Metals Selectivity from Natural Zeolite in Sewage Sludge Compost. A Function of Temperature and Contact Time

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ABSTRACT

It is well known that the application of Natural Zeolite in sewage sludge compost processes has the ability (a) to remove and/or uptake heavy metals in significant levels and not let them past to the groundwater, (b) to take up all the metals, which are bound to the most mobile forms while the rest remain to an inert forms. Hence, there are a lot of studies that show the selectivity of natural zeolite in metals, which are presented, in liquid waste or liquid prepared samples in laboratories but no research was carried out, for the selectivity of metals from zeolite in the process of sewage sludge compost. The paper focuses on the determination of the selectivity of heavy metals from natural zeolites in the first steps of the composting process, which the substrate is unstable. A number of experiments were carried out in different conditions in order to indicate how the temperature (20, 40 and 60°C) of composting and the contact time (1 - 30 d) of the clinoptilolite affected the uptake of the heavy metals. The selectivity series for the removal of heavy metals is different from temperature to temperature and from day to day. The optimum result was carried out in 30 d and for 60 ± 2°C. In those conditions 70% of Cd, 67% of Cr and Mn, 62% of Co, 46% of Zn, 43% of Ni, 41% of Pb, 37% of Fe and 27% of Cu were taken up from clinoptilolite. The results are very useful for the determination of the best conditions of the composting of a heavy polluted waste with zeolites.

INTRODUCTION

The mineralization of biogenic substances is a part of the natural recycling processes, which occurs at any place where organic material is synthesized by plants and degraded by animals and micro flora. Environmental problems associated with sewage sludge disposal have prompted legislative actions. At the same time, the upgrading and expansion of wastewater treatment plants have greatly increased the volume of sludge generated. Sludge is composed of by-products collected at different stages of the wastewater treatment process. It contains compounds of agricultural value (including organic matter, nitrogen, phosphorus and potassium, and to a lesser extent calcium, sulphur, magnesium), and pollutants, which usually include heavy metals, organic pollutants and pathogens. Characteristics of sludge depend on the original pollution load on the treated water, and also on the technical parameters of the wastewater and sludge treatment process. Sludge is usually treated, before disposal or recycling, in order to reduce its water content, its fermentation propensity or the presence of pathogens. Several different treatment processes can be employed at the processing stage i.e. thickening, dewatering, stabilisation, disinfection, and thermal drying. After treatment, sludge can be recycled or disposed of using the following approaches: recycling for agriculture landspreading), incineration, land filling, silviculture, land reclamation, wet oxidation, pyrolysis and gasification.

The total amount of sludge produced in the 15 European Union countries is about 7 million tons of dry matter (t DM). Germany is the first sludge producer, followed by the United Kingdom, France, Italy and Spain, all producing more than 500,000 t DM in a year. These five countries generate altogether nearly 75% of the European sewage sludge. All other countries produce less than 250,000 t DM each.

This situation roughly reflects the demography of each country. The amount of sludge is usually presented in tons of dry matter that should be multiplied tenfold to obtain the amount of raw sludge produced. The total amount of raw sludge produced in the EU should be around 70 million t. However, it is only a theoretical approach, as the original water content of the sludge depends on its type and the treatment applied (EU 2008).

Sludge characteristics depend on many factors such as the degree of the composition of the wastewater, the wastewater treatment processes and sludge treatment processes. The composition of the wastewater depends on the various inflows and its treatment may have one to three stages; the primary, the secondary and the tertiary process. Each treatment plant operates with different types of processes and the technology that is applied is not always the same. Even in one plant the composition of the sludge produced can vary daily, weekly or annually. The need for finding new treatment and utilisation methods is imperative as the capacity of the landfill is limited and the EU Directives have set restrictions on the wastewater treatment, which impacts the disposal management of the sludge produced. The Directives also impose limitation of the biodegradable waste in landfills to 25% until 2010. Thereby, the EU members are obligated to develop new methods of sludge disposal in order to comply with the EU regulations.

European Commission Directives regulating sludge materials are translated into national legislations by Member states and accession countries. The most relevant Directives for sludge management are: (i) Council Directive 86/278/EEC on protection of the environment refers, in particular, to the soil when sewage sludge is used in agriculture. The main objective of the Directive is the control of heavy metals (PTEs), and is thought to be the main contaminants of concern when biosolids are being applied to land. The

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regulatory controls introduced address the potential impact of biosolids addition to soil from both the immediate application and also any possible cumulative effects. Minimum quality standards for the soil and sludge, and also monitoring requirements are specified in that Directive (86/278/EEC). It also contains limits for heavy metals concentration in sewage sludge, as well as in soil, when sewage is used on land, and the maximum annual heavy metals load through the application of sewage sludge. (ii) The Waste Framework Directive (91/156/EEC amending 75/442/EEC on waste) defines the waste management hierarchy, according to which preferences are given to prevention from waste followed by waste reduction, re-use, recycling and energy recovery. Principles of the use and disposal of waste, waste management plans, approval procedures, and monitoring, are also mentioned in this Directive. Also "waste" definition, a list of different types of waste, is provided by Commission Decision 2001/118/EEC.

Composted sludge presents a higher agricultural value, reaches a good level of disinfections, and is stabilized, reducing therefore the arising of odors. It also has a humus-like aspect, which, together with the reduction of odors, makes the acceptance of its use easier. Lastly, composting is used to reduce the water content of the product, as it may reach over 60% of dry matter, making also its handling easier. Composting is implemented in many cases throughout the world because it has several advantages over conventional disposal strategies. Firstly, composting can reduce the waste volume by 40 to 50% and thus require less landfill space for disposal (Wong *et al.* 1995; Zorpas 2008). Secondly, pathogens can be killed by the heat generated during the thermophilic phase (Finstein *et al.* 1992; Furhacker and Heberl 1995; Wong *et al.* 1995). Finally, composting has been well established and currently it is used to provide a final product, which can act as a soil conditioner or fertilizer. Compost contains major plant nutrients such as N, P and K, micro nutrients such as Cu, Fe and Zn and humic substances which improve the physical properties of soils such as aeration and saturation capacity (Wong *et al.* 1995; Zorpas *et al.* 2003; Zorpas 2008).

