were releasing from zeolite filter. According to the Table 3, where numerous technological samples and analysed heavy metal data from specific 5 days filtration, regeneration, backwashing and grained as well as powdered zeolite tap water eluates are presented, following conclusions were drawn. Except the arised aluminum content including slight increase of Ni in the alkalic recycled and recovered regenerants and in 2.5 h lasted tap water eluates, any other heavy metal concentrations over the hygienic limitation occurred in water treated by clinoptilolite-rich tuff (Directive 2000/60/EC of the European Parliament and of the Council, 2000; <http://www.atsdr.cdc.gov/phs/phs.asp?id=575&tid=107>, 2013; Melicherčíková and Melicherčík, 2011; <http://www.dhs.wisconsin.gov/eh/HlthHaz/fs>, 2013). The high pH of regenerant solution (over 9) worked onto the zeolitic rock destructive, while with the higher probability the not zeolitic rock's components dealuminated much easier (Horváthová, 1989). Such problem was proposed to solve by the utilization of less aggressive regenerant, alternatively using the additional step of water purification. The 6th day zeolite filtration in this case was done for verification of comparable metal eluation by breakthrough steady state only.

Table2 Chemical and bacteriological composition of water treated by means of laboratory zeolite equipment during the common 5 days operating cycle

Component in mg/L	Influent 1 - 5 th day					Effluent 1 - 5 th day				
	NH ₄ ⁺	3.1	3.5	3.4	3.3	3.3	0	0	1.2	2.6
NO ₂ ⁻	0	0	0	0	0	0	0	0	0	0
NO ₃ ⁻	2.8	18.8	21.6	23.5	15.5	7.8	21.6	27.0	23.5	22.0
O ₂	10.1	14.1	8.6	8.6	9.0	9.5	10.6	8.7	10.9	9.0
Ca ²⁺	58.1	59.1	65.1	53.1	54.1	52.1	51.1	40.1	64.1	65.1
Mg ²⁺	17.6	1.2	0	13.9	5.1	12.1	5.5	20.6	0	0
Na ⁺	15.5	15.5	17.0	17.0	16.9	44.0	25.5	25.5	20.0	17.5
K ⁺	5.3	4.8	5.3	5.3	5.2	1.0	1.0	1.0	2.2	2.6
Fe ³⁺	0	0	0	0	0	0	0	0	0	0
COD	1.5	1.3	1.5	1.5	1.4	1.5	1.8	1.5	1.5	1.4
Alkalinity, mmol/L	3.8	3.8	3.8	4.0	3.9	4.1	4.4	3.8	4.1	4.2
Mn (total)	0	0	0	0	0	0	0	0	0	0
Psychrophil bacteria/mL	0	0	0	0	0	143	0	0	0	33
Mesophil bacteria/mL	0	0	0	0	0	23	47	0	0	1
Coli index	0	0	0	0	0	0	0	0	0	0
Flagellata	0	0	2	0	0	0	13	0	4	0
Other physiologic bacteria	0	0	0	0	0	0	0	0	0	0

Table 3 Analysed heavy metal data from the common 5 days zeolitic filtration, regeneration, backwashing and grained as well as powdered zeolite tap water eluates

