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Application of Hellenic Natural Zeolite in Thessaloniki industrial area wastewater treatment

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ABSTRACT

The treatment of wastewater (initial pH 7.7) from Sindos industrial area of Thessaloniki (Greece) with different proportions (0.1, 0.2, 0.4, 0.8, 1.6, 3.2, and 6.4 g) of Hellenic natural zeolite (HENAZE), resulted in overflowed clear water of pH 7.4–7.3, free of odours and improved by 69–76% for the chemical oxygen demand, 54–70% for nitrate (NO_3^-), over than 97% for the P_2O_5 content, 33% to over than 50% for Pb and 77% to over than 88% for Cr. The treatment process gave also as precipitate an odourless and cohesive zeosludge which is suitable for safe disposal. The HENAZE comprises very high-quality HEU-type zeolitic tuff, containing 86 wt.% HEU-type zeolite (clinoptilolite-heulandite), 4 wt.% mica + clay minerals, 5 wt.% quartz + cristobalite + tridymite, and 5 wt.% feldspars. The HENAZE cannot be used as feed additive for animals and consequently as nutrition supplements, since it contains SiO_2 minerals (quartz, cristobalite, tridymite), while chemically, is suitable for use as soil conditioner, since the concentration of trace elements (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) are lower than the maximum allowable concentrations for agricultural soils.

Keywords: HEU-type zeolite; Clinoptilolite; Heulandite; Hellenic Natural Zeolite; Wastewater purification; Water quality

1. Introduction

During the last decades, fast growth population and industrial development were reflected in a considerable rise in both freshwater consumption and wastewater production. Freshwater demand has already exceeded supply, and currently special treatments on water reserves and wastewaters are more often required in order to obtain drinking water of high quality as well as to produce environmentally acceptable effluents. Wastewaters of industrial origin may contain a variety of suspended, dissolved, colloidal or emulsified organic and inorganic harmful compounds, some of which could be successfully

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separated out with the use of very high-quality zeolitic tuffs.

Zeolitic tuff deposit corresponds to a rock, which contains high amounts of one or more from the different (>65) phases of zeolites. The zeolite with the numerous applications is the HEU-type zeolite (clinoptilolite–heulandite) that shows tabular crystals and contains micro/nanopores in a framework of channels with 10- and 8-member rings, in dimensions of 7.5 × 3.1, 4.6 × 3.6, and 4.7 × 2.8 Å [1,2]. Only zeolitic tuffs with ≥80 wt.% clinoptilolite, ≤20 wt.% clay minerals, free of fibers and quartz can be used as feed additive for all animal species and consequently as nutrition supplements [3]. The presence of fibrous zeolites (erionite, mordenite, roggianite, mazzite, etc.) and of SiO_2 minerals (quartz, cristobalite, tridymite) in the HEU-type zeolitic tuff, is inhibitory for use as feed additive for animals and as nutrition supplements [4–6]. In humans and animals, inhaled or injected or swallowed, fibrous zeolites (mainly erionite and mordenite, and to a lesser extent roggianite and mazzite), as well as the SiO_2 minerals (quartz, cristobalite, tridymite), were proved to be toxic, carcinogenic and highly pathogenic [7–9].

Almost every industrial area is served by wastewater treatment facilities that aim to treat wastewater in a safe manner using a variety of techniques (e.g. anaerobic, aerobic, coagulation/precipitation). Very-high quality HEU-type zeolitic tuffs, display unique physical and chemical features and have a great variety of environmental, industrial and agricultural applications [4–6,10–22].

The production of odourless-cohesive zeosludge using sludge from Sindos industrial area in proportions 20:80 and 40:60 (sludge/natural zeolite), as well as the purification of 300 mL Sindos industrial area wastewater using 0.4 and 0.8 g of natural zeolite, have been previously investigated [23,24]. The present study investigates, in seven (7) different experiments, the purification of 300 mL Sindos industrial area wastewater using 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, and 6.4 g of the Hellenic Natural Zeolite (HENAZE).

2. Materials and methods

The HENAZE sample used was supplied by GEO-VET N. Alexandridis & Co. O.E. The mineralogical composition of HENAZE sample was determined by X-ray powder diffraction (XRPD). The XRPD analysis was performed using a Philips PW1710 diffractometer with Ni-filtered CuK_α radiation on randomly oriented samples. The counting statistics were as follows: start angle 3˚, end angle 63˚ (2θ), step size 0.02˚ (2θ), time per step 1 s and scan speed 0.02˚/s. Semiquantitative estimates of the abundance of the mineral phases were derived from the XRPD data, using the intensity (counts) of certain reflections, the density and the mass absorption coefficient for CuK_α radiation of the minerals present. Clay mineralogy was identified from air-dried, glycolated and heat-treated oriented samples scanned from 3˚ to 23˚ 2θ at a scanning speed of 1.2˚/min [14].

The microanalyses of the minerals contained in the HENAZE were performed on polished thin section by scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS) with LINK-AN 10000 EDS system. To minimize volatilization of alkalis in the HEU-type zeolite, the electron beam spot size was enlarged and the counting time decreased.

The chemical composition (major oxides and trace elements) of the HENAZE was determined by the following methods: fusion-mass spectrometry (FUS-MS), fusion-inductively coupled plasma (FUS-ICP), total digestion-inductively coupled plasma (TD-ICP), instrumental neutron activation analysis (INAA), and fire assay (FA).

