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NEUTRALIZATION OF SLUDGE AND PURIFICATION OF WASTEWATER FROM SINDOS INDUSTRIAL AREA OF THESSALONIKI (GREECE) USING NATURAL ZEOLITE

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Abstract

The commixture of sludge from Sindos industrial area of Thessaloniki with high quality HEU-type natural zeolite (tuff with 86 wt.% clinoptilolite-heulandite) in equal proportions, resulted in odourless and cohesive zeosludge. Also, the treatment of wastewater of pH 7.8 from the same area with high quality HEU-type natural zeolite (88 wt.% clinoptilolite-heulandite) resulted in production of clear water of pH 7.3, free of odours and improved quality parameters by 60% for the NO_3^- content, 76% for the chemical oxygen demand (COD), 100% for P_2O_5 and Cr contents. Simultaneously, a precipitate of odourless and cohesive zeosludge was produced. The odourless and cohesive zeosludge produced either by the commixture of sludge with the natural zeolite or as precipitate from the treatment of industrial wastewater with the natural zeolite and coagulants, is suitable for safe deposition, since the fixation of the hazardous components in the micro/nano-pores of the HEU-type zeolite, as well as the meso- and macro-porous of natural zeolite, prevents their leaching by the rain water, protecting thus the quality of soils, surface and ground waters.
Key words: *Economic Geology, Waste treatment, environmental mineralogy, waste management.*

Περίληψη

Η ανάμειξη λάσπης από τη βιομηχανική ζώνη Σίνδου Θεσσαλονίκης με υψηλής ποιότητας φυσικό ζεόλιθο τύπου-HEU (τόφφος με 86 %κ.β. κλινοπτιλόλιθο-ευλανδίτη) σε ίσες ποσότητες, έδωσαν άοσμη και συνεκτική ζεολάσπη. Επίσης, η κατεργασία υγρών αποβλήτων pH 7,8 από την ίδια βιομηχανική ζώνη με υψηλής ποιότητας φυσικό ζεόλιθο τύπου-HEU (88 %κ.β. κλινοπτιλόλιθο-ευλανδίτη), έδωσε διαυγές νερό pH 7,3, ελεύθερο από οσμές και βελτιωμένες τις ποιοτικές παραμέτρους κατά 60% για τα NO_3^-, 76% για το χημικά απαιτούμενο οξυγόνο (COD), 100% για τα P_2O_5 και το Cr. Ταυτόχρονα, προέκυψε άοσμη και συνεκτική ζεολάσπη ως ίζημα. Η άοσμη και συνεκτική ζεολάσπη που προέκυψε είτε από την ανάμειξη της λάσπης με τον φυσικό ζεόλιθο, είτε ως ίζημα από την κατεργασία των βιομηχανικών υγρών αποβλήτων με φυσικό ζεόλιθο και κροκιδωτικά, είναι κατάλληλη για ασφαλή απόθεση, επειδή η καθήλωση των επιβλαβών συστατικών στους μίκρο/νάνο-πόρους του ζεόλιθου τύπου-HEU καθώς και στους μέσο- και μάκρο-πόρους του φυσικού ζεόλιθου, αποτρέπει την έκπλυσή

τους από το νερό της βροχής, προστατεύοντας έτσι την ποιότητα των εδαφών, επιφανειακών και υπόγειων υδάτων.
Λέξεις κλειδιά: *Κοιτασματολογία, Κατεργασία αποβλήτων, περιβαλλοντική ορυκτολογία, διαχείριση αποβλήτων.*

1. Introduction

Natural zeolite deposit corresponds to a rock which contains high amounts of one or more from the 80 natural phases of zeolites. The zeolite with the numerous applications is the HEU-type zeolite (clinoptilolite-heulandite) that shows tabular crystals and contains micro/nano-pores in a framework of channels with 10- and 8-member rings, in dimensions of 7.5x3.1 Å, 4.6x3.6 Å and 4.7x2.8 Å (Baerlocher et al. 2007; Mitchell et al. 2012). For nutritional, pharmaceutical, medical, environmental, cattle-raising, agricultural, aqua-cultural and industrial uses, the required HEU-type zeolite (clinoptilolite-heulandite) content should be greater than 75 wt.%. The presence of fibrous zeolites (e.g., erionite, mordenite, scolecite, mesolite, natrolite, roggianite, mazzite, ferrierite) is inhibitory for the use of natural zeolite (Tsirambides and Filippidis 2012).

Almost every industrial area is served by sludge and wastewater treatment facilities that aim to treat sludge and wastewater and dispose them in a safe manner using a variety of techniques (e.g., anaerobic, aerobic, coagulation/precipitation, composting). High quality HEU-type natural zeolites, display unique physical and chemical features and have a great variety of environmental, industrial, aquacultural and agricultural applications (e.g. Tserveni-Gousi et al. 1997; Colella and Mumpton 2000; Bish and Ming 2001; Kallo 2001; Ming and Allen 2001; Tchernev 2001; Filippidis and Kantiranis 2007; Filippidis et al. 2008; Filippidis 2010; Tzamos et al. 2011; Vogiatzis et al. 2012). 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 0.1 and 0.2 g of natural zeolite, have been previously investigated (e.g. Filippidis et al. 2011a,b, 2012).

