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TREATMENT AND RECYCLING OF MUNICIPAL AND INDUSTRIAL WASTE WATERS USING HELLENIC NATURAL ZEOLITE: A REVIEW

A. Filippidis

Aristotle University, Faculty of Sciences, Department of Mineralogy-Petrology-Economic Geology, 54124 Thessaloniki, Hellas, 2310-998468, anestis@geo.auth.gr

ABSTRACT

Hellenic Natural Zeolite (HENAZE) in specific location of Petrota (Evros), contains 89 wt. % HEU-type zeolite (clinoptilolite), shows ion exchange capacity of 226 meq/100g and regulates to the neutral the pH of waters. Treatment of municipal sewages with pH 8.4-8.9 by the HENAZE resulted to production of clear waters of pH 7.4-7.8, free of odors and improved by 90-97 % for the color, 92-100 % for the suspended particles, 94-97 % for the chemical oxygen demand (COD), 950 % for the dissolved oxygen, 95-99 % for the P_2O_5, 99-100 % for the NH_4, 92 % for the NO_3, 94 % for Mn and 100 % for the SO_4, NO_2, Cr, Ni and Cu contents. Treatment of dye-work waste waters of pH 7.9-9.0 by the HENAZE resulted to production of clear waters of pH 7.5-8.3, free of odors and improved by 97 % for the color, 92-93 % for the suspended particles, 94-95 % for the chemical oxygen demand (COD) and 98 % for the P_2O_5 and the NH_4 contents. Treatment of tanning-work waste water of pH 8.8 by the HENAZE resulted to production of clear water of pH 7.2, free of odors and improved by 98 % for the color and 99 % for the suspended particles and the P_2O_5 contents. These final values of the pH and of the previous mentioned quality parameters, measured in the overflowed clear waters, are fulfilling the requirements for disposition as downstream, irrigation, swimming and fish waters.

1. INTRODUCTION

In the Trigono Municipality (Evros, N.E. Greece) and around the villages of Petrota and Pentalofos, seven different occurrences show varying zeolite contents, on average 39-74 wt. % [1]. In specific location of Petrota has been located a HEU-type zeolite deposit, the Hellenic Natural Zeolite (HENAZE) of GEO-VET N. Alexandridis & Co O.E. concession [2-4]. Some high quality HEU-type natural zeolites, displays unique physical and chemical features and has a great variety of environmental, industrial, aquacultural and agricultural applications [1, 4]. The purification of industrial and urban wastewaters, using the HENAZE, has been successfully investigated [5-13].

The present review paper presents the treatment and recycling of municipal and industrial waste waters using the HENAZE of GEO-VET N. Alexandridis & Co O.E.

2. MATERIALS, TREATMENT AND RESULTS

The Hellenic Natural Zeolite (HENAZE) on average contains 89 wt. % HEU-type zeolite clinoptilolite and shows ammonia ion exchange capacity of 226 meq/100g [1-4]. Municipal and industrial (dye- and tanning-works) waste waters, were treated with HENAZE in butch-type experiments. The starting waste waters and the overflowed clear waters, were analyzed for (method): pH (Electrometric), Color (Photometric), Suspended Particles (Filtering and Centrifugation), Chemical Oxygen Demand (method of K_2CrO_6), Dissolved Oxygen (Electrochemical), P_2O_5, NH_4, SO_4, NO_3, NO_2, Cr, Mn, Ni and Cu (Molecular Absorption Spectrophotometry) [5-13].

Treatment of municipal sewages with pH 8.4-8.9 by the HENAZE resulted to production of clear waters of pH 7.4-7.8, free of odors and improved by 90-950 % for the quality parameters presented in Table 1. Simultaneously, the treatment gave as precipitate odorless and cohesive zeo-sewage sludge (Figure 1).