The HENAZE was powdered in agate mortar and passed all through sieve <0.5 mm (Fig. 1). The Sindos industrial area (Thessaloniki) wastewater was treated at room temperature with <0.5 mm grain size of HENAZE in batch-type experiments. In 300 mL of wastewater and in seven (7) different experiments, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2, and 6.4 g of HENAZE was added under continuous stirring for 3 min. At the final stage of each experiment, coagulants were added (0.1 mL of polyaluminium chloride and 2 mL of polyelectrolyte). The overflow clear water and the precipitated zeosludge were separated by filtering. The zeosludge was dried at room temperature.

The starting wastewater and the overflowed clear waters were analyzed for (method) the following: pH (Electrometric), chemical oxygen demand (COD) (method of K_2CrO_6), P_2O_5 molecular absorption spectrophotometry (MAS), NO_3^-, Zn, Cu, Pb and Cr atomic absorption spectroscopy (AAS).

Fig. 1. Powdered sample (grain size < 0.5 mm) of the HENAZE.

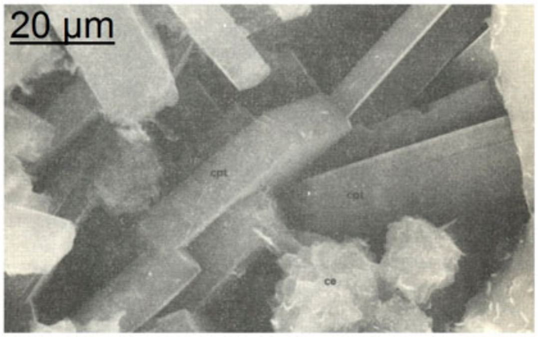

Fig. 2. SEM microphotograph of the HENAZE. cpt: Lath-tabular shaped crystals of HEU-type zeolite, ce: Celadonite.

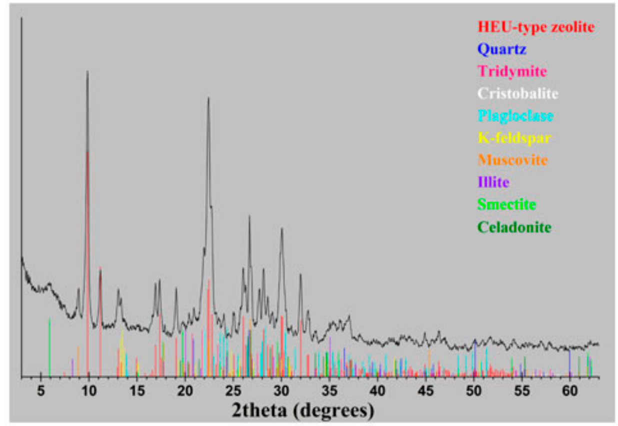

Fig. 3. XRPD pattern of the HENAZE.

3. Results and discussion

The HENAZE contains shards (0.1–2.0 mm in size), lath-tabular-shaped crystals of HEU-type zeolite (5–50 μm in size) (Fig. 2) as interstitial cements and as polycrystallites in the shards [5]. The HEU-type zeolite presents characteristics of group I zeolite (clinoptilolite) and of group II (intermediate heulandite) [18]. The ammonia ion-exchange capacity (sorption ability) of the HENAZE was measured to 187 meq/100 g [25]. The grain-size distribution of <0.5 mm HENAZE is, 6 wt.% (<500–250 μm), 28 wt.% (<250–125 μm), 30 wt.% (<125–63 μm) and 36 wt.% (<63 μm) [5].

The main exchangeable cations of the HEU-type zeolite are Ca, K, Mg, and Na. The chemical formula

Table 1
Microanalysis (average of 8 analyses) of the HEU-type zeolite

Oxide	wt.%	Ion	Numbers of ions on the basis of 72 oxygens
SiO_2	66.18	Si	29.5515
TiO_2	0.02	Ti	0.0067
Al_2O_3	12.10	Al	6.3679
$Fe_2O_{3\ tot}$	0.12	Fe^{3+}	0.0134
MnO	0.06	Mn	0.0227
MgO	1.09	Mg	0.7255
CaO	3.83	Ca	1.8324
Na_2O	0.59	Na	0.5108
K_2O	1.67	K	0.9513
H_2O[a]	14.34	H_2O	21.3562
Total	100.00		

[a]Estimated by difference, HEU-type zeolite: clinoptilolite-intermediate heulandite.

Table 2
Semiquantitative mineralogical composition of the HENAZE

Mineral	wt.%	Mineral	wt.%
HEU-type zeolite (clinoptilolite-intermediate heulandite)	86		
Mica + clay minerals (smectite, illite, celadonite)	4	Total microporous	90
Quartz + Cristobalite + Tridymite	5		
Feldspars (alkali-feldspar + plagioclase)	5	Total non-microporous	10
Total	100	Total	100
HENAZE: Hellenic Natural Zeolite			

Table 3
Chemical analysis[a] of the HENAZE[b]

Oxide	wt.%
SiO_2	65.89
TiO_2	0.19
Al_2O_3	12.09
$Fe_2O_{3\ tot}$	1.31
MnO	0.03
MgO	1.07
CaO	3.27
Na_2O	0.74
K_2O	1.83
P_2O_5	0.02
L.O.I.	13.40
Total	99.84

[a]FUS-ICP: fusion inductively coupled plasma.
[b]HENAZE: hellenic natural zeolite (average of 10 analyses).

