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ADVANCED WASTEWATER TREATMENT USING CLINOPTILOLITE

Review of industrial utilization of natural clinoptilolite in the process of wastewater treatment and the results obtained in Slovakia as well as the recent experience from Zeotrips to Water Reclamation Plant in Tahoe-Truckee (California) and Upper Occoquan Sewage Authority in Centreville (Virginia), USA, is presented.

The cation exchange selectivity of clinoptilolite for ammonia has been applied to remove ammonia nitrogen from the tertiary effluents of several wastewater treatment facilities, mostly pilot plants in Europe, Japan, South Africa and the USA, where only one plant in the world using natural zeolite over 15 years – Tahoe Truckee Sanitation Agency – is in operation up to the present. The use of clinoptilolite for an ion-exchange process has several advantages over other methods of ammonia removal.

Particular attention is focused on the pilot plant scale ion exchange technology which verified the applicability of the Slovakian clinoptilolite as a natural selective ion exchanger for removal of ammonia from tannery wastewater. The pilot treatment unit using zeolite in an advanced treatment process with complex regeneration and renovation of eluates by means of air-stripping was situated at the experimental unit of the wastewater treatment plant, Otrokovice, of Shoe Manufacturing Industry 'Svit'.

The economic efficiency of both conventional biological nitrification–denitrification method and the method of ammonia removal by means of clinoptilolite is compared.

1. INTRODUCTION

After exploration of huge natural zeolite deposits in Eastern Europe, interest in the zeolitic minerals has been intensively developed in these regions. In many industrialized countries, natural zeolites, especially clinoptilolite, have been exploited for many years and applied in wastewater treatment processes for ammonia removal [1]–[3].

Due to economic reconstruction of the market in Central Europe countries, where within the framework of the Green Conception till the year 2005 the environmental protection legislation has to be coordinated with those in the other countries of European

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Community, nutrients in wastewaters seem to be the forthcoming problem. One of the several alternatives how to solve the water pollution problem is to apply clinoptilolite.

Technology with natural zeolites is developed first of all in the USA and Japan.

The USA Upper Occoquan Sewage Authority (UOSA) in Centreville recommends two conventional processes (figure) followed by five advanced treatment systems. In conventional treatment system, primary and secondary treatment processes take place. In secondary treatment, biological reactors with activated sludge and secondary clarifiers are involved. Preaeration basins (selectors) are used to promote a more efficient microbial culture.

Activated sludge is separated from the liquid phase by settling in secondary clarifiers and a portion of the settled sludge is returned to the selectors to inoculate their content or to activate biological reactions.

Treatment in the advanced systems consists in chemical processes, multimedia filtration, activated carbon adsorption, ion exchange by means of clinoptilolite and breakpoint chlorination.

In chemical treatment system, the wastewater treated is subjected to high-energy mixing, flocculation, chemical clarification and two-stage recarbonation with intermediate settling. Mechanical mixers completely mix the coagulant with the secondary effluent raising the pH to 11.3, thereby destroying viruses and precipitating and coagulating phosphorus, heavy metals and suspended soils. The coagulated particles are then flocculated to enhance settling characteristics prior to chemical clarification. The pH of water is restored to neutral by the addition of carbon dioxide in the recarbonation basins in two steps.

The effluent from chemical treatment system is pumped at a uniform rate and then undergoes the remaining advanced treatment processes. Multimedia pressure filtration removes the remaining particulate matter. Three media of various sizes and specific gravities are utilized to enhance filtration.

Ion exchange reactors with clinoptilolite were in operation only several months and removed ammonia, and activated carbon fines. In August 1979, as the system was being optimized, a pipeline break occurred in the regenerant basins, which caused the system to be shut down. UOSA's unoxidized nitrogen standard was normally met by nitrification in the secondary treatment system. However, during extreme droughts nitrogen was removed in the ammonia form in the ion exchange vessels. Breakpoint chlorination was replaced by ion exchange allowing removal of any trace amounts of ammonia remaining after nitrification. The water is then dechlorinated prior to being discharged into the final effluent reservoir [4].

