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PURIFICATION OF URBAN WASTEWATERS BY HELLENIC NATURAL ZEOLITE

Filippidis A.[1], Papastergios G.[1], Apostolidis N.[1], Filippidis S.[1], Paragios I.[1] and Sikalidis C.[2]

[1] *Aristotle University, Department of Mineralogy-Petrology-Economic Geology, 54124 Thessaloniki, Greece, anestis@geo.auth.gr*

[2] *Aristotle University, Department of Chemical Engineering, 54124 Thessaloniki, sikalidi@eng.auth.gr*

Abstract

Treatment of urban wastewaters ($pH_{initial}$ 8.2), with 6 g of Hellenic Natural Zeolite (HENAZE) of an grain-size < 1.5 mm, gave overflowed clear water of pH 7.5, free of odors and improved quality parameters by 87% for the suspended particles, 88% for the color, 91% for the P_2O_5 content, 93% for the chemical oxygen demand (COD) and 97% for the NH_4 content. Compared to previous experiment, the decrease of the amount of HENAZE by 1.5 g (20%) resulted to the purification worsening only by 1-2%. The HENAZE comes from Ntrista stream of Petrota village of Trigono Municipality of Evros Prefecture, Northeastern 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 urban 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 an 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 urban 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 29-57% and improves the quality of agricultural products by 4-46%, reduces the use of fertilizers by 55-100%, reduces the usage of irrigation water by 33-67%, prevents the seepage of dangerous species into the water environment (e.g., NO_3^- by 55-57%), 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.

Key words: *natural zeolite, urban wastewaters, sewage, sewage-sludge, Evros, Greece.*

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., 2008e-g).

In the Trigono Municipality (Evros Prefecture, Northeastern Greece) 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, 2007, 2008a-d, 2009). The purification of urban wastewaters, as well as the production of odorless zeo-sewage sludge, using 7.5 g of HENAZE and stirring time 5-60 min, has been investigated (Filippidis et al., 2008a-d, 2009). The present study investigates the purification of urban wastewaters, using 6.0 g of HENAZE and stirring time of 5 min.

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 (Filippidis and Kantiranis, 2007). 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. 1a, Filippidis and Kantiranis, 2002; Filippidis, 2005, 2007). 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 (Filippidis and Kantiranis, 2002, 2007; Filippidis, 2005). 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 ammonia ion exchange capacity of 226 meq/100g, as well as an ability to neutralize the pH of basic water (pH 9.5) from the lake Koronia (Prefecture of Thes-

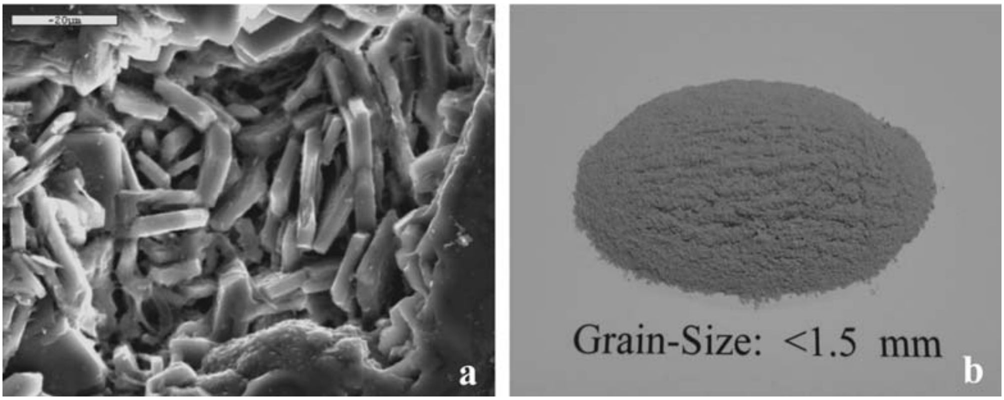

Fig. 1: a) SEM microphotograph of typical platy crystals of HEU-type zeolite of the HENAZE. b) The grain-size < 1.5 mm of HENAZE, used for the butch-type experiments.

saloniki) and of acidic stream mine water (pH 5.5) from NE Chalkidiki Prefecture, exhibiting an amphoteric character (Filippidis and Kantiranis, 2002, 2007; Filippidis, 2005). 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 (Northern Greece) urban wastewaters of pH 8.2, were treated at room temperature with < 1.5 mm grain-size HENAZE (Fig. 1b), in butch-type experiment. In 300 ml municipal sewage 6.0 g of HENAZE was added, the whole was stirred for 5 minutes 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 urban wastewater and the overflowed clear water, 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).