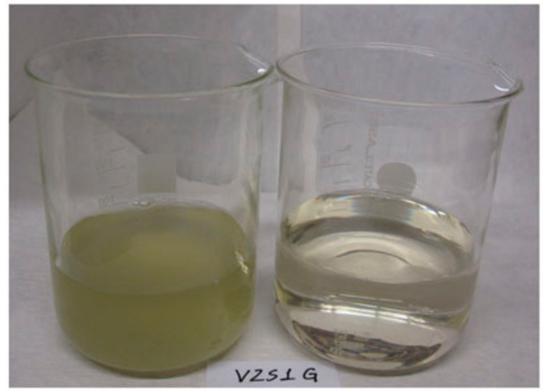

Fig. 4. (Left) Initial Sindos industrial area wastewater (VZS1) and (Right) The overflowing clear water after the treatment with 6.4 g of HENAZE (VZS1G).

Table 4
Trace element contents of HENAZE (ppm = mg/kg, average of 10 analyses)

Element	Analytical method	Detection limit	HENAZE	Element	Analytical method	Detection limit	HENAZE
Ag	FUS-MS	0.5	<0.5	Ni	TD-ICP	1	11
As	FUS-MS	5	<5	Pb	FUS-MS	5	47
Ba	FUS-ICP	2	180	Pr	FUS-MS	0.01	7.08
Be	FUS-ICP	1	6	Rb	FUS-MS	1	76
Bi	FUS-MS	0.1	0.4	Sb	FUS-MS	0.2	0.3
Br	INAA	1	<1	Sc	FUS-ICP	0.1	3.4
Cd	TD-ICP	0.5	<0.5	Se	INAA	3	<3
Ce	FUS-MS	0.1	67.7	Sm	FUS-MS	0.01	3.73
Co	FUS-MS	1	3	Sn	FUS-MS	1	4
Cr	INAA	1	29	Sr	FUS-ICP	2	1,464
Cs	FUS-MS	0.1	11.0	Ta	FUS-MS	0.01	1.70
Cu	TD-ICP	1	7	Tb	FUS-MS	0.01	0.51
Dy	FUS-MS	0.01	3.44	Th	FUS-MS	0.1	30.9
Er	FUS-MS	0.01	2.29	Tl	FUS-MS	0.05	1.29
Eu	FUS-MS	0.005	0.308	Tm	FUS-MS	0.005	0.367
Ga	FUS-MS	1	14	U	FUS-MS	0.01	9.15
Gd	FUS-MS	0.01	3.12	V	FUS-ICP	5	20
Ge	FUS-MS	0.5	1.4	W	FUS-MS	0.5	1.9
Hf	FUS-MS	0.1	4.0	Y	FUS-MS	0.5	20.6
Ho	FUS-MS	0.01	0.72	Yb	FUS-MS	0.01	2.44
In	FUS-MS	0.1	<0.1	Zn	FUS-MS	1	50
La	FUS-MS	0.1	38.3	Zr	FUS-ICP	1	129
Lu	FUS-MS	0.002	0.411				
Mo	FUS-MS	2	<2	Au (ppb)	INAA	5	<5
Nb	FUS-MS	0.2	15.0	Hg (ppb)	FA	5	10
Nd	FUS-MS	0.1	23.9	Ir (ppb)	INAA	5	<5

Notes: FUS-MS: fusion mass spectrometry, FUS-ICP: fusion inductively coupled plasma, INAA: instrumental neutron activation analysis, TD-ICP: total digestion inductively coupled plasma, and FA: fire assay.

Table 5
Quality characteristics of Sindos (Thessaloniki) industrial area wastewater (VZS1), of the overflowing waters (VZS1A to VZS1G) with the relevant improvement (RI), after the treatment (0.1 to 6.4 g) by the HENAZE

Method of analysis	Electrometric		Method of K_2CrO_6		AAS		MAS		AAS		AAS		AAS		AAS	
Parameter (detection limit-unit)	pH (0.1)		COD (15 mg/L)		NO_3^- (0.3 mg/L)		P_2O_5 (0.3 mg/L)		Zn (0.1 mg/L)		Cu (0.1 mg/L)		Pb (1.5 μg/L)		Cr (5 μg/L)	
Experiment (HENAZE added in g)		RI (%)	(mg/L)	RI (%)	(mg/L)	RI (%)	(mg/L)	RI (%)	(mg/L)	RI (%)	(mg/L)	RI (%)	(μg/L)	RI (%)	(μg/L)	RI (%)
VZS1 (0)	7.7	–	255	–	35.4	–	9.3	–	<0.1	–	<0.1	–	3.0	–	40	
VZS1A (0.1)	7.4	4	78	69	16.2	54	0.3	97	<0.1	–	<0.1	–	2.0	33	9	78
VZS1B (0.2)	7.4	4	67	74	15.3	57	<0.3	>97	<0.1	–	<0.1	–	<1.5	>50	7	83
VZS1C (0.4)	7.3	5	60	76	14.7	58	<0.3	>97	<0.1	–	<0.1	–	<1.5	>50	<5	>88
VZS1D (0.8)	7.3	5	60	76	13.8	61	<0.3	>97	<0.1	–	<0.1	–	<1.5	>50	<5	>88
VZS1E (1.6)	7.3	5	60	76	12.3	65	<0.3	>97	<0.1	–	<0.1	–	<1.5	>50	<5	>88
VZS1F (3.2)	7.3	5	60	76	12.0	66	<0.3	>97	<0.1	–	<0.1	–	<1.5	>50	<5	>88
VZS1G (6.4)	7.3	5	60	76	10.5	70	<0.3	>97	<0.1	–	<0.1	–	<1.5	>50	<5	>88

