Desalination and Water Treatment
www.deswater.com
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doi: 10.1080/19443994.2012.664724
41 (2012) 335–341
March
Taylor & Francis
Taylor & Francis Group

Natural zeolite—a versatile commodity—some retrospectives in water cleanup processes

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Received 9 November 2011; Accepted 22 January 2012

ABSTRACT

The objective of this paper is to review some of the practical applications of clinoptilolite-rich tuff, deposited at the Eastern Slovakian repository Nižný Hrabovec, which has been used for inland water treatment and purification processes in the last 25 years. Since this field is wide, this overview is limited and highlighting only those water purification and treatment processes, which have been realized in industrial scale up or pilot applications. The zeolite ion exchange pilot installation with a hydraulic loading rate of 900 L/h was situated at the field experimental facility of Water Research Institute in Vajnory, the closed vicinity of Bratislava, during the autumn of 1986. Surface water purification by means of chemical coagulation and flocculation supported by the powdered natural zeolite was carried out in 1984 to save the drinking water reservoir (upper part of Ondava river) settled by about 10,000 equivalent inhabitants. Ammonia removal from tannery wastewater using the clinoptilolite-rich tuff with chemical regeneration and regenerant recovery by air stripping was carried out for several months in 1987 at the mixed Wastewater Reclamation Facility in Zlin (Moravia region). Zeocem company is currently producing manganese-dopped grain-sized clinoptilolite-rich tuff under the trade mark Clinopur, purchased for water purification and for the removal of Mn with Fe pollutants removal.

Keywords: Clinoptilolite-rich tuff; Ammonia removal; Ion exchange; Regenerant recovery
Water purification; Air stripping; Coagulation and floculation; Fe and Mn removal

1. Introduction

In the last several decades, natural zeolites have been upgraded to a commodity of great potential, more or less due to the progress permanently reached by their marketing, e.g. as building stone, as lightweight aggregate and pozzolans in cements and concretes, as filler in paper, in the uptake of radiocesium and strontium from nuclear waste and fallouts, as soil amendments in agronomy and horticulture, in the removal of ammonia from municipal, industrial or agricultural waste and drinking waters, as energy supplier in solar refrigerators, as dietary supplements in animal diets and as zeoponic substrate for growing plants on space missions to their recent application in the healing of human cuts and wounds [1].

These volcanogenic sedimentary rocks may potentially record, in an improving price–performance position compared to the increasing number of crystalline zeolite-type or other porous carbon- or silica-based synthetic materials, perspective uptake rates even in the future. China is currently the giant of natural zeolites production with an estimated output of 2.5 Mtpa or 65% of the world output. Cuba accounts for a further 15% of the world's production of natural zeolites [2,3] .

Other significant producers include Germany, Japan and South Korea. Pet litter, animal feed and water purification nowadays account for more than 70% of the market sales tonnage. Despite the versatility of surface-modified clinoptilolite, this field is still not fully explored, except the low-cost surfactant-modified zeolites which have been prepared in multi-ton quantities in USA for its use as subsurface-permeable barriers against ground water contaminant migration [4,5].

Based on the chemical and mineralogical variabilities of the zeolitic rocks and thus their moderate ion exchange and selectivity properties including the exploration of some new zeolite ores in individual countries, an unpredictable wide national research and versatile industrial applications of these unique tuffaceous materials have been initiated all over the world since the last several decades. Topic of this paper therefore is to review some of the practical applications of clinoptilolite-rich tuff, originated from the Eastern Slovakian repository Nižný Hrabovec, which has been used for inland water treatment and purification processes in the last 25 years.