Heavy metals are toxic priority pollutants that commonly interfere with the beneficial use of wastewater for irrigation and industrial applications. Heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders (Bailey *et al.* 1999; Al-Degs *et al.* 2001; Wei and Liu 2005). These metals may leach from sludge and enter the ecosystem, the food chain and finally the human body. However, the total concentration of heavy metals cannot provide useful information about the risk of bioavailability, toxicity and capacity for remobilisation of heavy metals in environment (Fernández-Alborés *et al.* 2000; Kunito *et al.* 2001; Liu *et al.* 2007; Zorpas 2008; Zorpas *et al.* 2008a, 2008b). In the past two decades, research has been carried out and focused on using low-cost effective sorbents for heavy metal adsorption and the sorption behavior of several natural materials and waste products has been investigated (Al-Degs *et al.* 2001; Wand and Xing 2002). These cost-effective materials range from industrial byproducts or waste, such as waste rubber tires, to agricultural products such as wool, rice straw, coconut husks and peat moss. Other known natural materials like clay and zeolite have been investigated for their potential use as adsorbents for heavy metals. In addition, zeolite has a high sorption capacity and selectivity result from high porosity and sieving properties. Zeolites are natural silicate minerals; their capability to exchange cations is one of their most useful properties and determines their ability to remove heavy metals from industrial wastewater (Zorpas and Inglezakis 2009).

The heavy metal content of wastewater treatment sludge limits the possibilities for using and even disposing this waste. Application to soils for increasing their organic matter is restricted by metal content because it may indirectly be incorporated into the food chain or transported to aquifers. Composting of sewage sludge with natural zeolite (cli-

noptilolite) can enhance its quality and suitability for agricultural use (Zorpas 2008). Zeolites have been world-wide used for the last decades, either for their cation exchange or molecular sieving properties. Natural zeolites nowadays are mostly used in catalysis, in air enrichment, as filers in paper and rubber industry, in soil benefication, as animal feed supplements, as well as in water and wastewater treatment for the ammonia and heavy metal removal (Zorpas and Inglezakis 2009).

At present, the zeolite group includes more than 40 naturally occurring species and is the largest group of minerals among the silicates. Before 1960s, zeolite minerals were thought to be mainly distributed in hydrothermal veins and geodes in basalts, andesites and other volcanic rocks (Tsitsishvili *et al.* 1992; Zorpas 2008; Zorpas and Inglezakis 2009). Zeolite in such settings forms large, well-shaped crystals and druses. Due to the usual small size of veins and because of poly-minerality, these deposits have no practical importance, but samples of vein origin have been used to establish the properties of the mineral and the possibility of their utilization in industry. According to the bibliography (Tsitsishvili *et al.* 1992; Zorpas 2008), in the 1980s, more than 300000 t of natural zeolites were used in world market (150,000 t in Europe and 90,000 in Japan) and the most common zeolites were: clinoptilolite, mordenite, phillipsite, chapazite. Zeolite minerals are known to distribute rather unevenly in nature. Clinoptilolite, mordenite, phillipsite, chapazite, stilbite, analcime and laumontine are very common whereas offretite, paulingite, barrerite and mazzite, for example, are much rarer, and sometimes limited to single occurrences. According to Zorpas and Inglezakis (2009) and Tsitsishvili (1992) zeolites can be used as structural materials, in paper industry, to improve soil properties, in the animal feed industry, in wastewater treatment plants, for cleaning and improvement of drinking water properties, for metal removal, etc.

It is well known that the application of Natural Zeolite in sewage sludge compost processes has the ability to remove and/or uptake heavy metals in significant levels and not let them past to the groundwater. It is also well known that the zeolite has the ability to take up all the metals, which are bound to the most mobile (exchangeable and carbonates) forms, while the rest are remain to an inert forms (organic and residual) (Zorpas *et al.* 1999, 2000; Zorpas 2008; Zorpas *et al.* 2008a, 2008b). Therefore, the natural zeolites may be considered as one of the best amendment materials for co-composting with sewage sludge taking into account their high efficiency and low cost (Stylianou *et al.* 2007).

This paper focuses on the determination of the selectivity of heavy metals from zeolites in the first steps of the composting process during which the substrate is unstable, for several temperatures and contact times. The results are very useful for the determination of the best conditions of the composting of sewage sludge with zeolite in order to optimize the process.

MATERIALS AND METHODS

In the greater region of Athens, with almost 5,500,000 inhabitants, the main wastewater treatment plant operating is at the rock-island of Psittalia. At Psittalia, approximately 1,000,000 m^3/d consisting mainly of municipal wastewater and some industrial wastewaters, are subjected to primary treatment, producing approximately 350 t/d of dewatered anaerobically stabilized primary sewage sludge (DASPSS) (Zorpas 2008). Until now, landfilling was the main disposal route for sewage sludge in Athens generating potential environmental hazards which included the production of odor, methane gas, and leachates, while a small, however ever increasing amount is used as alternative fuel in the cement industry (Zorpas 2008).

DASPSS samples were sampled for a period of six month (April – September: 200-250 kg every 2 d) from the Psittalia wastewater treatment plant. Then, samples were dried, homogenized and stored in 4 ± 0.5°C. Natural zeolite, clinoptilolite (Cli), used as a bulking agent, was collected from Evros (Region in

Table 1 Selected physicochemical properties of sewage sludge, clinoptilolite.