Notes: AAS: atomic absorption spectroscopy and MAS: molecular absorption spectrophotometry.

Fig. 5. The odourless and cohesive zeosludge of the experiment VZS1G, dried for 24 h at room temperature.

of HEU-type zeolite, contained in the HENAZE is $Ca_{1.8}K_{1.0}Mg_{0.7}Na_{0.5}Al_{6.4}Si_{29.6}O_{72}\cdot 21H_2O$ (Table 1).

The chemical formulae for the rest of the minerals contained in the HENAZE, are: $Mg_{1.4}Fe_{1.1}K_{0.8}Na_{0.1}Mn_{0.1}Ti_{0.3}Al_{1.4}Si_{2.6}O_{10}(OH)_2$ for mica, $Fe_{1.0}K_{0.9}Mg_{0.4}Ca_{0.2}Al_{2.4}$ $(Al_{0.2}Si_{7.8})O_{20}(OH)_4\cdot 3H_2O$ for clay mineral, $K_{0.6}Na_{0.4}Al_{1.0}Si_{3.0}O_8$ for alkali-feldspar (sanidine), $Na_{0.5}Ca_{0.5}Al_{1.4}Si_{2.6}O_8$ for plagioclase (andesine) and SiO_2 for quartz, cristobalite, and tridymite.

The HENAZE sample used contains 86 wt.% HEU-type zeolite (clinoptilolite-intermediate heulandite), 4 wt.% mica + clay minerals, 5 wt.% quartz + cristobalite + tridymite and 5 wt.% feldspars (Fig. 3 and Table 2).

HENAZE cannot be used as feed additive for animals and consequently as nutrition supplements, since it contains 5 wt.% quartz + cristobalite + tridymite. Only zeolitic tuffs with ≥80 wt.% clinoptilolite, ≤20 wt.% clay minerals, free of fibers and quartz, can be used as feed additive for all animal species and consequently as nutrition supplements [3].

Chemically, the HENAZE consists mainly of SiO_2, Al_2O_3, CaO, K_2O, Fe_2O_3, MgO, and Na_2O (Table 3). The most abundant trace elements contained in the HENAZE are Sr, Ba and Zr (1,464, 180, and 129 ppm, respectively). The concentration values of Rb, Ce, Zn, Pb, La, Th, Cr, Nd, Y, V, Nb, Ga, Cs, and Ni are between 76 and 11 ppm, while the remainder 34 trace elements show concentration values <9.15 ppm (Table 4).

Concerning the trace elements measured in the wastewater, the concentration values in the HENAZE are 50 ppm Zn, 7 ppm Cu, 47 ppm Pb, and 29 ppm Cr (Table 4). Considering the high sorption and fixation ability of major and trace elements by the HEU-type zeolite and the HENAZE, the very low concentration of elements in seepage waters [4–6], as well as the very low bioavailability of elements, the concentration of