The present study investigates the neutralization of sludge from Sindos industrial area of Thessaloniki using high quality natural zeolite in proportion 50:50 (sludge:natural zeolite), as well as the purification of 300 mL Sindos industrial area wastewater using 0.4 g of high quality natural zeolite.

2. Materials and Methods

The natural zeolite samples used (Fig. 1) were supplied by GEO-VET N. Alexandridis & Co O.E. The mineralogical composition of natural zeolite samples were determined by X-Ray Powder Diffraction (XRPD). The XRPD analysis was performed using a Philips PW1710 diffractometer with Ni-filtered CuK_{α} radiation. The counting statistics were: start angle 3°, end angle 65° 2θ and scanning speed 1.2°/min. Semi-quantitative 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. The combined methods of SEM-EDS, thermal treatment and XRPD, revealed that the HEU-type zeolite contained in the zeolitic tuffs, presents characteristics of group I zeolite (clinoptilolite) and of group II (intermediate heulandite) (Kantiranis et al. 2006, Filippidis and Kantiranis 2007).

The natural zeolite was powdered in agate mortar and passed all through sieve < 0,5 mm. The sludge was mixed with natural zeolite in equal proportions, in a high-speed shaker for 5 seconds. The produced zeosludge was left to dry at room temperature for 24 hours. The wastewater was treated at room temperature with < 0.5 mm grain-size of natural zeolite in batch-type experiment. In 300 mL wastewater 0.4 g of natural zeolite was added under continuous stirring for 3 minutes followed by the addition of 0.1 mL of polyaluminium chloride and 2 mL of cationic polyelectrolyte. The overflow and the precipitated zeosludge were separated by filtering. The zeosludge was dried overnight at room temperature. The starting wastewater and the overflowed clear water, were analyzed for (method): pH (Electrometric), Chemical Oxygen Demand (method of K_2CrO_6), P_2O_5 (Molecular Absorption Spectrophotometry), NO_3^-, Cu, Zn and Cr (Atomic Absorption Spectroscopy).

Figure 1 - Natural zeolite rock (left) and its powdered sample with grain-size <0.5 mm (right).

3. Results

The semi-quantitative mineralogical composition of natural zeolite samples used are presented in Table 1. The natural zeolite used for the sludge treatment contains 86 wt.% HEU-type zeolite (clinoptilolite-heulandite), 4 wt.% mica + clay minerals, 5 wt.% feldspars (plagioclase + alkali-feldspar) and 5 wt.% SiO_2-phases (quartz + cristobalite). The natural zeolite used for the wastewater treatment contains 88 wt.% HEU-type zeolite, 4 wt.% mica + clay minerals, 5 wt.% feldspars and 3 wt.% SiO_2-phases. The small differences observed between the natural zeolite samples concerning their semi-quantitative mineralogical composition are within the standard deviation of the XRPD method.

Table 1 - Semi-quantitative mineralogical composition (wt.%) of the natural zeolite samples.

Minerals	**Natural zeolite used for sludge treatment**	**Natural zeolite used for wastewater treatment**
HEU-type zeolite (clinoptilolite-heulandite)	86	88
Mica + Clay minerals	4	4
Feldspars (plagioclase + alkali-feldspar)	5	5
SiO_2-phases (quartz + cristobalite)	5	3
Total	100	100

The commixture of sludge from Sindos industrial area of Thessaloniki with the high quality HEU-type natural zeolite (86 wt.% clinoptilolite-heulandite) in equal proportions, resulted to odourless and cohesive zeosludge (Fig. 2).

The treatment of wastewater of pH 7.8 from Sindos industrial area of Thessaloniki with the high quality HEU-type natural zeolite (88 wt.% clinoptilolite-heulandite) resulted in production of clear water of pH 7.3, free of odours and improved quality parameters by 60% for the NO_3^- content, 76% for the chemical oxygen demand (COD), 100% for P_2O_5 and Cr contents (Table 2 and Fig. 3). Simultaneously, a precipitate of odourless and cohesive zeosludge was produced, after drying for 24 hours at room temperature (Fig. 4).

Figure 2 - Left: Raw sludge from Sindos industrial area of Thessaloniki, Right: Odourless and cohesive zeosludge (sludge:natural zeolite 50:50).

Table 2 - Quality characteristics of Sindos Industrial Area Wastewater (SIAW), overflowing Clear Waters treated with 0.1g (CW-0.1), 0.2g (CW-0.2) and 0.4g (CW-0.4) of natural zeolite and relevant improvement (±%).