Parameters	Mean Values of 20 homogenized samples			
	DASPSS	SD	Clinoptilolite	SD
Moisture, %	70.10	2.50	7.15	0.50
pH (solid : distilled water = 1:10)	7.05	0.05	7.85	0.05
EC mS/cm (solid : distilled water = 1:10)	1.001	0.002	0.155	0.002
Organic Mater, % dry weight	45.10	1.25		
Ash, % dry weight	24.50	1.50	80.65	1.50
TOC, % dry weight	26.10	0.50		
TKN, % dry weight	1.75	0.25	0.032	0.002
C/N	14.91	0.25		
NH_4-N, mg/kg	957	35	140	15
Total humics, % dry weight	2.45	0.05		
Humification Index	0.04	0.001		
Total Exchange Capacity, according to its chemical composition, meq/g			2.4	0.3
Cd, mg/kg	2	0.1	n.d	
Cr, mg/kg	552	20	n.d	
Cu, mg/kg	258	25	n.d	
Fe, mg/kg	5098	250	1964	150
Mn, mg/kg	150	15	10	1.5
Ni, mg/kg	41	2	n.d	
Pb, mg/kg	326	21	111	15
Zn, mg/kg	1739	30	5	1.8
Co, mg/kg	603	60	n.d	
Na, mg/kg	724	23	1786	33
K, mg/kg	723	22	5493	41
Mg, mg/kg	1382	200	2030	50
Ca mg/kg	14854	1050	1502	61

Significant different at $p < 0.05$, n.d: not detected, SD: standard deviation

Table 2 Chemical composition of natural clinoptilolite. N = 20

Oxide	% w/w
SiO_2	66.5 ± 0.8
Al_2O_3	12.8 ± 1.3
Na_2O	1.2 ± 0.4
K_2O	1.4 ± 0.3
CaO	2.7 ± 0.6
MgO	1.5 ± 0.2
FeO	1.2 ± 0.4
H_2O	12.1 ± 0.2

North Greece). Selected composition characteristics of the materials used (Zorpas 2008; Zorpas *et al.* 2008a, 2008b) are given in **Tables 1** and **2**.

In order to observe how temperature and contact time of the mineral with the sewage sludge affected the uptake of the heavy metals, the following experiments were carried out in an in-vessel reactor: Temperature was set at 20 ± 2, 40 ± 2 and $60 \pm 2°C$ for contact times of 1, 2, 3, 4, 5, 6, 7, 10, 20 and 30 d, respectively. These temperatures are chosen according to the following principles: (i) $60 \pm 2°C$ corresponds to the thermophilic phase of the composting process where organic mater is decomposed and discharged in lower molecular weight, (ii) $40 \pm 2°C$ corresponds to the mesophilic phase where humic substances are formulated and (iii) $20 \pm 2°C$ corresponds to ambient conditions, because at the end the substrate is remaining under ambient conditions either for further stabilization or for storage. These experiments were carried out using the 25% w/w clinoptilolites (2.5 - 2.7 mm) and 75% w/w sewage sludge. The composting process was carried out in the laboratory using three in-vessel reactors of 1 m^3 active volume each (Finstein *et al.* 1992; Zorpas 1999). The first step of composting in the reactor lasted for 30 d. The temperature in the center of the reactor was set at 20 ± 2, 40 ± 2 and $60 \pm 2°C$, with the moisture content between $47 \pm 5\%$. The samples were aerated with oxygen concentration ranging between 5 - 8% vol. A temperature indicator controller was controlling the operation of the fan in order to maintain the set up temperature. The substrates were mechanically mixed every 6 h. During this period a small quantity of samples (five samples per sampling time and for each day) were taken every 1, 2, 3, 4, 5, 6, 7, 10, 20 and 30 d for several analyses and in order to estimate the selectivity of zeolite in metals.

After 30 d of composting, during which the organic material was biodegraded, the compost was piled to an enclosed package where it remained for further maturation under ambient conditions.

Methods of analysis

For the characterization of all compost samples, zeolites were manually removed from the final products using sieving with diameters of the sieve being 2.3 mm.

For determining the total metal concentration, a known quantity (1 g) of sample was digested with 10 mL of conc. HNO_3 and 2 mL of H_2SO_4 according to Zorpas *et al.* (1998b). After the completion of the digestion, samples were vacuum-filtered and the filtrate was used for the determination of heavy metal concentration by flame atomic absorption spectroscopy, using a Perkin Elmer 2380 spectrophotometer.

pH, electronic conductivity and ammonia content were determined according to Adams (1990) and Zorpas *et al.* (1998a, 1998b). Statistical analysis was performed using Microsoft Excel (2003).

RESULTS AND DISCUSSION

It is well known from previous reports (Zorpas *et al.* 2000, 2003, 2008, 2008a, 2008b) that 25% w/w of zeolite in the composting process of sewage sludge takes up from the final mature product 100% of Cd, 20% of Co, 36% of Cu, 12 % of Cr, 10% of Mn, 40% of Fe and Zn, 32% of Pb and 53% of Ni. Those are the results of the composting of sewage sludge with zeolite after 15 d in the thermophilic phase where temperature was varying between 45 - 70°C every 24 h in the center of the reactor, while at the end the compost was piled into an enclosed package where it remained for further mature in ambient conditions. The clinoptilolite has the ability to uptake and selectively extract heavy metals in different conditions. Under constant temperature and for a specific contact time, the clinoptilolite has the ability to uptake certain metal in higher amounts than under changeable conditions.