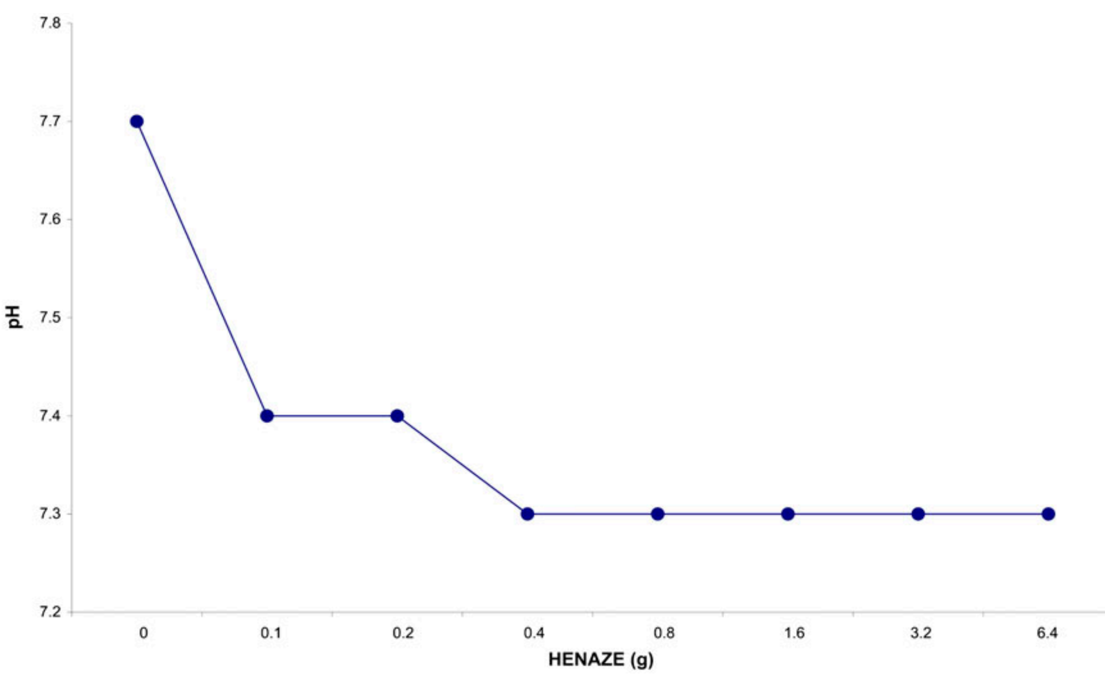

Fig. 6. pH improvement with the addition of variable HENAZE proportions.

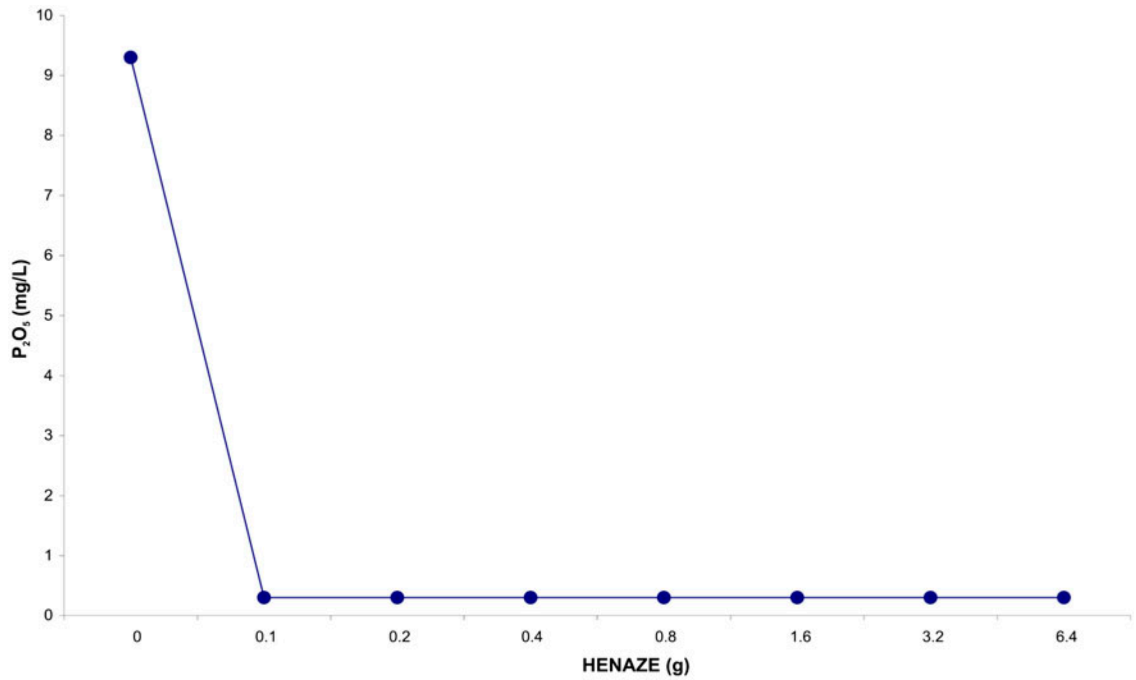

Fig. 7. Decrease in P_2O_5 concentration with the addition of variable HENAZE proportions.