Parameter (detection limit)	**SIAW**	**CW-0.1[1]**	**±%**	**CW-0.2[2]**	**±%**	**CW-0.4[3]**	**±%**
pH (0.1)	7.8	7.3	6	7.4	5	7.3	6
Chemical Oxygen Demand (COD), mg/L (15)	239	73	69	63	74	58	76
P_2O_5, mg/L (0.3)	9.1	bdl	100	bdl	100	bdl	100
NO_3^-, mg/L (2)	35	16	54	15	57	14	60
Cu, mg/L (0.1)	bdl	bdl	-	bdl	-	bdl	-
Zn, mg/L (0.1)	bdl	bdl	-	bdl	-	bdl	-
Cr, μg/L (5)	35	8	77	6	83	bdl	100

[1]Filippidis et al. (2011a), [2]Filippidis et al. 2011b, [3]Present study, bdl: below detection limit.

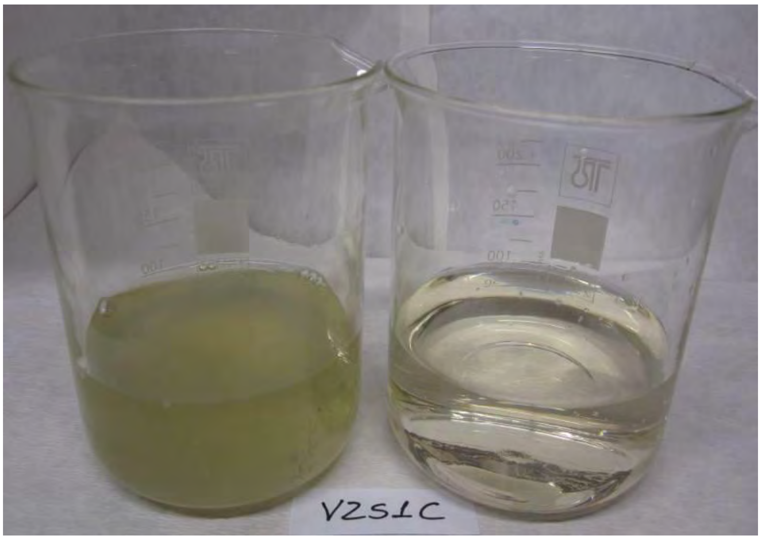

Figure 3 - Raw wastewater from Sindos industrial area of Thessaloniki (left) and clear water after the natural zeolite treatment (right).

Figure 4 - Odourless and cohesive zeosludge, dried at room temperature for 24 hours.

4. Discussion and Conclusions

The natural zeolite is of high quality, on average contains 87 wt.% HEU-type zeolite (clinoptilolite-heulandite), 4 wt.% mica + clay minerals, 5 wt.% feldspars (plagioclase + alkali-feldspar) and 4 wt.% SiO2-phases (quartz + cristobalite).

The commixture of industrial sludge with high quality natural zeolite produced odourless and cohesive zeosludge, suitable for safe disposal. The treatment of industrial wastewater of pH 7.8 with high quality HEU-type natural zeolite resulted in the production of clear water of pH 7.3, free of odours and improved quality parameters by 60% for the NO_3^- content, 76% for the chemical oxygen demand (COD), 100% for P_2O_5 and Cr contents. Simultaneously, a precipitate of odourless and cohesive zeosludge was produced. The increase of the added amount of natural zeolite from 0.1g to 0.4g, resulted in purification improvement by 6% for NO_3^-, 7% for COD and 23% for Cr, while for pH and P_2O_5 improvement was almost the same (Table 2).

The odourless and cohesive zeosludge produced either by the commixture of sludge with the natural zeolite or as precipitate from the treatment of industrial wastewater with the natural zeolite, is suitable for safe disposal, since the fixation of the hazardous components in the micro/nano-pores of the HEU-type zeolite, as well as the meso- and macro-porous of natural zeolite, prevents their leaching by the rain water, protecting thus the quality of soils, surface and ground waters (Filippidis 2010).

High quality HEU-type natural zeolite, sorb bacteria, fungi, gases, inorganic, organic and organometallic compounds, controls to neutral the pH of soils and waters, enriching in oxygen the waters (oxygenous currents), acting as acceptor and donor of protons, exhibiting thus an amphoteric character. The pH increase of the acidic waters is attributed to the binding of H^+ to the Lewis basic active sites of the HEU-type zeolite, while the pH decrease of the basic waters is attributed to the removal of OH^- from Brønsted acidic active sites and/or from the exchangeable hydrated cations of the HEU-type zeolite. The sorption of gases results in the oxygen enrichment of air and in remarkable malodour decrease (e.g. Filippidis et al. 1996, Charistos et al. 1997, Godelitsas et al. 1999, 2001, 2003, Filippidis and Kantiranis 2007).

The sorption and fixation of the different components by the micro/nano-pores of the HEU-type zeolite, as well as the meso- and macro-pores of the natural zeolite, are attributed to absorption (ion exchange), adsorption and surface precipitation processes. Important role in these processes play the surface Brønsted acidic and Lewis basic sites of the HEU-type zeolite structure. Due to the existence of these active sites, HEU-type zeolite reacts with the positively or/and negatively charged chemical species, 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/nano-pores) and the surface of the HEU-type zeolite crystals, consequently the meso- and macro-pores of the natural zeolite (e.g. Misaelides et al. 1995, Godelitsas et al. 1999, 2001, 2003, Kallo 2001, Kantiranis et al. 2011).

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