2. Ammonia removal from drinking water using the ion exchange technology with clinoptilolite-rich tuff including mass recycling loop

The zeolite ion exchange pilot installation (ZIEPI) with a hydraulic loading rate of 900 L/h (~13 Bed Volumes [BV] per hour) was situated at the field experimental facility of Water Research Institute in Vajnory, the closed vicinity of Bratislava, during the autumn of 1986. This pilot facility treated the tap water which was enriched with ammonium chloride to the initial concentration of 1 mg of ammonium per litre (Table 1). Two pressure steel columns operating in a series, each one filled with 70 L or 56 kg of clinoptilolite-rich tuff of size-granulation 0.4–1 mm, as a part of the above described pilot facility, provided the drinking water purification with 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 in upflow mode during the chemical regeneration. For the chemical regeneration of the loaded zeolite filter 2% NaCl solution of pH ~ 9 was used. The chemical regeneration process lasted for two hours and required approximately 25 BV of 2% NaCl solution to regenerate a zeolite filter by 85% or to elute the ammonia from the loaded zeolite bed by this method effectively and satisfactorily for 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 thereafter need to get recovered by means of air stripping, to be again recycled for filter regeneration. HDPP plastic tower with a total height of 6.5 m, assembled from six modules of the ground-plane measures 980 × 650 mm, was applied for ammonia stripping. To strip ammonia out of the regenerant brine, a large quantity of air trough the tower was necessary, therefore, the design of stripping tower was improved by the 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 counter-current tower 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 zeolite beds (ZB) i.e. 900 L/h) and falled across the vertical waves-like shaped laminated slats to the bottom of the tower (Fig. 1). 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 significantly. The stripped ammonia was discharged simple into the atmosphere. The entire volume of regenerants (1800 L) was recycled through the tower for 150 min to decrease the initial ammonia concentration from 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 also necessary. The major factors which affected the design and process performance of air stripping tower were tower configuration, air

Table 1
Average water quality of influents for pilot plant in Vajnory and waste water treatment facility in Zlin

Index mg/L	Inorganic substances	COD	BOD	NH_4^+	NO_3^-	K^+	Na^+	Ca^{2+}	Mg^{2+}	pH	Cr^{3+}	Cl^-	SO_4^{2-}
Waste water	1026	108	17	50	22	11	26	139	17	7.4	2.4	301	156
Drinking water	–	1.5	–	1	2.8	5.3	15.5	58.1	17.6	7.2	–	26	31

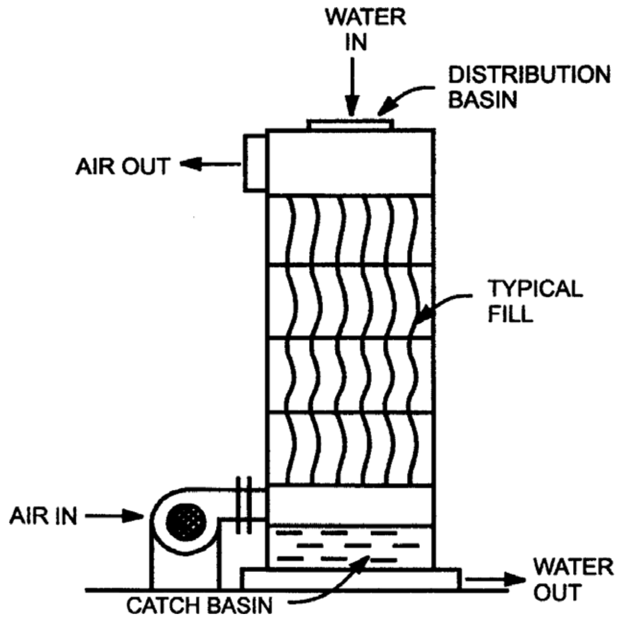

Fig. 1. Principle sketch of pilot air stripping tower for removal of ammonia from elutriants (regeneration) solution applied by the drinking water purification at the field laboratory.

flow and pH. For the recovery of 1 L of regenerant solution, the consumption of 3.8 m^3 of air was necessary. To maintain pH of 11 of regenerant solutions in the stripping process and to compensate some loss of sodium ions in the regenerant effluents, regular addition of NaOH to the effluents was provided during the operation of ZIEPI.

In the above described operation, one zeolite column was able to treat 85 m^3 of drinking water with enhanced ammonium concentration up to the limited value of 0.5 mg/L, which means that the 4 days operated zeolite filter removed 81 g of ammonium from the whole treated volume of water. The operation principle of two pilot zeolite columns (ZB) was as follows: single or one ZB was under the operation service till the ammonium concentration in the effluent reached the limited value of 0.5 mg/L and then the second new ZB was connected to 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 a single column. There was sufficient time for the column to get regenerated by the ammonium-loaded ZB and to prepare it for the sequenced operation in the overall 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%.