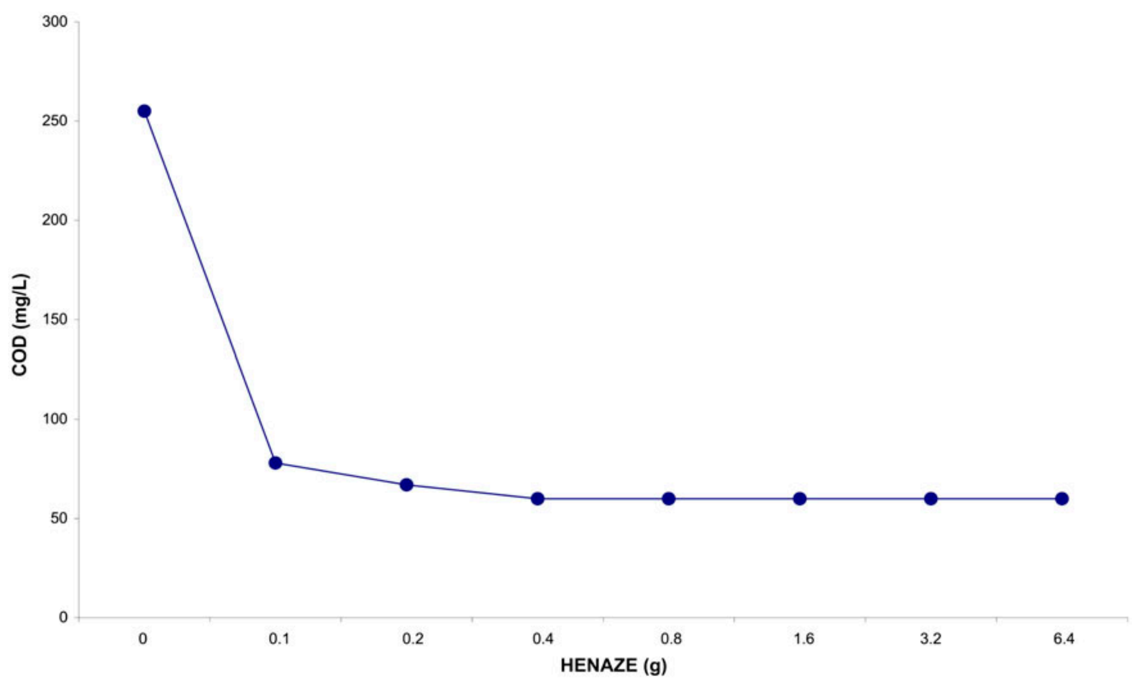

Fig. 8. Improvement of COD with the addition of variable HENAZE proportions.

elements in the zeolitic tuffs should not be enriched compared to the crustal average and should not exceed the maximum allowable concentrations (MAC) of trace elements in agricultural soils. The HENAZE can be used as soil conditioner in agriculture, since the concentrations of trace elements are lower than MAC:

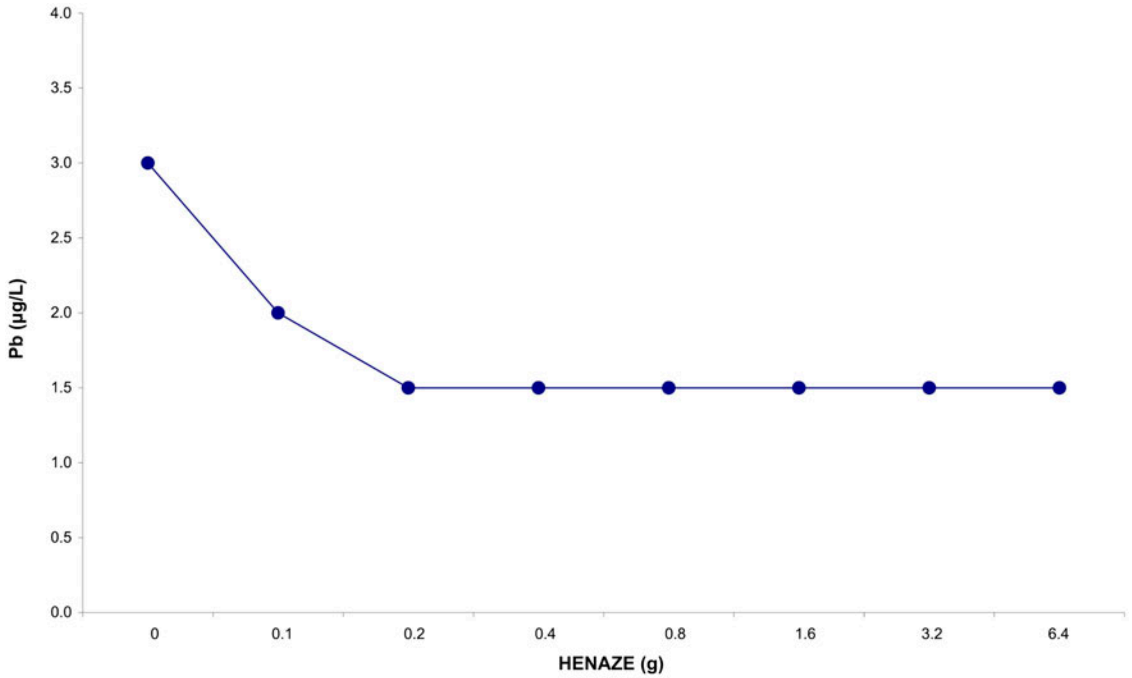

Fig. 9. Decrease in Pb concentration with the addition of variable HENAZE proportions.