The adsorption behavior of different metal ions on natural zeolite has been determined at different temperatures and contact times of sludge with zeolites. **Tables 3-5** present the heavy metals' uptake (%) at 20 ± 2, 40 ± 2 and $60 \pm 2°C$, respectively with respect to the contact time and also in respect to the initial concentration of metals in raw mate-

Table 3 Metals uptake (%) by clinoptilolites at 20 ± 2°C with respect to the initial amount of metal in DASPSS.

Time, d	Co	Cd	Cr	Cu	Fe	Ni	Mn	Pb	Zn	K	Na	Ca	Mg
1	0	0	0	2.32	0.54	0	6	0	0	83.95	100.13	0	86.36
2	0	0	0	3.10	1.53	0	7.33	0	0.46	88.105	100.27	0	86.51
3	0.33	5	0.36	3.87	8.00	2.43	8.66	0.30	0.57	90.871	108.70	0.55	86.59
4	0.33	5	0.36	5.03	9.96	2.43	9.33	0.61	2.18	103.31	108.83	4.83	86.66
5	0.50	15	0.54	10.85	10.945	4.87	9.33	0.92	3.10	104.70	112.43	5.97	86.99
6	0.50	15	0.54	12.79	11.141	4.87	9.33	0.92	5.29	107.46	113.53	7.04	87.04
7	0.50	20	0.54	14.34	12.318	4.87	9.33	1.84	5.52	121.30	114.77	7.82	87.27
10	1.16	25	1.26	15.11	33.50	4.87	10.66	2.45	12.93	157.67	120.85	9.44	87.57
20	3.17	30	3.44	21.7	39.58	14.63	13.33	8.58	17.82	179.39	124.44	10.00	95.22
30	4.00	50	4.34	22.86	41.15	17.07	13.33	8.89	17.82	198.75	130.66	11.47	95.30
Initial concentration in mg/kg dry mater													
	603	2	552	258	5098	41	150	326	1739	723	724	14854	1382

Significant different at p < 0.05

Table 4 Metals uptake in % by clinoptilolites at 40 ± 2°C with respect to the initial amount of metal in DASPSS.

Time, d	Co	Cd	Cr	Cu	Fe	Ni	Mn	Pb	Zn	K	Na	Ca	Mg
1	0.66	0	0.72	3.48	0.74	0	20	17.17	2.35	96.40	101.51	0	86.96
2	2.83	5	3.07	3.87	1.72	2.43	21.33	18.71	3.39	106.08	101.93	4.83	90.90
3	5.34	5	5.79	5.03	3.49	2.43	22	20.24	3.68	114.38	108.70	5.97	93.56
4	12.02	10	13.04	6.97	3.68	4.87	23.33	20.55	5.11	119.91	111.04	7.04	97.57
5	16.02	15	17.39	12.28	4.27	4.87	24	20.85	5.34	133.74	119.88	7.82	98.71
6	25.37	25	27.53	14.34	6.63	4.87	24	21.77	5.98	137.89	122.23	9.44	110.37
7	27.37	30	29.71	15.50	8.59	7.31	24.66	23.312	6.55	150.34	124.44	10.00	118.03
10	39.56	30	42.93	21.70	29.18	12.19	26.66	24.23	16.10	174.2	130.52	11.47	127.65
20	40.40	55	43.84	22.48	37.03	24.39	28	26.99	18.63	237.48	132.04	13.20	143.93
30	41.56	60	45.10	24.80	38.21	31.70	28	38.34	18.63	299.72	139.77	14.47	144.01
Initial concentration in mg/kg dry mater													
	603	2	552	258	5098	41	150	326	1739	723	724	14854	1382

Significant different at p < 0.05

Table 5 Metals uptake in % by clinoptilolites at 60 ± 2°C with respect to the initial amount of metal in DASPSS.

Time, d	Co	Cd	Cr	Cu	Fe	Ni	Mn	Pb	Zn	K	Na	Ca	Mg
1	34.55	5	37.5	7.75	1.92	2.43	34	18.71	2.87	119.91	101.5	0.28	90.98
2	41.56	5	45.10	8.52	2.31	2.43	35.33	20.24	3.62	130.99	110.35	6.06	93.56
3	42.40	10	46.01	8.91	2.51	4.87	46.66	20.55	7.53	133.74	111.18	7.82	97.57
4	48.91	15	53.07	9.96	3.29	7.31	50	20.85	10.40	147.57	113.81	9.44	101.89
5	50.58	20	54.89	13.56	6.82	7.31	53.33	21.77	14.43	155.87	122.09	10.00	117.80
6	52.25	30	56.70	15.89	7.61	9.75	60	23.31	16.56	160.02	126.51	11.47	136.43
7	55.42	35	60.14	18.99	9.76	14.63	61.3	24.22	20.29	166.94	132.04	13.20	143.10
10	58.26	50	63.22	24.80	24.87	24.39	62.66	26.99	40.42	198.75	136.87	14.47	151.59
20	62.10	70	67.39	25.58	34.28	31.70	67.33	28.22	46.23	249.93	140.60	15.20	168.18
30	62.10	70	67.39	27.13	36.83	43.90	67.33	41.71	46.23	309.40	154.00	16.01	169.62
Initial concentration in mg/kg dry mater													
	603	2	552	258	5098	41	150	326	1739	723	724	14854	1382

Significant different at p < 0.05

rial. Efficiency of the heavy metals removal by the clinoptilolites during the equilibrium studies is demonstrated in **Fig. 1A-I**, which presents the behavior of the removal of metals from sewage sludge using zeolite in respect to the contact time and temperature during the first 30 d of composting.