A half-an-hour lasted ZB backwashing using the tap water with about 30% bed expansion following the chemical regeneration with alkalic NaCl solution additively, due to the necessity of pH decrease of the treated water filtered through ZB, left after its contact with the alkalic brines (Fig. 2).

3. Surface water purification by means of chemical coagulation and floculation supported by the powdered natural zeolite

The coagulation and flocculation in drinking water purification process are a classical or traditional method in water technology, which is used for removal of suspended particles and coloids. These entities used to cause the enhanced turbidity and unwanted colouring of waters; therefore, the coagulation and flocculation are mostly employed for the entire surface water treatment (pretreated with the sedimentation and sand filtration in the common Water Works). The technique is able to remove total turbidity with about 90% efficiency and 50–70% of the total organic matter (as chemical oxygen demand [COD]).

To save one of the Eastern Slovakian surface water reservoirs (upper part of the river Ondava) in 1984, in the region with a critical deficiency of high quality water resources, the local Water Works applied for surface water purification a powderized natural zeolite (clinoptilolite-rich tuff) from the nearby repository Nižný Hrabovec together with the primary coagulant $Al_2(SO)_3 \cdot 18H_2O$. The zeolite was added to the water during the coagulation step of the water purification process for several months until the ammonia contamination in the reservoir, caused probably by the local agricultural company, get disappeared. To support a better aggregation of suspension and facilitate a larger size and higher density floccs, the amount of zeolite added to the treated water represented a maximum amount of 5 g/L.

4. Drinking water with enhanced Fe and Mn concentrations treated with zeolitic Clinopur

Zeocem company is currently producing manganese-dopped grain-sized clinoptilolite-rich tuff under the trade mark *Clinopur* which is beneficial for water purification and for the removal of Mn with Fe pollutants [6].

