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PURIFICATION OF MUNICIPAL WASTEWATERS AND PRODUCTION OF ODORLESS AND COHESIVE ZEO-SEWAGE SLUDGE, USING HELLENIC NATURAL ZEOLITE

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Abstract: Treatment of municipal wastewaters ($pH_{initial}$ 8.2-8.9), with 7.5 g of Hellenic Natural Zeolite (HENAZE) of a grain-size < 1.5 mm, gave overflowed clear water of pH 7.3-7.8, free of odors and improved quality parameters by 89.9-96.7 % for the color, 89.0-98.5 % for the suspended particles, 93.7-97.2 % for the chemical oxygen demand (COD), 92.9-99.3 % for the P_2O_5 content and 98.3-99.9 % for the NH_4 content. The improvement of the quality parameters for the clear water increases with increasing stirring time of the treatment experiments. The correlation coefficient is 0.9423 for the P_2O_5 content, 0.9323 for the suspended particles, 0.9282 for the chemical oxygen demand (COD) and 0.8854 for the color. The correlation coefficient for the NH_4 content and pH are < 0.60. The HENAZE comes from Ntrista stream of Petrota village of Trigono Municipality of Evros Prefecture, North-eastern Greece. HENAZE contains 89 wt. % HEU-type zeolite and exhibit an ammonia ion exchange capacity (sorption ability) of 226 meq/100g. The mineralogical composition and the unique physico-chemical properties, make the HENAZE suitable material for numerous environmental, industrial, agricultural and aquacultural applications, such as: Animal nutrition, soil amendment for agriculture, pH soil regulation, greenhouse and flowers substrates, durability and health improvement of lawn, purification of industrial and municipal wastewaters, treatment of sewage sludge, odor control, fishery and fish breeding, gas purification and drying systems, oxygen enrichment of aquatic ecosystems, improvement of drinking water quality, constructed wetlands and wastewater treatment units. The treatment gave as precipitate odorless and cohesive zeo-sewage sludge, suitable for safe deposition and also for the reclamation of agricultural soils. The zeo-sewage sludge produced either from the municipal wastewater treatment or from the mixing of HENAZE and sewage sludge, can be used for the reclamation of agricultural soils. The presence of HENAZE in the agricultural soils, increases the crops yield by 17-66 % and improves the quality of agricultural products by 4-46 %, reduces the use of fertilizers by 56-100 %, reduces the usage of irrigation water by 33-67 %, prevents the seepage of dangerous species into the water environment (e.g., NO_3^- by 55-92 %), protecting thus the quality of surface and underground waters. The usage of HENAZE in vivarium units and in the animal nutrition increases the production and improves the quality of the relevant products, reduces the feed cost, the animal diseases and medication, the new-born animal's death-rate and the malodor, converting thus the manure to odorless fertilizer.

Key words: natural zeolite, municipal wastewaters, sewage, sewage-sludge, Evros, Hellas.

1. Introduction

Zeolite comprises a special solid crystalline microporous material, with open structure and void space. Some high quality HEU-type natural zeolites, displays unique physical and chemical features and have a great variety of environmental, industrial, aquacultural and agricultural applications. The large natural zeolite deposits and the low cost of mining, gave access to large-scale utilization (e.g., Pond and Mumpton, 1984; Tsitsishvili et al., 1992; Carr, 1994; Collela and Mumpton, 2000; Filippidis and Kassoli-Fournaraki, 2000; Bish and Ming, 2001; Harben, 2002; Savvas et al., 2002; Inglezakis and Grigoropoulou, 2004; Inglezakis et al., 2004, 2005; Filippidis, 2008; Filippidis et al., 2008g-i).

In the Trigono Municipality (Evros Prefecture) and around the villages of Petrota and Pentalofos, eight different occurrences show varying zeolite contents, on average 39-76 wt. % (e.g., Kirov et al., 1990; Marantos and Perdikatsis, 1994; Filippidis et al., 1995; Arvanitidis, 1998; Stamatakis et al., 1998, 2001; Filippidis and Kassoli-Fournaraki, 2000; Hall et al., 2000; Kassoli-Fournaraki et al., 2000; Yannakopoulos et al., 2000; Zorpas et al., 2000a,b; Barbieri et al., 2001; Moirou et al., 2001; Vlessidis et al., 2001; Koshiaris et al., 2002; Kyriakis et al., 2002; Papaioannou et al., 2002a,b; Savvas et al., 2002; Christidis et al., 2003; Katranas et al., 2003; Krestou et al., 2003; Perraki et al., 2003; Fokas et al., 2004; Inglezakis and Grigoropoulou, 2004; Inglezakis et al., 2004, 2005; Perraki and Orfanoudaki, 2004; Kantiranis et al., 2006; Warchol et al., 2006).