As observed from **Tables 3-5** and **Fig. 1A-I**, temperature and contact time affect the amount of heavy metals taken up by clinoptilolite. It is obvious that the selectivity series vary from day to day and from temperature to temperature. At lower temperatures, metals' removal from clinoptilolite is lower than in higher temperatures. For example, at 20 ± 2°C and for a 5 d contact time, the percentage removal of all examined metals is less than 11% (from 0.5 for Co up to 11% for Fe), while at 40 ± 2°C and for the same contact time the percentage removal of all the examined metals ranges between 4.7% for Fe and 24% for Mn. Finally, for the same contact time but at 60 ± 2°C, the percentage removal of all examined metals ranged between 6.82% for Fe to 53% for Mn. Similar behavior was observed for a contact time of 30 d and at 20 ± 2°C, with the lowest concentration of metal removal present for Co (only 4%) and the highest for Fe (almost 42%). At 40 ± 2°C and for a 30 d contact time, the lowest percentage metal removal is obtained for Zn (18.63%) and the maximum for Cr

(45.1%). Cu presented the lowest percentage removal (27.13%), while Cr and Mn both showed maximum removal percentages (67% both) at 60 ± 2°C and for a 30 d contact time. In highest temperatures and in a relative moisture of 47 ± 5%, the mobility of metals is highest than in lower temperatures. Kocaoba *et al.* (2007) state that the adsorption process of heavy metal ions by the different natural materials (zeolites) was affected by various parameters such as sorbent amount, agitation speed, contact time, temperature, pH and initial concentration of heavy metals solution in kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite.

In this study the selectivity series at 20 ± 2°C is:

In 1 d: Mn > Cu > Fe
In 5 d: Cd > Fe > Cu > Mn > Ca > Ni > Zn > Pb > Cr > Co
In 10 d: Fe > Cd > Cu > Zn > Mn > Ca > Ni > Pb > Cr > Co
In 20 d: Fe > Cd > Cu > Zn > Ni > Mn > Ca > Pb > Cr > Co
In 30 d: Cd > Fe > Cu > Zn > Ni > Mn > Ca > Pb > Cr > Co

while the selectivity series at 40 ± 2°C is:

In 1 d: Mn > Pb > Cu > Zn > Fe = Cr > Co
In 5 d: Mn > Pb > Cr > Co > Cu > Cd > Ca > Zn > Ni > Fe
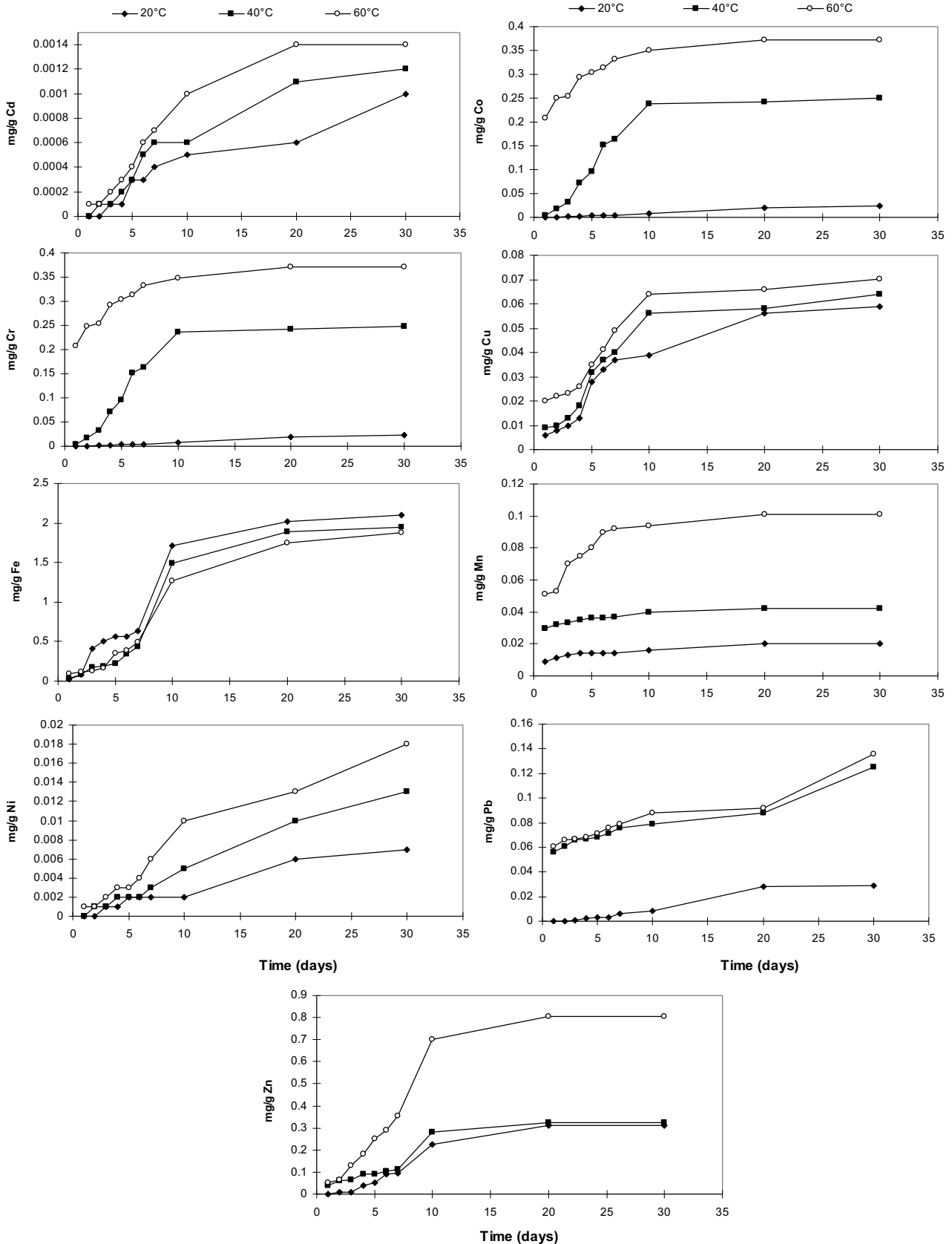
Fig. 1 Equilibrium removal from zeolite in different temperatures and contact times.