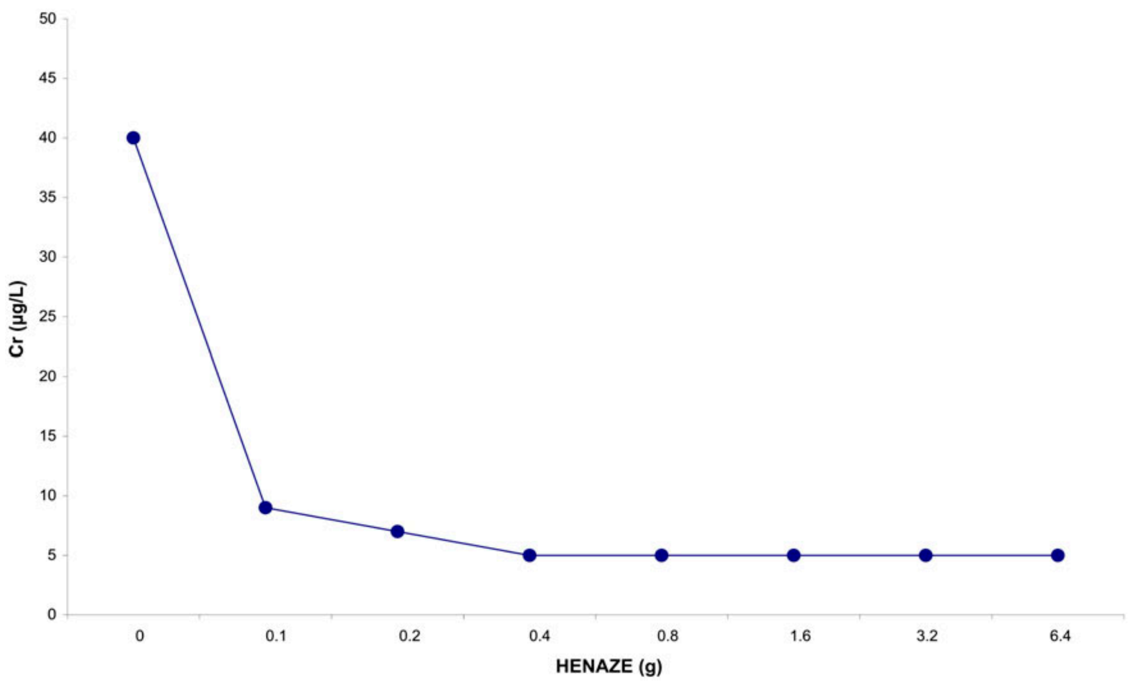

Fig. 10. Decrease in Cr concentration with the addition of variable HENAZE proportions.

<0.5 ppm Cd (MAC 1–3 ppm), 29 ppm Cr (MAC 50–150), 7 ppm Cu (MAC 50–140), 0.01 ppm Hg (MAC 1–1.5), 11 ppm Ni (MAC 30–75), 47 ppm Pb (MAC 50–300), and 50 ppm Zn (MAC 150–300) [26–28].

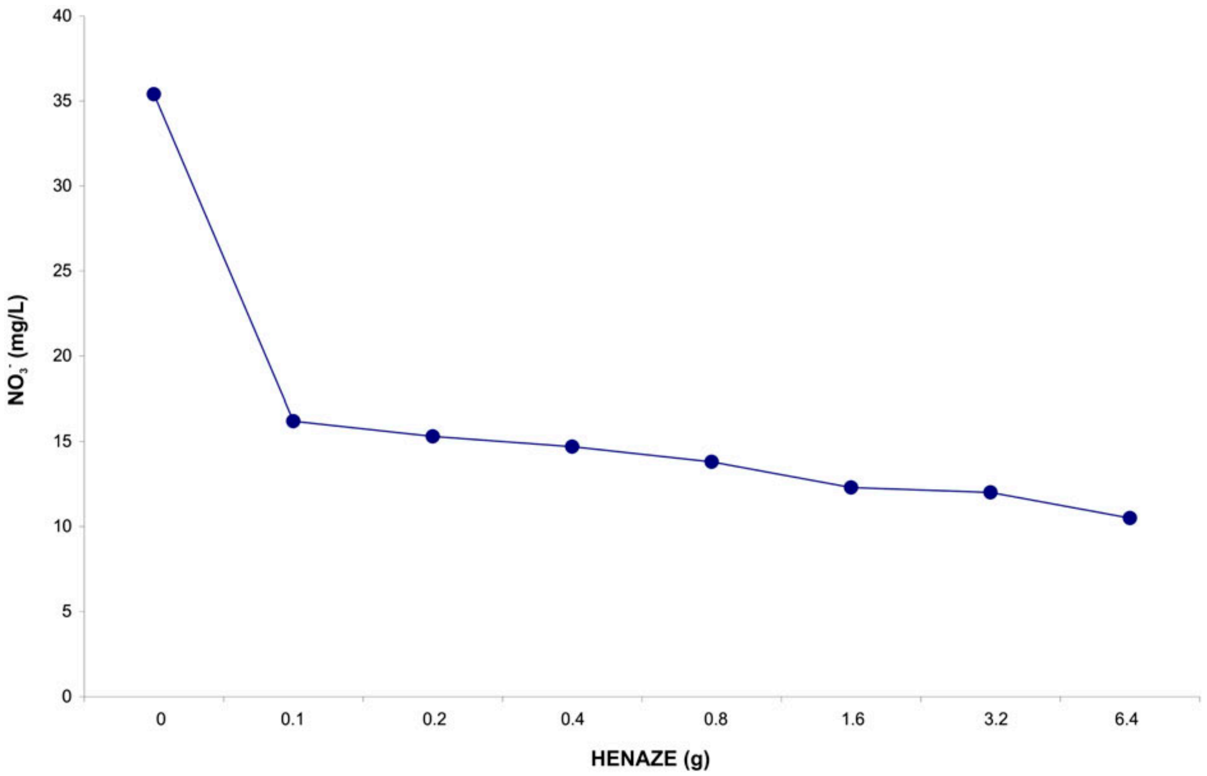

Fig. 11. Decrease in NO_3^- concentration with the addition of variable HENAZE proportions.

The treatment of wastewater of pH 7.7 from Sindos industrial area of Thessaloniki with 6.4 g of HENAZE (the 7th experiment), resulted in production of clear water (Fig. 4) of pH 7.3, free of odours and improved quality parameters by 70% for the NO_3^- content, 76% for the COD, >97% for P_2O_5, >50% for Pb and >88% for Cr contents (Table 5). The precipitated zeosludge is odourless and cohesive (Fig. 5).