The Tahoe Truckee Sanitation Agency in California (TTSA) is only one facility in Northern America using continuously natural zeolite for ammonia removal for about last 15 years. The table illustrates general criteria and particular treatment processes of this facility. TTSA as sister's company of UOSA has the conception of wastewater treatment very similar to that described above. The ion-exchange system for ammonia removal is designed to accommodate a mainstream flow rate of 26 100 m^3/d of wastewater with concentration about 25 mg NH_4^+/dm^3 and consists of 5 horizontal

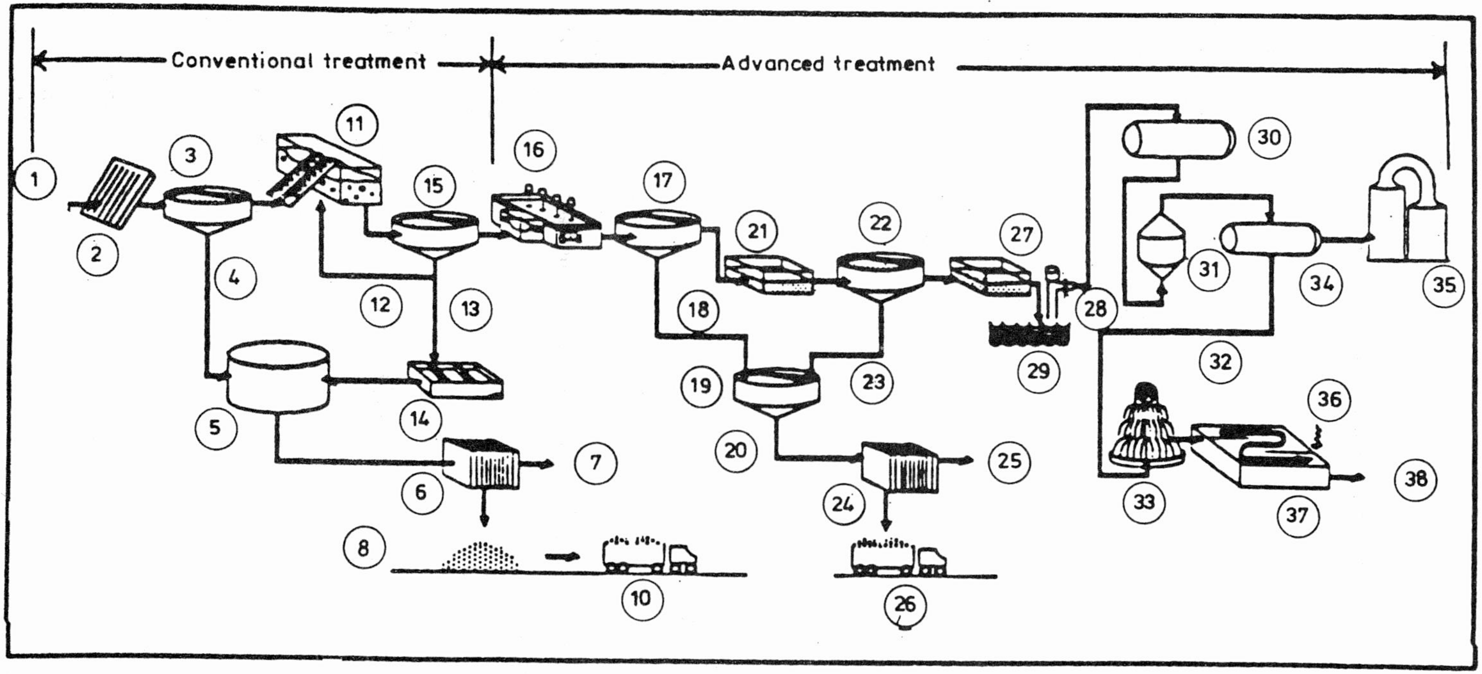

Fig. Treatment of wastewaters according to Upper Occoquan Sewage Authority
1 – plant influent, 2 – headworks, *3* – primary clarifiers, *4* – primary sludge, *5* – anaerobic digestion, *6* – filter process, *7* – filtrate to headworks, *8* – composting, *10*– compost, *11* – aeration basins, *12* – return activated sludge, *13* – waste activated sludge, *14* – flotation thickeners, *15* – secondary clarifiers, *16* – rapid mix and flocculation basins, *17* – chemical clarifiers, *18* – chemical sludge, *19* – thickened chemical sludge, *20* – chemical sludge thickeners, *21* – first-stage recarbonation, *22* – recarbonation clarifiers, *23* – recarbonation sludge, *24* – filter process, *25* – filtrate to rapid mix, *26* – dewatered solids, *27* – second stage recarbonation, *28* – balast pond pumps, *29* – balast ponds, *30* – pressure filters, *31* – activated carbon reactors, *32* – gravity mixer, *33* – chlorination, *34* – post-carbon filtration and ion exchange, *35* – ARRP, *36* – dechlorination, *37* – chlorine contact basins, *38* – final effluent reservoir

Table 1

General criteria and particular treatment processes of TTSA

Raw sewage flows	
Maximum day, Q	18 300 m^3/d
Sewage loadings	
BOD_5	3659 kg/d
Suspended solids	4206 kg/d
Primary and secondary treatment	
Primary clarifiers	
Retention time	2.3 h
Oxygenation basins	