metal mg/L sample	Al	Fe	Cu	Ag	Pb	Zn	Cd	Ni	Co	Cr	Sr	Cs	Ba	Se	As	Hg	V
tap water	0.04	0.56	0.008	0.001	0.004	0.29	<0.001	0.015	<0.002	<0.002	0.08	<0.002	-	-	-	-	-
synthetic tap water	0.07	0.28	0.009	0.001	0.005	0.39	<0.001	0.005	0.02	<0.002	0.32	<0.002	-	-	-	-	-
zeolite filtered water	0.16	0.06	0.005	0.002	0.005	0.04	<0.001	0.02	0.01	<0.002	0.02	<0.002	-	-	-	-	-
tap water	0.05	0.09	0.01	<0.001	0.012	0.11	<0.001	0.01	<0.002	0.002	0.32	-	-	-	-	-	-
zeolite filtered water	0.12	0.08	0.009	<0.001	0.006	0.07	<0.001	0.005	0.004	<0.002	0.03	<0.002	-	-	-	-	-
tap water	0.07	0.13	0.006	<0.001	0.004	0.13	<0.001	0.005	0.002	<0.002	0.34	-	-	-	-	-	-
zeolite filtered water	0.09	0.07	0.005	<0.001	0.002	0.07	<0.001	0.005	0.002	<0.002	0.12	-	-	-	-	-	-
tap water	0.05	0.08	0.004	<0.001	<0.002	0.12	<0.001	0.01	0.004	0.002	0.34	-	-	-	-	-	-
zeolite filtered water	0.14	0.09	0.007	0.001	<0.002	0.08	<0.001	0.01	<0.002	0.002	0.12	<0.002	-	-	-	-	-
tap water	0.05	0.08	0.004	<0.001	<0.012	0.12	<0.001	0.005	0.002	0.002	0.34	<0.002	-	-	-	-	-
zeolite filtered water	0.06	0.06	0.005	<0.001	<0.012	0.08	<0.001	0.01	<0.002	<0.002	0.2	-	-	-	-	-	-
tap water	0.07	0.06	0.003	0.001	0.008	0.14	<0.001	0.005	0.008	<0.002	0.34	<0.002	-	-	-	-	-
zeolite filtered water	0.08	0.1	0.005	<0.001	0.006	0.09	<0.001	0.005	0.002	0.054	0.26	<0.002	-	-	-	-	-
Recycled and recovered	40.6	0.48	0.028	0.003	0.04	0.31	<0.001	0.70	0.102	0.028	0.04	-	-	-	-	-	-
regeneration (alkalic 2% NaCl)	3.12	0.36	0.02	<0.001	0.01	0.29	<0.001	0.65	0.10	0.032	0.002	-	-	-	-	-	-
counter-current	pH= 10.8; 3.75	0.17	0.016	<0.001	0.005	0.1	<0.001	0.01	0.02	0.002	<0.002	<0.002	-	-	-	-	-
backwashing of zeolite	pH= 10.2; 1.12	0.15	0.010	<0.001	0.005	0.07	<0.001	<0.005	0.004	0.002	0.008	<0.002	-	-	-	-	-
filter with tap water	pH= 7.2; 0.14	0.18	0.016	<0.001	0.005	0.05	<0.001	<0.005	<0.002	<0.002	0.042	<0.002	-	-	-	-	-
tap water eluate of	1.62	0.1	0.005	0.003	0.002	0.10	<0.001	0.015	0.002	0.004	0.14	0.008	0.013	<0.001	<0.001	<0.001	<0.005
grain sized 0.2-0.7 mm																	
zeolite after 2.5 h	0.42	0.09	0.009	0.002	0.004	0.06	0.012	0.01	0.008	0.002	0.32	0.002	0.027	<0.001	0.003	<0.001	<0.005
tap water eluate of																	
powder (<0.125 mm)																	
zeolite after 2.5 h																	

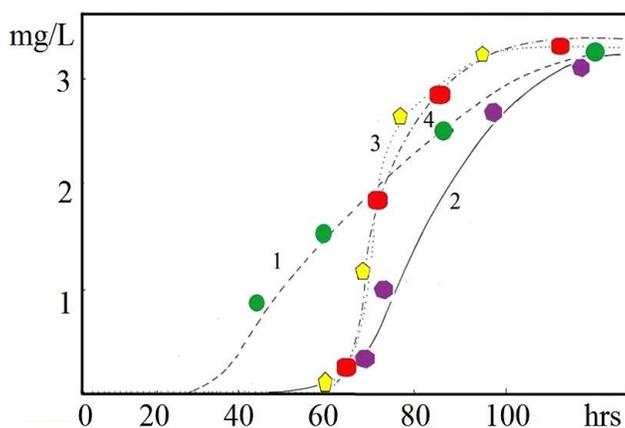


Fig.1. Typical breakthrough curves measured by means of laboratory zeolite bed and tap water with ammonium content of 3.2 mg/L (curve 1 was the first and curves 2 – 4 subsequently obtained, i.e. after the zeolite bed regeneration with 2% NaCl)