In 10 d: Cr > Co > Cd > Fe > Mn > Pb > Cu > Zn > Ni > Ca
In 20 d: Cd > Cr > Co > Fe > Mn > Pb > Ni > Cu > Zn > Ca
In 30 d: Cd > Cr > Co > Pb = Fe > Ni > Mn > Cu > Zn > Ca

Finally, the selectivity series at 60 ± 2°C is:

In 1 d: Cr > Co = Mn > Pb > Cu > Cd > Zn > Ni > Fe > Ca
In 5 d: Cr > Mn > Co > Pb > Cd > Zn > Cu > Ca > Ni > Fe

In 10 d: Mn > Cr > Co > Cd > Zn > Pb > Fe = Cu = Ni > Ca
In 20 d: Cd > Cr = Mn > Co> Zn > Fe > Ni > Pb > Cu > Ca
In 30 d: Cd > Cr > Mn > Co > Zn > Ni > Pb > Fe > Cu > Ca

The changeable conditions, which affect the system (and the selectivity series mentioned above) include temperature, pH (**Fig. 2A**) and concentration of ammonia (**Fig. 2B**) which absorbs and dis-absorbs at any time due to chan-
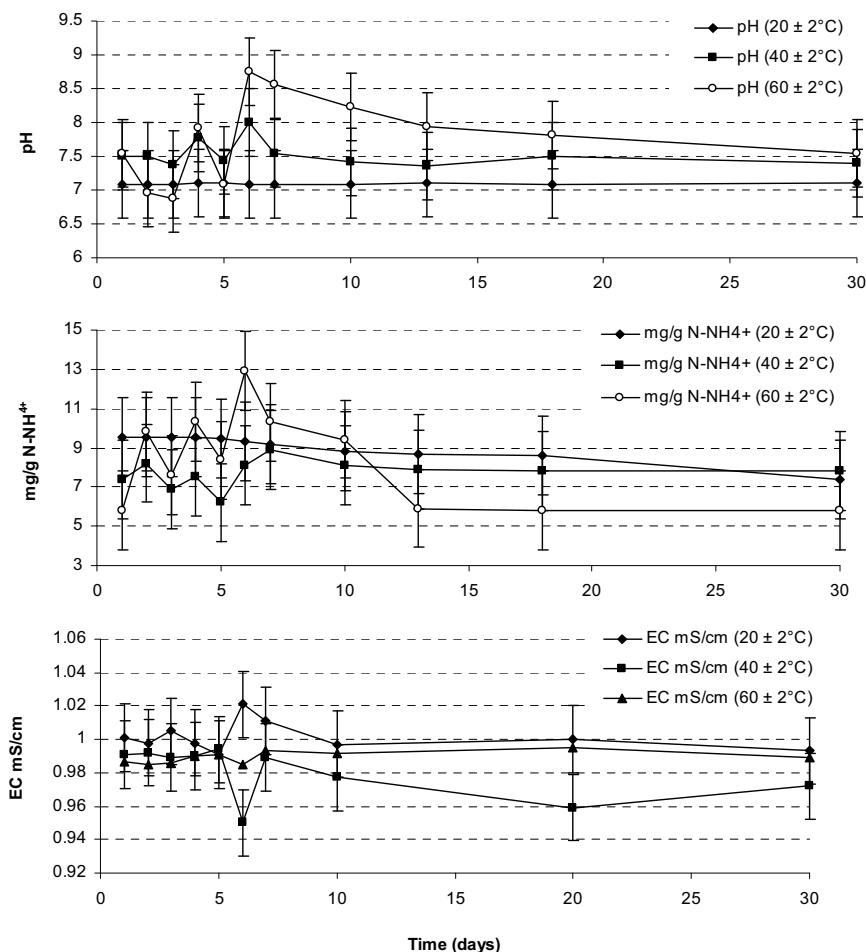
**Fig. 2 pH, NH$_4^+$ and EC variation at different temperatures.**

ges in microorganisms. Hence, acetic and reductive conditions due to the formation of the acetic acid (disruption of the organic matter from the *Bacillus Bacterium*) from the oxidation of lignin (Lynch 1986) and ammonia (in the first step of the composting process) may be a reasonable hypothesis. It is obvious that at lower temperatures, the selectivity of zeolites is completely different than in higher temperatures and for the same time.

This behavior is a result of two parallel uptake phenomena: ion exchange and adsorption. A constant conductivity value throughout the uptake process could be an indication that ion exchange is the predominant mechanism. Ion exchange resembles sorption in that, in both cases, a solid takes up a dissolved species. The characteristic difference between the two phenomena is that ion exchange, in contrast to sorption, is a stoichiometric process. Every ion, which is removed from the solution, is replaced by an equivalent amount of another ionic species of the same sign, while in sorption a solute (an electrolyte or non-electrolyte) is taken up without being replaced by another species. Conductivity, which is the ability of aqueous solutions to carry an electric current, is presented as a factor that affects the selectivity of metals in aqueous solutions according to Stylianou *et al.* (2007). This ability depends on the presence of the ions, on their total concentration, mobility and valence and on the temperature of the measurement. Solutions of most inorganic compounds are relatively good conductors. The conductivity according to **Fig. 2C** remains stable during the whole process.

The pH values of the experiments are presented in **Fig. 2A**. It is well known that natural zeolites tend to elevate the pH in acidic solutions. This is due to the H$^+$ exchange with Na$^+$, the binding of H$^+$ to the Lewis basic sites linked to the framework oxygen atoms of the clinoptilolite and the presence of OH$^-$ in solution deriving from hydrolysis of some species present in natural zeolite (Kurtoglu and Atun 2006;

Stylianou *et al.* 2007).