Type	Pure oxygen
Retention time	2.2 h
Oxygen generation	
Type	Pressure swing adsorption
Capacity	4 t/d
Chemical treatment	
Rapid mix basins	
Retention time	4.1 min
Flocculation basins	
Retention time	10.9 min
Advanced waste treatment	
Carbon adsorption	
Contact time	30 min
Ion exchange ammonia removal	
Type of media	Clinoptilolite
	5 horizontal pressure vessels 12×3 m, 40 tons of zeolite, grain size 0.4–0.8 mm
Filter flow rate	270 m^3/h
Influent $NH_4^+ - N$ concentration	25 mg/dm^3
Percent of ammonia removal	95%
Regenerant recovery system	ARRP
	5 stripping and absorber modules, 29 m^3 of synthetic media
Liquid loading rate	0.003 $m^3/min/m^2$
Gas loading	125 $m^3/min/m^2$
Effluent disposal	
Type	Subsurface leach field
Length of pipe	23 km
Area of field	9 h
Raw sewage total nitrogen	43 mg/dm^3
Total nitrogen in effluent	9 mg/dm^3
COD in effluent	45 mg/dm^3
Suspended solids in effluent	10 mg/dm^3
Total phosphorus in effluent	0.8 mg/dm^3
Total dissolved solids in effluent	600 mg/dm^3
Chlorides in effluent	200 mg/dm^3

pressure vessels with about 40 tons of 0.4–0.8 mm grained clinoptilolite per bed. Ammonia removal recovery process (ARRP) proceeds in 5 ammonia stripping and exchange modules, each of them contains 29 m^3 of synthetic media. The absorber counterpart has the same diameter, medium type and gas flow rate as the stripper, but its depth and volume are smaller by 1/3.

Once an ammonia discharge in the bed is established on the level of 12 mg/dm^3, the unit is considered to be exhausted. It is then isolated from the main stream and regenerated with 1760 m^3 of 3% NaCl solution. This regenerate is applied in a 4-phase elutriation of 10 bed volumes (440 m^3) per phase. Duration of the regeneration cycle depends upon the number of ARRP modules in service and is 606 minutes for 2 and 402 minutes for 4. About 2 tons of concentrated ammonium sulphate is produced daily and used as a basic ingredient in agricultural fertilizer [5].