The treatment of wastewater sample with various proportions of HENAZE resulted in a significant improvement of its quality characteristics as presented in Table 5. The reference value of pH (VZS1) is nearly neutral without any remarkable deviation from the pH of pristine waters, and thus, no assess can be made to the potential influence of HENAZE, but just a general remark of a minor decrease after the first zeolite addition (0.1 g) and a slight further improvement with the addition of 0.4 g of HENAZE (Fig. 6). The P_2O_5 concentration is decreased over than 97% and falls above the detection limit of 0.3 mg/L after the addition of 0.2 g of HENAZE (Fig. 7). Regarding COD, an increase in the added amount of HENAZE from 0.1 g to 0.4 g, resulted in improvement by 7% (from 69 to 76%) (Fig. 8). The Pb concentration is decreased over than 50% and falls above the detection limit of 1.5 μg/L (Fig. 9) after the addition of 0.2 g of HENAZE. The Cr concentration is decreased over than 88% and falls above the detection limit of 5 μg/L (Fig. 10) after the addition of 0.4 g of HENAZE.

Nitrates are considered as a key factor for environmental sustainability [29,30] and are related with major environmental pressures like eutrophication and groundwater quality deterioration. The present batch-type treatment of Thessaloniki industrial area wastewater (35.4 mg/L initial nitrate concentration, contact time 3 min) by HENAZE (<0.5 mm grain size and 86 wt.% HEU-type zeolite) and coagulants resulted to nitrate removal by 54–70%. In batch-type treatments of urban wastewater (75.70 mg/L initial nitrate concentration, contact time 2 min) by the same HENAZE and coagulants, resulted to nitrate removal by 86% [5]. In batch and column treatments of South African groundwater (50–190 mg/L initial nitrate concentration) by surfactant modified clinoptilolite, resulted to nitrate removal by 91–97% [31], while nitrate removal from shallow-well water (74–288 mg/L initial nitrate concentration) carried out under static conditions (contact time 60 min) and sedimentation time of 30 min, using 0.315 mm particle-sized zeolitic rock (70–75 wt.% clinoptilolite), achieved removal percentage < 10% [32].

Nitrates reduction is considerable (54%) even with the minimum addition of HENAZE (0.1 g), and consequently, the solution quality is further improved but with a noticeable smaller removal rate which is nearly linear (Fig. 11).

The HENAZE of very high-quality HEU-type zeolitic tuff, sorb bacteria, gases, inorganic, organic and organometallic compounds, controls to neutral the pH of soils and waters e.g. [4–6,14,15,17]. The sorption and fixation of the different components from their solutions by the micro/nanopores of HEU-type zeolite, as well as the meso- and macropores of the HENAZE, is attributed to absorption (ion exchange), adsorption and surface precipitation processes [18,33–37]. The HEU-type zeolite, because of the existence in its structure, of the Brønsted acidic active sites and the Lewis basic active sites, reacts with the negatively or/and positively charged chemical components, even with molecules in gas condition. These chemical processes are related to sorption and fixation physicochemical phenomena of ions and molecules, and concerns both the structural void spaces (micro/nanopores) and the surface of the HEU-type zeolite crystals, consequently the meso- and macropores of the HENAZE. The HENAZE shows an ability to neutralize the pH of acidic and basic waters, acting either as a proton acceptor or donor, exhibiting thus an amphoteric character [18,33–35,38–40]. The sorption of gas phases results in the oxygen enrichment of air and in remarkable malodour decrease [2,4–6,11,12,14,15,17,18].

4. Conclusions

The HENAZE is of very high-quality zeolitic tuff containing 86 wt.% HEU-type zeolite (clinoptilolite-heulandite), 4 wt.% mica + clay minerals, 5 wt.% quartz + cristobalite + tridymite and 5 wt.% feldspars. The total amount of microporous minerals (HEU-type zeolite, mica, clay minerals) is 90 wt.%. The HENAZE, mineralogically cannot be used as feed additive for animals and consequently as nutrition supplements, since it contains SiO_2-minerals (quartz, cristobalite, tridymite), while chemically, is suitable for use as soil conditioner, since the concentration of trace elements (Cd, Cr, Cu, Hg, Ni, Pb, Zn) are lower than the MAC in agricultural soils. The treatment of 300 mL of wastewater from Sindos industrial area of Thessaloniki (initial pH 7.7) with different proportions (0.1, 0.2, 0.4, 0.8, 1.6, 3.2, 6.4 g) of HENAZE with a grain size of < 0.5 mm, resulted in overflowed clear water of pH 7.4–7.3, free of odours and improved by 69–76% for the COD, over than 97% for the P_2O_5 content, 33 to over than 50% for Pb and 77% to over than 88% for Cr. The present batch-type treatments of industrial wastewater with initial nitrate (NO_3^-) concentration of 35.4 mg/L by 0.1–6.4 g of HENAZE and coagulants resulted to nitrate removal by 54–70%. The treatment gave also as precipitate, an odourless and cohesive zeosludge, which is suitable for safe deposition since the fixation of dangerous species into the HENAZE, prevents the seepage by run-off or leaching, thus protecting the quality of soils, surface and groundwaters.

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