The pH range under which ion exchange takes place should be specified. Several reports tried to determine the optimum pH value of the aqueous solution to be treated with natural zeolite, focusing on copper, lead and zinc (Mier *et al.* 2001; Inglezakis *et al.* 2003; Wingenfelder *et al.* 2005; Stylianou *et al.* 2007). At lower pH, more highly charged metal complexes are formed, a fact beneficial for the exchange (Inglezakis *et al.* 2003). H$^+$ cations should be considered as competitive ones in ion-exchange processes and, consequently, ion exchange of metals is favored by high pH (which is presented in our study), which should, however, be lower than the minimum pH for precipitation. Another factor that should be taken into account in ion exchange studies is that in metal ion solutions, pH is affected by hydrolysis, according to the following two-way reversible reaction, giving acidic properties to heavy metal solutions:

$$[M(H_2O)_x]^{n+} + H_2O \leftrightarrow [M(H_2O)_{x-1}(OH)]^{(n-1)+} + H_3O^+ \qquad [1]$$
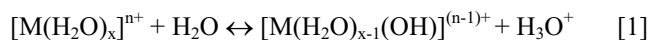
As the zeolite is gradually loaded with metals, as the time passes, pH may decrease (5 - 6.5) due to hydrolysis for 60 ± 2°C and for the first 5 d of contact time. The ion exchange process does not seem to have an effect from pH at 20 ± 2°C and for the first 5 - 10 d of contact time (except from Cu and Fe). As the temperature is very low, the pH is remaining stable and the discharge of the organic matter is reaming constant no acetic conditions is available in order to affect the system. Also, in these conditions the hydrolysis phenomenon is absent which leads to more acidic conditions.

The amount (%) of the removal metals from the sewage sludge in relation with the initial amount of metal in the raw materials is presented to be higher in higher temperatures. These results may be very useful for the optimization of the composting process of sewage sludge. It is obvious that in

$60 \pm 2°C$ and for 10 days of contact time, zeolites have the ability to remove 63% of Cr and Mn, 58% of Co, 50% of Cd, 40% of Zn, 25% of Cu, Fe, Ni and Pb, while for the same contact time but in $40 \pm 2°C$ the zeolites has the ability to remove 42% of Cr, 40% of Cd, 30% of Fe and Cd, 25% of Mn and Pb, 21% of Cu, 16% of Zn and 12% on Ni. In lower temperatures and for the same contact time except for Cd and Fe (which is about 25 and 30%, respectively), the rest of the metals are removed by the zeolite from 1 – 16%.

Another reason for the different selectivity that zeolites present may be the effect of the exchangeable fraction in which metals are bound. According to Zorpas et al. (2000, 2008a, 2008b) metals used to be bound in mobile and less mobile forms. Those fractions (according to the extraction scheme) are: the exchangeable, carbonates, oxidized/reducible, organic and residual forms (Tessier et al. 1979; Zorpas et al. 2000, 2008b). According to the same researcher (Zorpas et al. 2000, 2008a, 2008b) and some others (Wegner et al. 1990; Kapetanios et al. 1993) the changes, which are observed in metal partitioning of the sewage sludge compost (during, before and after the composting of sewage sludge), are the results of several factors which may be the same for the different selectivity of zeolite: (i) the thermophilic phase of composting, which was the first step in composting and which affected the exchangeable fraction. During the first step in composting changes in pH (acetic acid formation) and in ammonia content (affected by the action of the proteolytic bacteria and by the temperature), (ii) the pH changes, which occurred at the beginning of the composting process, affected the exchangeable and carbonate fraction. The pH changes may be due to acid formation during the decomposition of organic matter contained in the sludge and (iii) the oxic and anoxic conditions (produced by acetic acid and ammonia) at the first step of composting affected the reducible and organic fractions. Zeolite has the ability to take up all the dispensable metals and especially from the most mobile fractions (exchangeable and carbonates) while the rest metal are remain in an inert form (residual fraction). For the same reasons may be the different selectivity of metals from zeolite. Also, at higher pH the adsorption percentage of metals is relatively slow (Kocaoba et al. 2007) but according to the same researchers on equilibrium studies on metal removal from natural zeolite was found that the adsorption of heavy metal ions increased by increasing the pH value. Also, most of the heavy metal ions tend to form precipitation at pH higher than 6.0, which limits this process greatly. Therefore, the adsorption of metals ions on zeolite is difficult to be quantified at the higher pH value than 6, and the "true" adsorption could be potential by precipitation. Although various groups of microorganisms contribute in biosorption of heavy metals are usually the center of attention as additives (Ryu et al. 2003; Wong et al. 2004), mineral sorbents are also used to minimize the mobility of heavy metals in the compost (Zorpas et al. 2003; Wong and Selvam 2006; Zorpas et al. 2008b). Natural zeolites and the clinoptilolite in particular seem to be appropriate amendment materials for sewage sludge taking into account their sorption and exchangeable properties towards the heavy metals. Addition of the clinoptilolite to sewage sludge might change chemical speciation of heavy metals in composts and decrease their mobility and bioavailability (Sprynskyy et al. 2007). The sewage sludge is a source of nitrate, sulphate ions and houmic substances. Another reason of the differences that is presented especially at 40 ± 2 and $60 \pm 2°C$ may be the result of the formation of humic substances due to the decomposition of organic matter. Humics are complex substances with highs molecular and is clogging part of the pore openings in zeolite structure, leading in slower ion exchange kinetics. Increase of the zeolite sorption properties (more metals removal from other metals) may be connected by effect of polarization of water molecules sorbed onto the clinoptilolite surface as well as by cleavage intensification in the micro crystals. A sodium form of the clinoptilolite is somewhat more effective for the

metals sorption than hydrogen one. This state is also supported by Sprynskyy (2009). Another reason for several selectivity may be the surface dust. Surface dust (Inglezakis et al. 1999) is clogging part of the pore openings in zeolite structure, leading in slower ion exchange kinetics. Lower kinetics, is leading in lower uptake of metal ions.