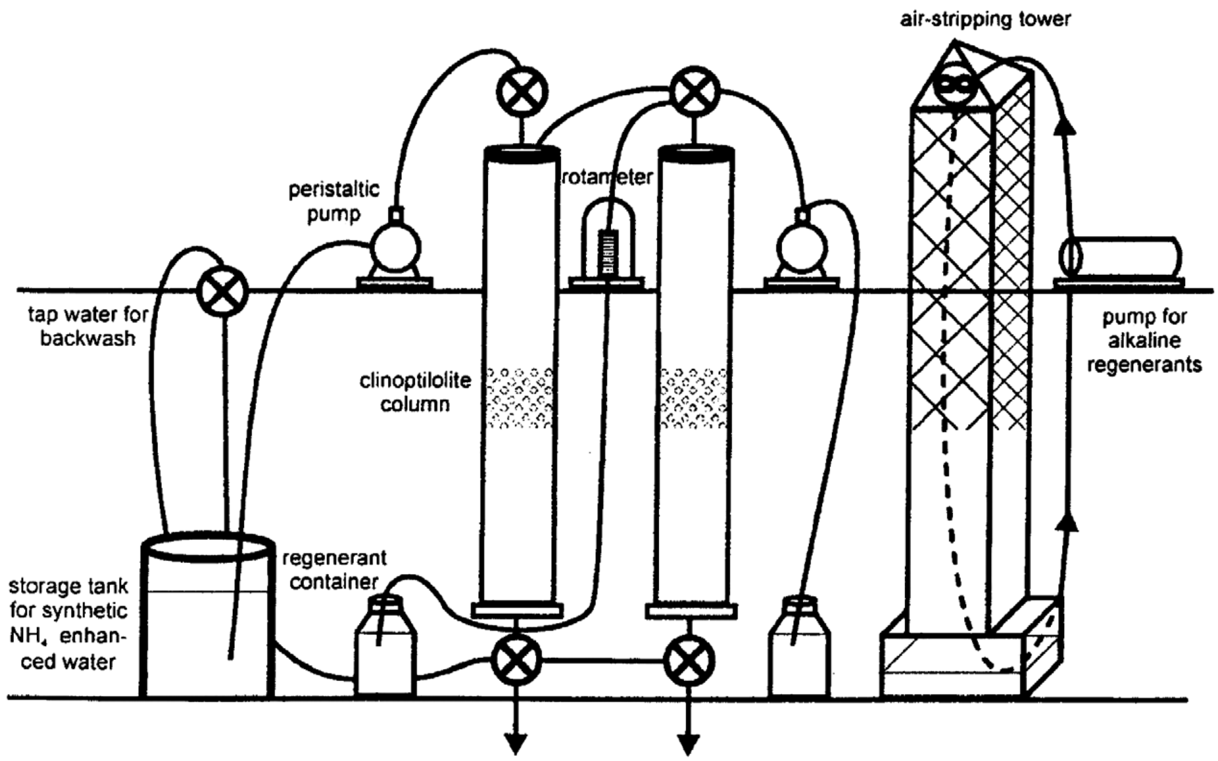

Fig. 2. Principle sketch of zeolite ion exchange pilot plant using the clinoptilolite-rich tuff, chemical regeneration and air stripping recovery of ammonia-rich regenerant solution installed at the field laboratory.

In underground waters which are characterized by low oxygen content, a dissolved Fe(II) species usually appears in contrary to the surface water resources where some hydrated oxides of Fe(III) states, their coloidal entities or different forms bound into organic complexes occur. The reason for that phenomenon is mainly the higher oxygen concentration in those waters. Manganese used to be present exclusively in dissolved Mn(II) state. While the presence of iron without manganese is common, manganese alone in waters occurs rarely.

Removal of the above entities out of the waters proceeds by various routes of oxidation reactions after which precipitated hydrated oxides allow the sedimentation and filtration steps. Nevertheless, the manganese in regard to iron oxidation proceeds more slowly. For the simultaneous removal of iron and manganese out of the waters a higher valency MnO_2-coated filtration materials which are available in the market, manufactured mainly with the activation of adsorbent surface by $KMnO_4$ solutions, are used. Besides a plenty of costly commercial products like Kemira, GEH, Bayeroxide, Greensand and others, purchased for such a water purification worldwide, domestic market offers this cost-effective Clinopur.

Thus, in water, rather fast ongoing autocatalytic oxidation of Mn(II), by the presence of higher valency MnO_2, may be expressed by the following equation:

$$MnO_2 + Mn^{2+} + \frac{1}{2}O_2 + H_2O \rightarrow 2MnO_2 + 2H^+ \ (pH \approx 8.3)$$

5. Ammonia removal from tannery wastewater using the clinoptilolite-rich tuff with chemical regeneration and regenerant recovery by air stripping

Similar operation with the same hydraulic loading rates through the zeolite beds as by the drinking water purification units was used for the removal of ammonia from the mixed tannery and sewage sludge waste waters at the Shoe Manufactury Wastewater Reclamation Plant in Zlin (former Czechoslovakia) in the 1987 (Table 1) [7]. A higher ammonium concentration in waste water (in average, 50 mg/L) considerably increased the ion exchange capacity of zeolite (approximately 10 times higher in regard to drinking water purification).

Operation of three columns (two ZB under stream while the third ZB being regenerated) as well as much more complicated management of the entire ZIEPI valving and piping was required at this wastewater treatment facility. In comparison with the sufficiently long, i.e. 4 days long drinking water service of ZB, ammonia removal from the waste water by ZB already reached the limited value of 3 mg/L in the effluent after 15 h. Consequently, the time of regeneration including ammonia stripping was needed to be shortened to keep the entire operation system permanently running [8]. The sketch in Fig. 3 illustrates the three-fractional regeneration and ammonia stripping process which was used for regenerant recovery and recycling in the ZIEPI. Only the highest, on ammonia mostly concentrated elutriant solution (the first fraction of the whole volume consisted from three portions) was stripped in air stripping tower. The stripping process of ammonia was intensified and considerably shortened by the injection of the mixed hot waste steam and air at the bottom of the tower against the regenerant solution pumped to the top of this tower. The stripped ammonia was proposed to get absorbed into water