2. MATERIALS AND METHODS

The examined zeolite was found in the one industrial deposit of clinoptilolite tuff in Slovakia, in the locality of Nižný Hrabovec. Clinoptilolite content in zeolitic tuff ranges between 35–75%; in pilot facility about 60% clinoptilolite tuff was used, whose chemical and mineralogical compositions are described in paper [6].

In the case of ammonium ions, the maximum ion-exchange capacity of the zeolite tested was established to be 1.4 meq/g. Slovakian clinoptilolite exhibits high preference for some cations which can be presented according to the following selectivity sequence [6]:

$$Cs > Pb > NH_4 > Cu > Zn, Sr, Cd > Co.$$

The above mentioned capabilities enable us to apply clinoptilolite tuff in water treatment processes, especially for the removal of the first element introduced, i.e. Cs.

3. RESULTS AND DISCUSSION

Domestic utilization of natural zeolite on a commercial scale started in 1985, as the short-time contamination of surface water by ammonia occurred. Powdered clinoptilolite of grain size less than 200 μm was dosaged into water together with coagulant, soda and activated carbon to rescue a drinking water source of capacity 40 dm^3/s.

Removal of biotoxic radionuclides, especially Sr(90) and Cs(137), from wastewaters of low activity produced in some domestic nuclear processing plants has been examined.

The suitability of natural zeolite for coagulation, mechanical filtration, metal adsorption and ammonium exchange in the purification of drinking water has been investigated.

Recently, conditioning of sludge from paper and pulp industry occurred. In such cases, clinoptilolite was used as convenient ingredient allowing removal of fetid odour and composting of wastes.

In Otrokovice, former Czechoslovakia, in a pilot wastewater treatment facility (WWTFO) domestic clinoptilolite was used in an advanced treatment process consisting in chemical regeneration and ammonia recovery by air-stripping. This technology enabled treatment of mixed wastewaters (industrial and municipal wastes) [7], [8].

Prevailing wastewaters are produced in tanneries, textile plants, various chemical plants, rubber plants and paper-mills. Table 2 shows pollution of tannery wastewater after being subjected to mechanical and biological treatment in Otrokovice.

Table 2

Average values for parameters of wastewater at different points of a wastewater plant (industrial area Otrokovice)

Parameter [mg/dm^3]	Inflow to treatment plant	Effluent from mechanical step	Effluent from mechanical-biological step	Effluent from experimental unit
Dissolved matter	1997	1906	1317	1200
Inorganic substances	1500	1482	1117	1026
BOD$_5$	488	310	55	17
COD$_{Cr}$	2044	827	199	108
NH_4^+	61	55	43	40
Cl^-	482	508	465	301
SO_4^{2-}	278	259	206	156
Cr^{3+}	12	7.2	2.8	2.4
Ca^{2+}	138	141	135	139
Mg^{2+}	46	21	16	17
Petroleum substances	–	2.5	–	–
pH	9	8.9	7.2	7.4
Total hardness [mmol/dm^3]	5.3	4.4	4.0	4.2

Pilot plant in Otrokovice consisted of 2 pressure vessels connected in series and filled with grain-sized clinoptilolite, 1 counter-current air-stripping tower of 0.6 m diameter and operating volume of 0.9 m^3, filled with 32×50 mm PVC tubes and 4 storage tanks of 0.75 m^3 volume for regeneration solutions. Technological characteristics of the above mentioned pilot plant, which started the experimental work in the fall of 1987 and completed in the fall of 1988, presents table 3. The pilot treatment proved that the applicability of the Slovakian clinoptilolite as a natural selective ion exchanger for the removal of ammonia in tannery wastewater [8] is fully justified.