Application of different additives to sewage sludge for immobilization of the excessive amounts of heavy metals is one of the ways to improve physical and chemical properties of the substrate. Use of natural sorbents or related materials for heavy metals removal or immobilization seems to hold much promise for sewage sludge treatment. Specifically, Li et al. (2001) studied solidification of the sludge by cement. Results of this study indicated that the heavy metals (copper, zinc and lead) could exist in the solidified/ stabilized waste matrix as metal hydrated phases or metal hydroxides precipitating on the surface of calcium silicate hydrates and pulverized fly ash.

Application of the clinoptilolites according to Sprynskyy (2009) previously treated by 2 M NaCl, 2 M HCl solutions and by ultrasound demonstrates the biggest effect of 30 min ultrasound treatment on the clinoptilolites extraction ability. In this case the efficiency of uptake of Pb, Ni, Cd, Cu and Cr increase for 14, 10, 7, 6 and 4%, respectively. Efficiency of the metal uptake by the clinoptilolite evaluated in the equilibrium study grows with increase of the zeolite dose added to the sewage sludge. Addition of 25% of the zeolite provides extraction efficiency of cadmium and lead of about 84%, chromium, copper and nickel of 66, 61 and 50%, respectively (Sprynskyy 2009).

Other investigators elaborated methods of chemical fixation of heavy metals during co-composting of sewage sludge with natural materials, such as lime and clay. Investigation of co-composting of sewage sludge with lime showed that lime is a suitable material to reduce the availability of heavy metals in the sludge compost (Fang and Wong 1999; Wong and Selvan 2006). The use of clay as compost amendments in experiments led to reduce the labile metal species in the composted product (Lothenbach et al. 1997; Qiao and Ho 1997). The addition of clay minerals, especially of Na-bentonite, Ca-bentonite and natural zeolite to soil derived from sewage sludge caused decrease inwater-extractable and exchangeable forms of heavy metals (Zn, Cd, Cu, and Ni) (Usmaz et al. 2004). In this case the extent of decrease ranged from 14 to 75% for the water extractable form and from 12 to 42% for the exchangeable form of metals. The good effect of the metal removal from sewage sludges was obtained with the application of natural zeolite (clinoptilolite) in experiments (Sprynskyy et al. 2007; Zorpas et al. 2008b). Utilization of synthetic zeolite (Zeolite P) as an amendment for compost derived from sewage sludge also demonstrated satisfactory results (Nissen et al. 2000).

Kocaoba et al. (2007) investigated the efficiency of removal of heavy metals such as Cu^{+2}, Cd^{+2} and Ni^{+2} ions from aqueous solution using natural clinoptilolite, obtained from the Biga-Canakkale region of Turkey, under different experimental conditions [metal solutions ranging from 1 - 100 mg/L concentration at various pH values (1 - 10), agitation speed (100 - 500 rpm), zeolite amount (0 - 2 g) and temperature (20 - 50°C) for retention times]. The results were provided strong support for the adsorption of heavy metals into clinoptilolites. The selectivity of the studied metals was determined as $Cd^{+2} > Ni^{+2} > Cu^{+2}$.

CONCLUSION

The amount (%) of removed metals from sewage sludge in relation with the initial amount of metal in the raw materials is presented to be higher in higher temperatures. These results may be very useful for the optimization of the composting process of sewage sludge.

The adsorption behavior of different metal ions on natural zeolite has been determined at different temperature and contact time of sludge with zeolites. Optimum conditions

were determined for maximum removal of metal at the first steps of composting between zeolites and sewage sludge. The application of natural zeolite in the composting process seems to take up a significant ($p < 0.05$) quantity of heavy metals in several temperatures and contact times. Temperature and contact time seem to affect the ability of natural zeolite to uptake the heavy metals. The efficiency on zeolites' selectivity seems to be more obvious at 60 ± 2 than in 40 ± 2 and $20 \pm 2°C$. Specifically, at $60 \pm 2°C$ and for 30 d of contact time the effectiveness of zeolites is up to 70% for Cd, 67% for Cr and Mn, 62% for Co, 46% for Zn, 44% for Ni, 42% for Pb, 37% for Fe, 27% for Cu. At $40 \pm 2°C$ and for 30 d of contact time the effectiveness of zeolites is up to 60% for Cd, 45% for Cr, 42% for Co, 38% for Pb and Fe, 32% for Ni, 28% for Mn, 25% for Cu, and 19% for Zn. At $20 \pm 2°C$ and for 30 d of contact time the effectiveness of zeolites is up to 50% of Cd, 41% of Fe, 17% for Zn and Ni, 13% for Mn, 9% for Pb and 4% for Cr and Cd. The effectiveness of zeolites seems to have limited influences also from the initial amount of metals in the raw material. The concentration of metals in increasing order according to the initial amount in raw material: is Cd < Ni < Mn < Cu < Pb < Cr < Co < Zn < Fe. Other parameters which seem to affect the selectivity of metals from zeolite include pH, ammonia concentration and electric conductivity. The clinoptilolite has the ability to uptake and selectively extract heavy metals in different conditions. Under constant temperature and for a specific contact time, the clinoptilolite has the ability to uptake certain metal in higher amount than in changeable conditions. Composting may concentrate (Cr, Mn, Ni, Pb, Zn) or dilute (Cu, Fe) heavy metals presented in sewage sludge. The change in metal concentration depends also on the metal loss through leaching and on the overall concentration of metals due to organic matter destruction.

ACKNOWLEDGEMENTS

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