3. Results

Microscopic examination of thin sections reveals a fine-grained vitroclastic texture containing glass shards (Fig. 2), angular to subangular quartz and feldspar, as well as tabular mica crystals.

The lath- or tabular shaped crystals of HEU-type zeolite are very abundant as interstitial cements or as polycrystalline replacements of glass shards. The peripheral zone of the altered glass shards is often a rim containing clay minerals (Fig. 2).

The treatment of urban wastewater of pH 8.2 with the HENAZE gave overflowed clear water (Fig. 3a) of pH 7.5, free of odors and improved quality parameters by 87% for the suspended particles, 88% for the color, 91% for the P_2O_5 content, 93% for the chemical oxygen demand (COD) and 97% for the NH_4 content (Table 1).

Treatment with 7.5 g of HENAZE resulted to pH of 7.3 for the clear water and to improvement by 89% for the suspended particles, 90% for the color, 93% for the P_2O_5 content, 94% for the chemical oxygen demand (COD) and 98% for NH_4 content (Table 1, Filippidis et al., 2009).

Simultaneously, the treatment gave as precipitate odorless and cohesive zeo-sewage sludge, dried overnight at room temperature (Fig. 3b).

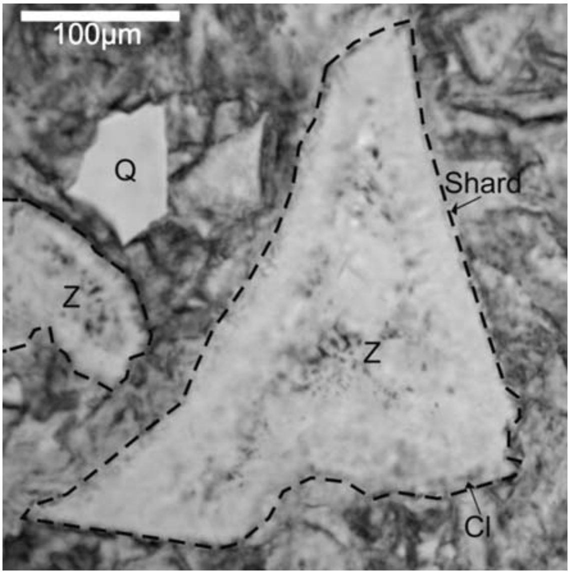

Fig. 2: Photomicrograph of thin section, altered glass shards (discontinuous line), lath-tabular shaped crystals of HEU-type zeolite (Z), angular-subangular quartz crystal (Q) and the peripheral rim of the shards containing clay minerals (Cl).

Fig. 3: a) Left: Starting urban wastewater (SUW), Right: Overflowed clear water (CW) after the HENAZE treatment. b) Odorless and cohesive zeo-sewage sludge, dried overnight at RT.

Table 1. Chemistry of starting urban wastewater (SUW) and overflowed relevant Clear Water treated with 6.0 g (CW-6) and 7.5 g (CW-7.5) of HENAZE at RT.

Quality parameters (detection limit)	**SUW**	**CW-6**	**± %**	**CW-7.5***	**± %**
pH (0.1)	8.2	7.5	- 9	7.3	- 11
Suspended Particles, mg/L (5)	210	28	- 87	23	- 89
Color, mg/L, Pt scale (5)	1180	143	- 88	119	- 90
Chemical Oxygen Demand (COD), mg/L O_2(15)	410	29	- 93	26	- 94
P_2O_5, mg/L (0.02)	9.24	0.80	- 91	0.66	- 93
NH_4, mg/L (0.02)	30.52	0.79	- 97	0.51	- 98

* Filippidis et al., 2009.

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 malodour. Also, they show an ability to neutralize the pH of acidic and basic waters, acting either 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. 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 urban 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., 2007, 2008a-g).

The HENAZE treatment of urban wastewater (pH initial 8.2) gave overflowed clear water of pH 7.5, free of odors and improved by 87% for the suspended particles, 88% for the color, 91% for the P_2O_5 content, 93% for the chemical oxygen demand (COD) and 97% for the NH_4 content. Treatment with 7.5 g of HENAZE resulted to pH of 7.3 for the clear water and to improvement by 89% for suspended particles, 90% for color, 93% for P_2O_5, 94% for COD and 98% for NH_4 (Filippidis et al., 2009). The decrease of the amount of HENAZE by 1.5 g (20 %) resulted to the purification worsening only by 1-2 %. 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 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 29-57% and improves the quality by 4-46% of agricultural products, reduces the use of fertilizers by 55-100%, reduces the usage of irrigation water by 33-67%, prevents the seepage of dangerous species into the water environment (e.g., NO_3^- by 55-57%), 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 their products (e.g., Filippidis, 2005, 2007; Filippidis et al., 2006, 2007, 2008c).

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