Figs. 1 and 2 present the typical breakthrough curves with actual cation exchange during the process studied. Recorded data clearly showed, that mostly the exchange of NH_4^+ , Ca^{2+} and K^+ ions with each other and the slight increase of NO_3^- anions in effluents by gradual reaching the steady state appeared. Nevertheless, after the alkalic regeneration of zeolite bed and backwashing with tap water, the not remarkable nitrate increase fell down to the former level. Moreover, drinking water is usually at the end disinfected, what means that potential biological pollution of water is expected to be diminished.

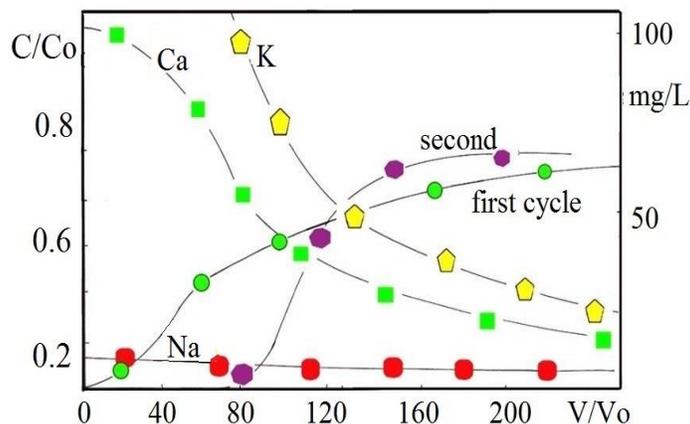


Fig. 2. Reverse cation exchange by ammonium removal from the tap water on laboratory zeolite bed (1. NH_4^+ curve means the use of native variety of zeolite or first cycle by which the simultaneous elution of mostly K^+ , Ca^{2+} and in less extent Na^+ ions proceeded)

Fig. 3 illustrates the standard regeneration cycles of the zeolite columns performed with 2% NaCl solution and alkalinized with NaOH for the pH ~ 9 . The use of economic lime for filter regeneration was excluded due to the identification of unwanted calcium carbonate in between zeolite grains, causing so-called „channelling effect“ or filter plugging, visible in the laboratory glass columns. For the total regeneration of zeolite filters 1.3 kg of NaCl was consumed. This quantity was sufficient for the whole and renewed regeneration periods as well as for the Na ions supply for the zeolite framework, respectively. Any other addition, except the alkalization with NaOH, was required in this regeneration process. Based upon the curves recorded at the Fig. 3, there is more or less evident that 2 h lasted regeneration was sufficient. In regard to synthetic ion exchanger, a specific lower concentration of regenerant solution for natural zeolite use to be chosen, in order to exclude the colmatation of zeolite bed. Also the regeneration curves depict the longer stationary as well as diffuse phases by the species exchange (Fig.3). Figs. 4 and 5 present the laboratory results of ammonia removal efficiency upon the various pH and temperature within the time tested for the final step, i.e. for the exhausted regenerant recovery. It seems clearly that the increased pH of regenerant brines positively influenced the ammonia removal efficiency. On the other hand, the high pH of solutions caused a structure breakdown or dealumination of zeolite framework (Table 3).

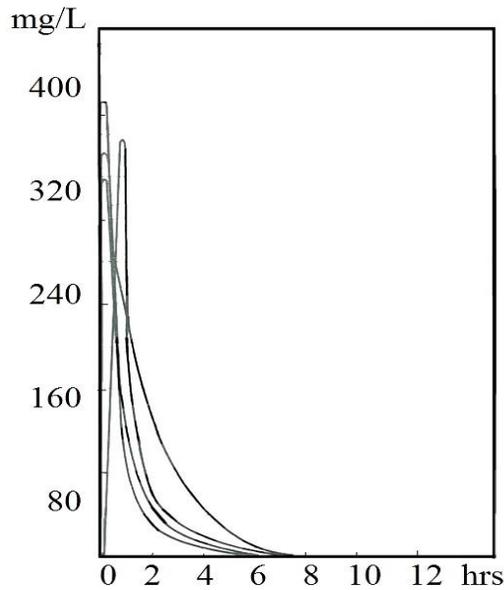


Fig. 3. The 4 standard regeneration curves of laboratory zeolite bed recorded or ammonia elution within the time using the alkalized 2% NaCl solution

Also the enhanced volume of tap water for filter backwashing and the alkalinity decrease is necessary. From this reason, the aqueous NaCl solution with pH = 9 was used for the zeolite bed regeneration.