In a specific ground of Petrota village (Ntrista stream) has been located a HEU-type zeolite deposit, the Hellenic Natural Zeolite (HENAZE) of GEO-VET N. Alexandridis & Co O.E. concession (e.g., Filippidis and Kantiranis, 2002, 2005, 2007; Deligiannis et al., 2005; Filippidis, 2005, 2007; Filippidis et al., 2006, 2007a,b, 2008a-f, 2009a,b). The purification of municipal wastewaters, as well as the production of odorless and cohesive zeo-sewage sludge, using 7.5 g HENAZE of grain-size <1.5 mm and stirring time 5-60 min, has been investigated (Filippidis et al., 2007a,b, 2008a-f, 2009a,b). The present study investigates the purification improvement of the municipal wastewaters versus the stirring time. Environmental, agricultural, aquacultural and industrial applications are proposed for the HENAZE.

2. Materials and methods

The Hellenic Natural Zeolite (HENAZE) sample used was selected from a vertical profile of the Ntrista stream within the GEO-VET's concession. Petrographic investigation of HENAZE was performed on thin and polished thin sections. The morphology and chemistry of the HEU-type zeolite were studied by Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) with Link-AN 10000 EDS system. To minimize volatilization of alkalis, the electron beam spot size was enlarged and the counting time decreased. The mineralogical composition was determined by X-Ray Powder Diffraction (XRPD). Semi-quantitative estimates were performed using external mixture standards of the identified mineral phases. The chemical composition of the HENAZE was determined by Atomic Absorption Spectrometry. The ammonia ion exchange capacity (sorption ability) of the HENAZE was determined according to the Ammonium Acetate Saturation (AMAS) method. The pH variations and the removal ability of metals and anions were performed through butch-type experiments at RT (Filippidis and Kantiranis, 2002, 2007; Filippidis, 2005; Filippidis et al., 2006).

The typical platy crystals of HEU-type zeolite have a grain-size of 5-25 μm (Fig. 1). The chemical formula of the clinoptilolite is $Ca_{1.5}K_{1.4}Mg_{0.6}Na_{0.5}Al_{6.2}Si_{29.8}O_{72}{\cdot}20H_2O$. The minerals content of HENAZE is 89 wt.% HEU-type zeolite, 3 wt.% mica + clays (92 wt.% microporous minerals), 6 wt.% feldspars and 2 wt.% quartz. HENAZE shows a remarkable ammonia ion exchange capacity of 226 meq/100g (Table 1).

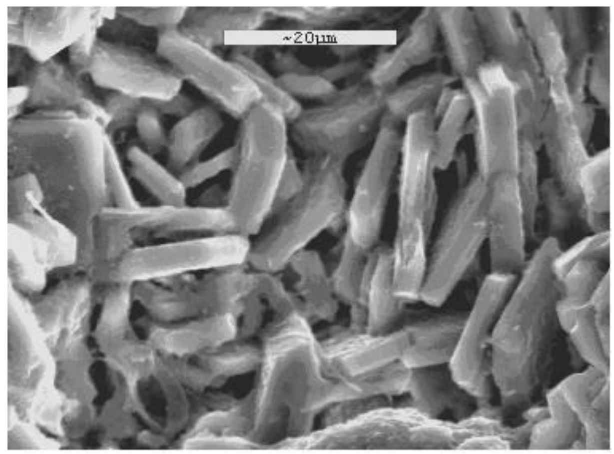

Fig. 1. SEM microphotograph of typical platy crystals of HEU-type zeolite of the HENAZE.

The chemical analysis of HENAZE gave: 68.62 wt.% SiO_2, 11.80 wt.% Al_2O_3, 2.92 wt.% K_2O, 2.14 wt.% CaO, 1.13 wt.% Na_2O and 0.75 wt.% MgO. HENAZE shows a remarkable ability to neutralize the pH of basic water (pH 9.5) from the lake Koronia (Prefecture of Thessaloniki) and of acidic stream mine water (pH 5.5) from NE Chalkidiki Prefecture, exhibiting an amphoteric character. Also found to remove from their aqueous solutions 74 % of Pb, 79% of Ag and 55-57% of NO_3^- (Filippidis and Kantiranis, 2002, 2007; Filippidis, 2005; Filippidis et al., 2006).