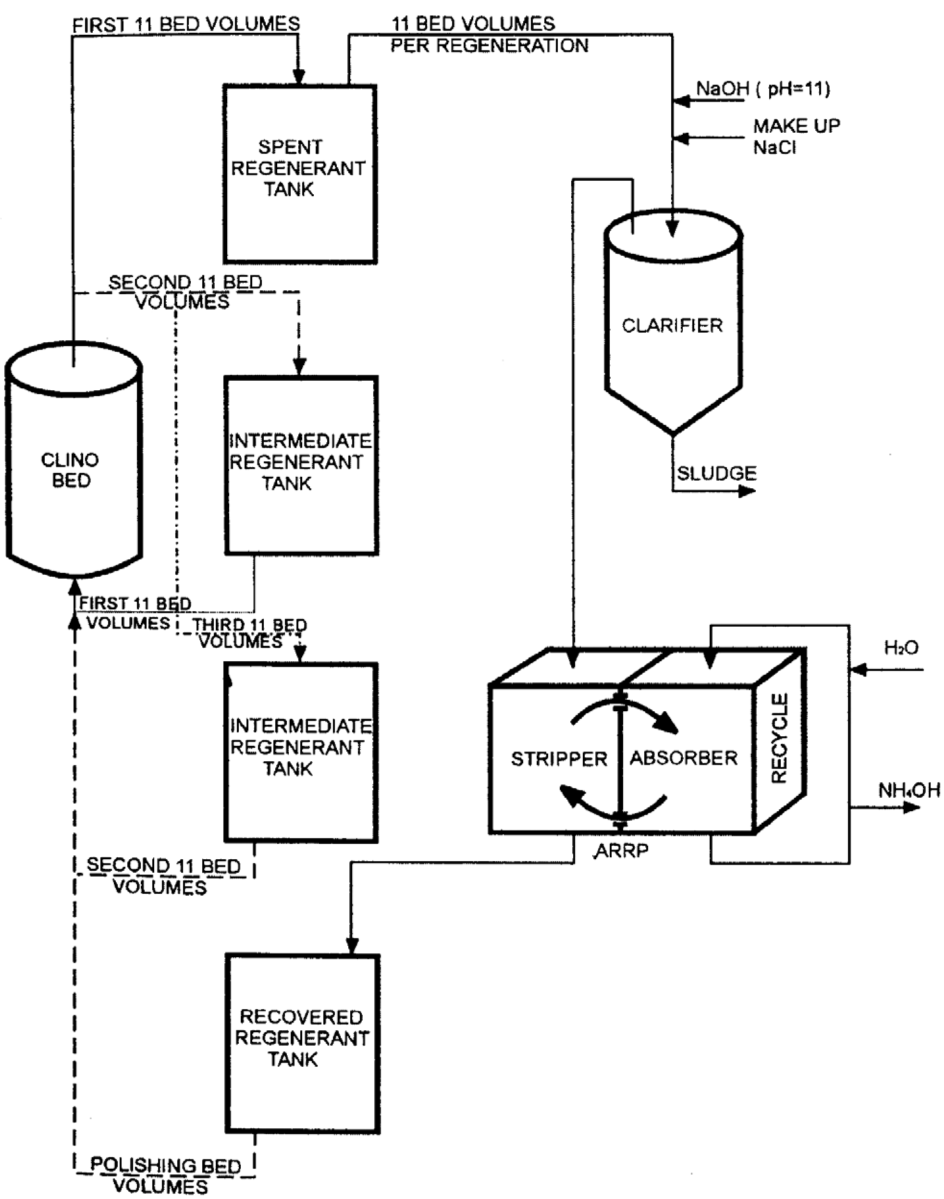

Fig. 3. Diagram of three-fractional zeolite regeneration and ammonia recovery system applied at the Tannery Wastewater Treatment Facility in Zlin (TWTF).