Table 1. Chemistry of Municipal Waste Waters and Overflowed Clear Waters

Quality Parameters (detection limit)	**Starting Waste Waters**	**Clear Waters**	**±%**	***Ref.***
pH (0.1)	8.4	7.8	- 7	*5,6*
	8.6	7.7	- 10	*9*
	8.4	7.5	- 11	*7, 8, 11, 12*
	8.9	7.4	- 17	*13*
Color mg/L Pt-scale (5)	1280	128	- 90	*9*
	1214	99	- 92	*7*
	1230	98	- 92	*11*
	1390	90	- 94	*5, 6, 8*
	1390	52	- 96	*12*
	1470	49	- 97	*13*
Suspended Particles mg/L (5)	272	22	- 92	*9*
	241	15	- 94	*11*
	283	15	- 95	*7*
	280	10	- 96	*5, 6, 8*
	280	9	- 97	*12*
	325	<5	- 100	*13*
Chemical Oxygen Demand (COD) mg/L O_2 (15)	512	29	- 94	*9*
	461	23	- 95	*11*
	670	19	- 97	*8, 12*
Dissolved Oxygen, mg/L (0.1)	0.6	6.3	+ 950	*13*
P_2O_5 mg/L (0.02)	13.26	0.66	- 95	*9*
	11.15	0.33	- 97	*11*
	11.22	0.36	- 97	*7*
	15.86	0.12	- 99	*5, 6, 8*
	15.86	0.11	- 99	*12*
NH_4 mg/L (0.02)	33.80	0.19	- 99	*11*
	36.92	0.21	- 99	*9*
	110.76	0.06	- 100	*12*
SO_4, mg/L (0.02)	0.74	<0.02	- 100	*13*
NO_3, mg/L (0.02)	46.50	3.90	- 92	*13*
NO_2, mg/L (0.02)	0.11	<0.02	- 100	*13*
Cr, mg/L (0.02)	0.20	<0.02	- 100	*13*
Mn, mg/L (0.02)	0.31	0.02	- 94	*13*
Ni, mg/L (0.02)	0.28	<0.02	- 100	*13*
Cu, mg/L (0.02)	0.05	<0.02	- 100	*13*

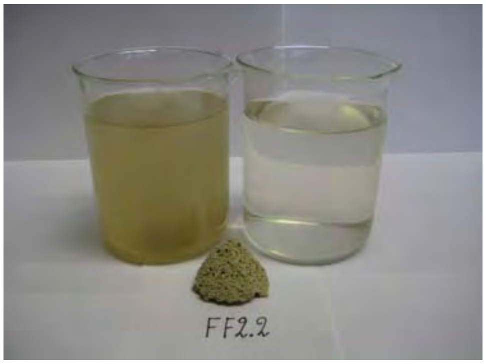

Figure 1.

Left: Starting Municipal Sewage.

Center: Odorless and Cohesive Zeo-Sewage Sludge.

Right: Overflowed Clear Water after the HENAZE treatment [9]

Treatment of dye-work waste waters of pH 7.9-9.0 by the HENAZE resulted to production of clear waters of pH 7.5-8.3, free of odors and improved by 92-98 % for the quality parameters presented in Table 2. Simultaneously, the treatment gave as precipitate odorless and cohesive zeo-sludge (Figure 2).

Table 2. Chemistry of Dye-work Waste Waters and Overflowed Clear Waters

Quality Parameters (detection limit)	**Dye-work Waste Waters**	**Clear Waters**	**±%**	***Ref.***
pH (0.1)	7.9	7.5	- 5	*6*
	9.0	8.3	- 8	*11*
	9.0	8.2	- 9	*10*
Color mg/L Pt-scale (5)	1035	34	- 97	*6*
	1232	37	- 97	*10*
	1524	48	- 97	*11*
Suspended Particles mg/L (5)	151	12	- 92	*11*
	105	7	- 93	*6*
	125	9	- 93	*10*
Chemical Oxygen Demand (COD) mg/L O_2 (15)	449	25	- 94	*10*
	415	21	- 95	*11*
P_2O_5 mg/L (0.02)	7.01	0.13	- 98	*6*
	8.34	0.18	- 98	*10*
	10.32	0.24	- 98	*11*
NH_4 mg/L (0.02)	19.50	0.39	- 98	*10*
	20.59	0.45	- 98	*11*

Figure 2.

Left: Starting Dye-work Waste Water.