Kilkis City municipal wastewaters of different pH were treated at room temperature with HENAZE of < 1.5 mm grain-size (Fig. 2), in butch-type experiments. In 300 ml municipal wastewater 7.5 g of HENAZE was added, the whole was stirred for 5 to 60 minutes (Table 2) and polyaluminium chloride as well as cationic polyelectrolyte was added. The overflowed clear water and the precipitated zeo-sewage sludge were separated by filtering. The zeo-sewage sludge was dried overnight at room temperature (RT). The starting municipal wastewaters and the overflowed clear waters, were analyzed for (method): pH (electrometric), color (photometric), suspended particles (filtering and centrifugation), COD (method of K_2CrO_6), P_2O_5 and NH_4 (molecular absorption spectrophotometry).

Table 1. Mineralogical composition and cation exchange capacity (CEC) of HENAZE.

Minerals	**Min-Max (wt. %)**	**Average (wt. %)**
HEU-type zeolite	87 – 93	89
Mica + Clays	2 – 4	3
Feldspars	3 – 8	6
Quartz	2 – 3	2
Total	**100**	**100**
Micro-porous minerals	90 – 95	92
CEC, meq/100g	***218 – 234***	***226***

3. Results

The treatment of municipal wastewaters of pH 8.2-8.9 (Table 2) with the HENAZE gave overflowed clear water (Fig. 3) of pH 7.3-7.8, free of odors and improved quality parameters by 89.9-96.7 % for the color, 89.0-98.5 % for the suspended particles, 93.7-97.2 % for the chemical oxygen demand (COD), 92.9-99.3 % for the P_2O_5 content and 98.3-99.9 % for the NH_4 content (Table 2). Simultaneously, the treatment gave as precipitate odorless and cohesive zeo-sewage sludge, dried overnight at room temperature (Fig. 4). The improvement of the quality parameters for the clear water increases with increasing stirring time of the treatment experiments. The correlation coefficient is 0.9423 for the P_2O_5 content (Fig. 5), 0.9323 for the suspended particles (Fig. 6), 0.9282 for the COD (Fig. 7) and 0.8854 for the color (Fig. 8). The correlation coefficient for the NH_4 content and pH are < 0.60.

Fig. 2. The grain-sizes of HENAZE (< 1.5 mm used for the butch-type experiments).

Fig. 3. Left: Starting municipal wastewater, Centre: Odorless and cohesive zoo-sewage sludge, Right: Overflowed clear water.

Fig. 4. Odorless and cohesive zeo-sewage sludge, dried overnight at RT.

4. Discussion and Conclusions

The natural zeolites show a remarkable ability to remove inorganic, organic, organometallic compounds, gas species, metals and radionuclides from their aqueous solutions. The sorption of the different species from their solutions by the micro- meso- and macroporous of natural zeolite can be attributed to absorption (mainly ion exchange), adsorption and surface precipitation processes (e.g., Tsitsishvili et al., 1992; Misailides et al., 1993, 1995; Godelitsas et al., 1999, 2001, 2003; Collela and Mumpton, 2000; Bish and Ming, 2001). The sorption of gas phases results to oxygen enrichment of the air and to the remarkable decrease of the malodor. Also, they show an ability to neutralize the pH of acidic and basic waters, acting either

Table 2. Chemistry of starting municipal wastewaters (SMW), clear water (CW) and relevant improvement (%). HENAZE-treatment: 7.5 g of < 1.5 mm grain-size at RT.

	Stirring time (min)	SMW	CW	± %	Ref.
pH	60	8.9	7.4	-16.9	1
	50	8.4	7.8	-7.1	2, 3
	50	8.4	7.5	-10.7	4, 5
	30	8.4	7.5	-10.7	6, 7
	7	8.6	7.7	-10.5	8
	5	8.2	7.3	-11.0	9
Color, mg/L, Pt scale	60	1470	49	-96.7	1
	50	1390	90	-93.5	2, 3, 4
	50	1390	52	-96.3	5
	30	1230	98	-92.0	7
	30	1214	99	-91.8	6
	7	1280	128	-90.0	8
	5	1180	119	-89.9	9
Suspended Particles, mg/L	60	325	5	-98.5	1
	50	280	10	-96.4	2, 3, 4
	50	280	9	-96.8	5
	30	283	15	-94.7	6
	30	241	15	-93.8	7
	7	272	22	-91.9	8
	5	210	23	-89.0	9
Chemical Oxygen Demand (COD), mg/L O_2	50	670	19	-97.2	4, 5
	30	461	23	-95.0	7
	7	512	29	-94.3	8
	5	410	26	-93.7	9
P_2O_5, mg/L	50	15.86	0.11	-99.3	5
	50	15.86	0.12	-99.2	2, 3, 4
	30	11.15	0.33	-97.0	7
	30	11.22	0.36	-96.8	6
	7	13.26	0.66	-95.0	8
	5	9.24	0.66	-92.9	9
NH_4, mg/L	50	110.76	0.06	-99.9	5
	30	33.80	0.19	-99.4	7
	7	36.92	0.21	-99.4	8
	5	30.52	0.51	-98.3	9