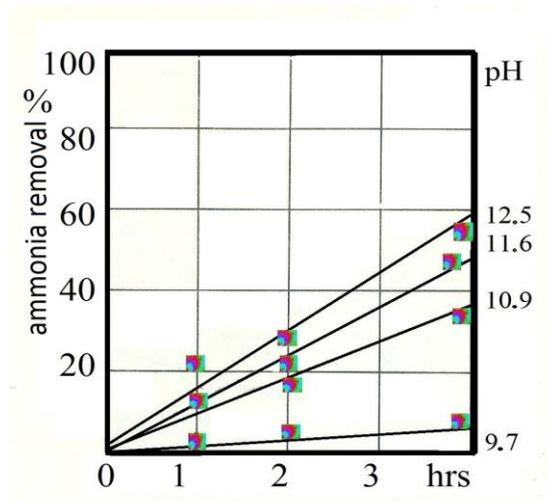


Fig. 4. Ammonia removal efficiency upon the pH within the time for the exhausted regenerant recovery

The main physicochemical factors, like temperature and pH on the ammonia removal efficiency, was examined at laboratory using the model cylindrical containers equipped with the bottom air diffusers, which were supplied from the central pressed air system and controlled by rotameter with the air flow of 500 L/h. To shorten the ammonia stripping out of the regenerant brines the

regenerants were heated by 2 thermostates, keeping the constant temperature at 36°C. The lab system was simplified in order to find out how much air is necessary to strip ammonia out of the regenerant brines and to reduce the air consumption, respectively. Fig. 5 depicts the considerably increase of ammonia removal efficiency within the time by the enhanced temperature, while showing the highest performance at 40°C. Based upon this arrangement, the consumption of about 1.5 m³ air to recover 1 L of regenerant solution or to remove the whole ammonia with the initial concentration of 40 mg/L was estimated. Therefore, for industrial scale treatment, some counter or parallel-flow double pipe waste heat exchanger was recommended to shorten the ammonia stripping process and thus to save the energy for pumping.

The major factors which affected design and process performance of pilot air stripping tower were the tower configuration, the air flow and the pH. For recovery of 1 L of regenerant solution in pilot air stripping tower, the consumption of 3.8 m³ air was necessary. To maintain pH ~ 11 of regenerant solutions in stripping process and to compensate some loss of sodium ions in regenerant effluents, regularly addition of NaOH into effluents was provided during the operation of ZIEPI.

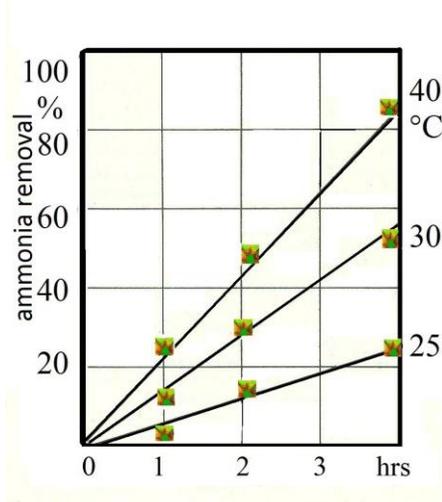


Fig. 5. Ammonia removal efficiency upon the temperature within the time for the exhausted regenerant recovery

According to the section Materials and Methods described operation of ZIEPI, the one zeolite column was able to treat 85 m³ of drinking water with enhanced ammonia concentration up to the limited value of 0.5 mg/L (the laboratory model only a volume of 675 L), what means that the 4 days operated zeolite filter removed from the whole treated volume of water 81 g of ammonia.