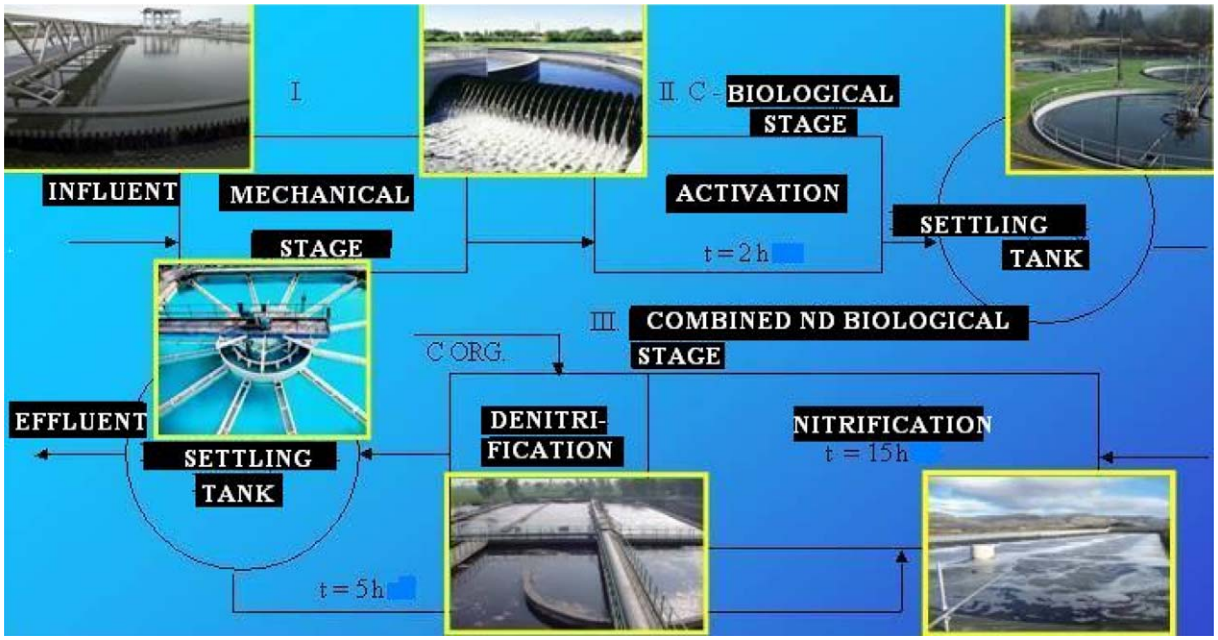

Fig. 4. Schematic illustration of conventional waste water treatment at the TWTF in Zlin.

to produce the agricultural fertilizer. For the recovery of 1 L of highly concentrated elutriants (regenerant solution), the consumption of 20 m^3 of air was necessary.

After several months of ZIEPI operation, the Centroproject Zlin provided, based on the submitted pilot experimental data, some economic calculations for model capacity of 6,000 m^3 of treated wastewater per day [9]. At that time, the investment for the construction of zeolite ion exchange and regeneration and air stripping recovery units for the proposed capacity was calculated to be 550,000 Euro, whereas the investment for ammonia removal by means of biological nitrification–denitrification method was estimated to be 700,000 Euro (see the schematic diagram at the Fig. 4). Nevertheless, the operation cost of ion exchange technology using the natural zeolite per cubic meter of treated water was a bit higher than the operation cost of the comparable biological nitrogen removal using the nitrification–denitrification method. Concluding, the examined technology of zeolitic ion exchange appeared technically and financially competitive towards traditional biological methods.

6. Conclusion

Nowadays, some updates or other zeolitic applications related to water treatment and purification processes are available in hundreds. However, recent literature reports the state of the art mainly in zeolite surface modification using the hydrophobization (sol-gel technique for coating the zeolitic surface by different surfactants) or peletization of zeolite matrices with some biopolymeric eco-friendly carbohydrates [10].

Since the last decade, by our investigations, several new surface-modified or hybridized zeolite adsorbents have been succesfully synthesized whose performance and favourably, much extended adsorption properties towards aqueous pollutants have been achieved (mostly with the octadecylammonium surfactant-coated clinoptilolite-rich tuff).

Nevertheless, natural zeolite of clinoptilolite type, deposited at the municipality by Nižný Hrabovec, may become a preferable adsorbent even without costly surface modification towards inorganic nutrients like ammonia and phosphate. The selectivity and effectivity of the removal of these pollutants out of the waters using the above natural mineral were already confirmed in the past for many times.

Acknowledgements

The project of natural zeolites utilization for water treatment processes is currently funded by the Slovak Scientific Council VEGA (Project No. 1/0185/12) and Slovak-Chinese Cooperation grant SK-CN-0002-09.

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