1) Filippidis et al. 2008e, 2) Filippidis et al. 2007a, 3) Filippidis et al. 2008c, 4) Filippidis et al. 2008f, 5) Filippidis et al. 2009a, 6) Filippidis et al. 2008b, 7) Filippidis et al. 2008d, 8) Filippidis et al. 2008a, 9) Filippidis et al. 2009b.

as a proton acceptor or donor, exhibiting thus an amphoteric character (e.g., Filippidis et al., 1996; Charistos et al., 1997).

The Hellenic Natural Zeolite (HENAZE) is of very high quality (> 85 wt. % HEU-type zeolite), removes inorganic, organic, organometallic, gas species, metals, cations and anions from their aqueous solutions. Also, shows an ability to neutralize the pH of acidic and basic waters. HENAZE removes from their aqueous solutions 74 % of Pb, 79 % of Ag and 55-57 % of NO_3^- (Filippidis, 2005; Filippidis et al., 2006). The increase of the pH in the acidic pH-range could mainly be attributed to the binding of the protons to the Lewis basic sites of the zeolite. The decrease of the pH in the basic pH-range could be the result of the removal of protons from surface Brønsted acidic sites or even of the detachment of protons from water molecules surrounding the exchangeable cations, caused by OH^- attack on the zeolite (e.g., Godelitsas et al., 1999, 2001, 2003). The mineralogical composition and the unique physico-chemical properties, make the HENAZE suitable material for numerous environmental, industrial, agricultural and aquacultural applications, such as: Animal nutrition, soil amendment for agriculture, conditioning of acid and basic soils, greenhouse and flowers substrates, durability and health improvement of lawn, purification of industrial and municipal wastewaters, treatment of sewage sludge, odor control, fishery and fish breeding, gas purification and drying systems, oxygen enrichment of aqua ecosystems, improvement of drinking water, constructed wetlands and wastewater treatment units (e.g., Collela and Mumpton, 2000; Harben, 2002; Filippidis, 2007; Filippidis et al., 2007a,b; 2008a-f; 2009a,b).

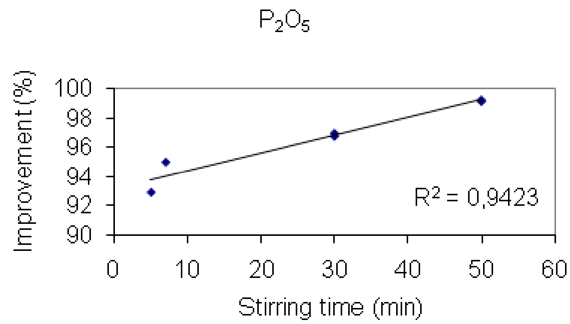

Fig. 5. The P_2O_5 content improvement of clear water vs stirring time of the HENAZE treatment.

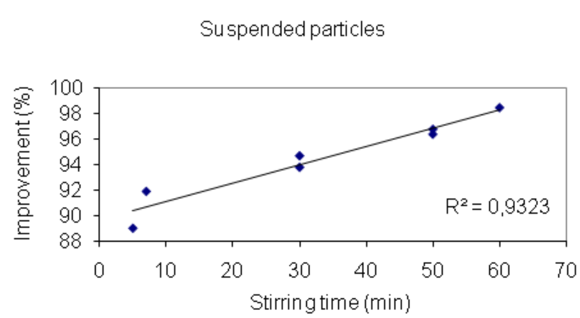

Fig. 6. The suspended particles content improvement of clear water vs stirring time of the HENAZE treatment.

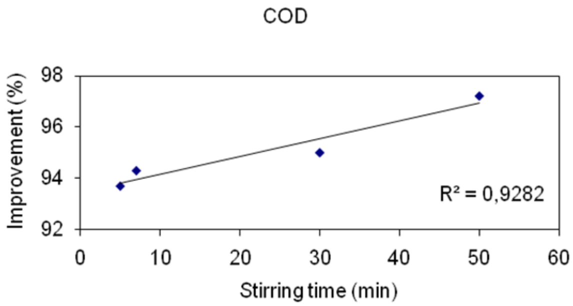

Fig. 7. The Chemical Oxygen Demand (COD) improvement of clear water vs stirring time of the HENAZE treatment.