The operation principle of two pilot zeolite columns (zeolite beds ZB) was as follows: Single or one ZB was under the operation service till the ammonia concentration in effluent reached the limited value of 0.5 mg/L and then the second new ZB was connected with the first one in series to load the capacity of the first ZB totally. When the first ZB was loaded to its maximum capacity, the column was disconnected from the operation in series and started to get regenerate, while the second ZB operated as single column. There was sufficient time to get regenerated the by ammonia loaded ZB and to prepare it for the sequenced operation in the next process of drinking water purification. The

longer time operating ZB was used to be joined in series always at the influent end, backed up by another ZB with lower loading level. Using this strategy of operation, the number of bed volumes throughput (volumes of treated water by ZB) during the operation service increased effectively by about 50% (Fig.6).

A half hour lasted ZB backwashing using the tap water with about 30% bed expansion followed the chemical regeneration with alkalic NaCl solution additively, due to necessity of pH decrease of the treated water filtered through ZB, left after its contact with the alkalic brines.

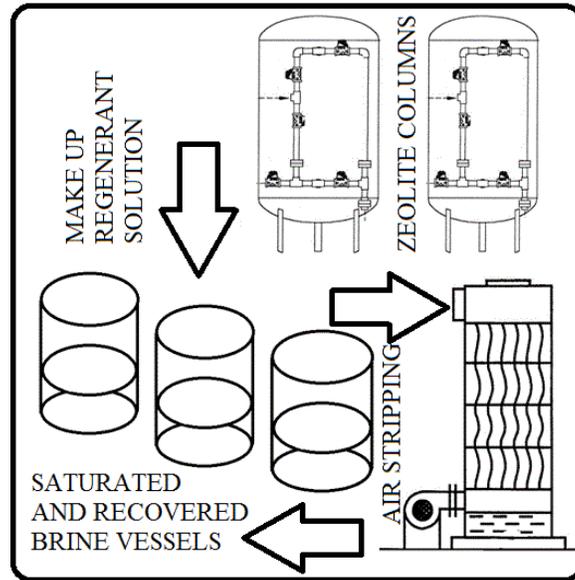


Fig. 6. Principle sketch of ion exchange technology for ammonia removal from water using the zeolitic filtration incl. its chemical regeneration and the used regenerant recovery by air stripping

4. Conclusion

In autumn 1986, the zeolite ion exchange pilot installation (ZIEPI) with a hydraulic loading rate of 900 L/h was successfully operated at the Water Research Institute field experimental facility in Vajnory, which is near Bratislava.

At that time, the cost to treat water by means of ion exchange utilizing clinoptilolite-rich tuff, including chemical regeneration and regenerant recovery by air stripping, was calculated as 0.37 Czechoslovakian crowns (0.012 Euro). It should be noted in respect to that time, the low per kilowatt cost of electricity made the cost of water purification low. To the total cost the consumption of zeolite, chemicals, energy for pumping, air stripping, filtering and backwashing was calculated.

No pathogenic microorganisms were detected during water purification by this method. According to the hygienic and sanitary procedures performed, this aluminosilicate was not classified as toxic or carcinogenic, nor did it demonstrate any oral or dermal toxicity. A standardized fibrogenicity procedure, using the intratracheal application of powdered zeolite with less than 5 µm grain-size in physiological solution, was tested using Whistar rats. Only the less than 3% of respirable, pure SiO₂ (free quartz) content in the zeolite samples was identified (Horváthová, 1989). Based upon this fact, it was concluded that the content may not expose or endanger human health during the treatment process.

Moreover, updated epidemiological studies have not revealed any evidence of a relation between exposure to natural clinoptilolite and diseases of the respiratory tract beyond general effects of dust.

Despite of the all positive results presented, ion exchange technology utilizing clinoptilolite-rich tuff has not been applied industrially since that time in Czech or Slovak Republics probably due to the rare or no occurrence of such a specifically polluted drinking water.

Acknowledgements

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