Center: Odorless and Cohesive Zeo-Sludge.

Right: Overflowed Clear Water after the HENAZE treatment [6].

Treatment of tanning-work waste water of pH 8.8 by the HENAZE resulted to production of clear water of pH 7.2, free of odors and improved by 98-99 % for the quality parameters presented in Table 3. Simultaneously, the treatment gave as precipitate odorless and cohesive zeo-sludge (Figure 3).

Table 3. Chemistry of Tanning-work Waste Water and Overflowed Clear Water

Quality Parameters (detection limit)	**Tanning-work Waste Waters**	**Clear Waters**	**±%**	***Ref.***
pH (0.1)	8.8	7.2	- 18	*7*
Color, mg/L Pt-scale (5)	11200	194	- 98	*7*
Suspended Particles, mg/L (5)	1955	24	- 99	*7*
P_2O_5, mg/L (0.02)	61.97	0.68	- 99	*7*

Figure 3.

Left: Starting Tanning-work Waste Water.

Center: Odorless and Cohesive Zeo-Sludge.

Right: Overflowed Clear Water after the HENAZE treatment [7].

3. DISCUSSION AND CONCLUSIONS

The Hellenic Natural Zeolite (HENAZE) from a specific location of Petrota (Evros, Greece), is a high quality HEU-type zeolite deposit. Treatment of municipal sewages (pH 8.4-8.9) by the HENAZE produced odorless clear waters (pH 7.4-7.8), improved by 90-100 % for the quality parameters (color, suspended particles, COD, P_2O_5, NH_4, SO_4, NO_3, NO_2, Cr, Mn, Ni and Cu) and 950 % for the dissolved oxygen. Treatment of dye-work waste waters (pH 7.9-9.0) by the HENAZE produced odorless clear waters (pH 7.5-8.3), improved by 92-98 % for the quality parameters (color, suspended particles, COD, P_2O_5 and NH_4). Treatment of tanning-work waste water (pH 8.8) by the HENAZE produced odorless clear water (pH 7.2), improved by 98-99 % for the quality parameters (color, suspended particles and P_2O_5). These final values of the pH and of the previous mentioned quality parameters, measured in the overflowed clear waters, are fulfilling the requirements for disposition as downstream, irrigation, swimming and fish waters. The HENAZE removes inorganic, organic, organometallic and gas species from the waste waters. The sorption of the different species by the micro- meso- and macroporous of the HENAZE can be attributed to absorption (mainly ion exchange), adsorption and surface precipitation processes, resulting to oxygen enrichment, decrease of the malodour and to the pH neutralization of the waters [1, 4].

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(2010) evaluated the RO concentrate treatment using lime-soda softening process and showed that efficiency of seawater desalination using lime-soda is 80-90%. Nkwonta and Ochieng (2010) designed a pilot plant for wastewater pretreatment using charcoal and gravel. They demonstrated that filters roughness enhances efficiency of pretreatment process for mine water. They also showed that in general, charcoal outperforms gravel.Â In this study, natural zeolites are chosen to adsorb the salty particles in the water. Zeolites have high cation exchange capacity and ion selectivity, which make them appropriate for removal of different ions from water and wastewater.Â Compost' leachate recycling through land treatment and application of natural Zeolite. Int. J. Recycl. Natural zeolites are abundant and low cost resources, which are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Due to their high cation-exchange ability as well as to the molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification processes in the past decades. In this paper, we review the recent development of natural zeolites as adsorbents in water and wastewater treatment. The properties and modification of natural zeolite are discussed. Various natura... Municipal Wastewater. Large-scale cation-exchange processes using natural zeolites were first developed by Ames (1) and Mercer et al. (2), who demonstrated the effectiveness of clinoptilolite for extracting NH4+ from municipal and agricultural waste streams.Â Hundreds of papers have dealt with wastewater treatment by natural zeolites. Adding powdered clinoptilolite to sewage before aeration increased O2-consumption and sedimentation, resulting in a sludge that can be more easily dewatered and, hence, used as a fertilizer (16).Â By using certain natural zeolites, however, researchers have made headway in the drying and purification of acid gases.