Otrokovice industrial area has delivered up to 55 000 m^3 of wastewaters per day, therefore the technology for the whole treatment capacity was designed. Such a project consisted of 3 series of zeolite filters, each of the weight of about 30 tons; each series comprises set of 5 filters operating in parallel.

Table 3

Technological characteristics of the final (tertiary) wastewater treatment using natural zeolite (clinoptilolite) (Wastewater Treatment Plant in Otrokovice)

Specific volume filter load, $V/V_0/h$	12.8
Volume of zeolite within filter bed, V_0	70
Particle size of zeolite applied, mm	0.3–1.0
Ion exchange capacity of zeolite in tannery wastewater, mg/g	ca. 10
Duration of operation cycle, h	20
Regeneration (fractional), h	2.5
Volume of pretreated water in the cycle, m^3	18
Regenerant fraction renovated by air-stripping, m^3	0.75
Air consumption for ammonia stripping from the eluate at 20 °C, m^3/dm^3	ca. 20

For estimating the economic efficiency of both ion exchange on clinoptilolite and biological nitrification–denitrification methods, the latter, i.e. suspension one with external carbon source, was selected and compared with the physicochemical method, only in the final treatment step. Operation costs of biological variant were lower than those of zeolitic ion exchange; however, investment costs for biological method were higher.

4. CONCLUSIONS

Comparison of existing ion-exchange facility for ammonia removal using natural zeolite in TTSA (USA) with the experimental WWTFO allows us to draw the following conclusions:

1. Technological differences between TTSA (USA) and the experimental WWTFO are first of all in the regeneration procedure as well as in wastewater quality entering the zeolitic ion-exchange system, resulting in higher exploitation of zeolite capacity. In Otrokovice, some improved regeneration was applied, therefore only the most concentrated fraction, represented by 1/3 of the entire solution volume, was stripped and finally, as third polishing fraction, cycled into regeneration process.
2. One of the preferential benefits of WWTFO was the recovery of the stripped ammonia into tannery processing plants, while TTSA technology enabled production of agricultural fertilizer.

3. Because of the lower operation costs in comparison to the clinoptilolite methods, biological methods are more efficient. On the other hand, the investment costs and the other advantages of the clinoptilolite methods (e.g. saving of construction area, temperature resistance, high selectivity) favourize that method. Nevertheless, biological technologies being more conventional allow a complex degradation of water pollutants.

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NOWOCZESNE UZDATNIANIE WODY ZA POMOCĄ KLINOPTILOLITU

Opisano przemysłowe wykorzystanie naturalnego klinoptilolitu do oczyszczania ścieków w Słowacji, a także ostatnie sukcesy w tym względzie odniesione w Kalifornii i Wirginii (USA).

Selektywność żywic kationitowych w odniesieniu do amoniaku wykorzystano do usuwania azotu amonowego w procesie oczyszczania trzeciego stopnia ścieków pochodzących głównie z zakładów doświadczalnych w Europie, Japonii, Południowej Afryce i USA. Tylko w tym ostatnim kraju istnieje zakład, w którym opisany sposób oczyszczania ścieków jest stosowany już przez 15 lat. Oczyszczanie ścieków z wykorzystaniem klinoptilolitu w procesie wymiany jonowej ma wiele zalet w porównaniu z innymi metodami.

Szczególną uwagę zwrócono na półprzemysłową skalę wymiany jonowej, która umożliwiła zweryfikowanie przydatności słowackiego klinoptilolitu jako naturalnego, selektywnego wymieniacza jonowego do usuwania amoniaku ze ścieków w garbarni. Jednostka w skali półprzemysłowej, w której zastosowano zeolit do procesów oczyszczania z kompleksową regeneracją i odnawianiem eluatów, jest częścią oczyszczalni ścieków w fabryce butów „Svit” w Otrokowicach.

W artykule porównano wydajność ekonomiczną tradycyjnej biologicznej nitryfikacji–denitryfikacji i metody usuwania amoniaku za pomocą klinoptilolitu.