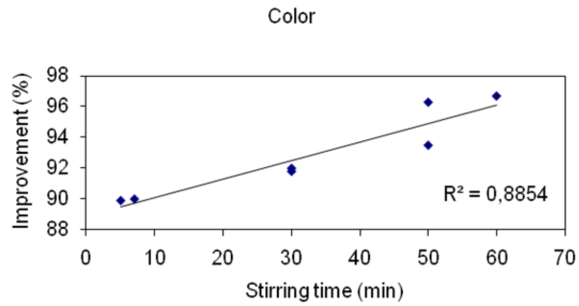

Fig. 8. The color improvement of clear water vs stirring time of the HENAZE treatment.

The HENAZE treatment of municipal wastewaters (pH initial 8.2-8.9) gave overflowed clear water of pH 7.3-7.8, free of odors and improved by 89.9-96.7 % for the color, 89.0-98.5 % for the suspended particles, 93.7-97.2 % for the chemical oxygen demand (COD), 92.9-99.3 % for the P_2O_5 content and 98.3-99.9 % for the NH_4 content. The improvement of the quality parameters for the clear water increases with increasing stirring time of the treatment experiments. Correlation coefficients > 0.88 are observed for the P_2O_5 content, the suspended particles, the COD and for the color, while those for the NH_4 content and pH where < 0.60. These final values of the pH and of the previous mentioned quality parameters, measured in the overflowed clear water, are fulfilling the requirements for disposition as downstream, irrigation, swimming and fish waters.

The HENAZE treatment gave also as precipitate, odorless and cohesive zeo-sewage sludge, suitable for safe deposition but also for the reclamation of

Table 3. The HENAZE in agricultural applications.

Addition of HENAZE in agricultural soils							
	Fertilizer		**Irrigations**		**Production (Kg/acre)**		
Species	**Kg/acre**	**± %**	**Nr.**	**± %**	**Without HENAZE**	**With HENAZE**	**± %**
Wheat [1]	20				170		+ 29
	0	- 100				220	
	10				70		+ 57
	0	- 100				110	
Rice [1]	90				880		+ 34
	40	- 56				1180	
Maize [1]	120		3		800		
	0	- 100	2	- 33		1200	+ 50
	0	- 100	1	- 67		800	± 0
Production increase (%) by addition of HENAZE in agricultural soils							
Species				**%**	**Species**		**%**
Grapes				48 - 66	Carnation (florescence increase) [2]		25
Tomato [1]				48 – 52			
Actinides [2]				45	Cotton [2]		17
Quality improvement of tomato by HENAZE addition in agricultural soils							
					Produced		
Quality parameters					**Without HENAZE**	**With HENAZE**	**± %**
Soluble solids (%) [1]					4.20	4.35	+ 4
Vitamin C (mg/100g) [1]					6.81	8.61	+ 26
Firmness (Kg) [1]					0.619	0.906	+ 46
HENAZE as feed additive and farm floor material							
17 % increase of milk production in cows [2]					Taste and quality improvement of products (meat, milk, eggs, etc)		
7 % increase of body weight in broilers [2]							
Reduction of feed cost					Reduction of new-born animals death-rate		
Reduction of animal diseases					Reduction of the malodor		
Reduction of animal medication					Conversion of manure to odorless fertilizer		

[1]Filippidis et al. 2007b, [2]Filippidis 2007.

agricultural soils. The same stands for the odorless and cohesive zeo-sewage sludge produced by mixing the sewage sludge and the HENAZE. The presence of HENAZE in the agricultural soils, increases the yield by 17-66 % and improves the quality by 4-46 % of agricultural products, reduces the use of fertilizers by 56-100 %, reduces the usage of irrigation water by 33-67 %, prevents the seepage of dangerous species into the water environment (e.g., NO_3^- by 55-92 %), protecting thus the quality of surface and underground waters (Tables 3). The usage of HENAZE in vivarium units and in the animal nutrition increases the production and improves the quality of their products (Table 3), reduces the feed cost, the animal diseases, animal medication, the new-born animals death-rate and the malodor, converting thus the manure to odorless fertilizer (e.g., Filippidis, 2005, 2007; Filippidis et al., 2006, 2007b, 2008e).

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