Use of clinoptilolite to improve and protect soil quality from the disposal of olive oil mills wastes

Maria K. Doula*, Kyriakos Elaiopoulos, Victor A. Kavvadias, Vasilis Mavraganis

National Agricultural Research Foundation of Greece, Soil Science Institute of Athens, 1 Sof. Venizelou St., 14123 Lycovrisi, Greece

ARTICLE INFO

ABSTRACT

In the framework of LIFE07 ENV/GR/000280 Project "*Strategies to improve and protect soil quality from the disposal of olive oil mills wastes in the Mediterranean*-PROSODOL", a laboratory experiment was conducted in order to investigate to which extent the natural zeolite clinoptilolite is capable of limiting environmental degradation caused by the uncontrolled disposal of olive oil mills wastes (OOMW). Clinoptilolite was added in various ratios (from 0% up to 30% w/w) to soil samples, which were collected from four OOMW disposal sites (from both the interior of the disposal ponds and the surroundings) located in a pilot Municipality in Rethymno, Crete, Greece. Water soluble K, Ca, Mg, Mn, Zn, Fe, Cu, polyphenols, NO_3^-, Cl^-, SO_4^{2-} and PO_4^{3-} were measured in leachates after equilibration of the soil samples with clinoptilolite It was observed that water soluble K, NO_3^-, Cl^-, SO_4^{2-} and polyphenols were decreased with an increase in zeolite percentage; Ca leaching was slightly increased or remained nearly constant; Mg leaching remained constant or increased, especially for pond soils; and PO_4^{3-} leaching was very low. Although the soil samples' content in available Mn, Cu, Zn, Fe was high, the metals were not detected in the leachates.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Natural zeolites have been the subject of investigation by many researchers who took advantage of zeolites' physical and chemical properties and used them in heavy metals adsorption, water purification and softening, soil remediation, etc. During these studies many experimental variables were investigated, such as solution pH, temperature, solution ionic strength, concentration of adsorbates, contact time and present cationic/anionic species. Results have shown that these naturally occurring materials could be used to provide satisfactory solutions for many environmental problems via low-cost procedures [1–6].

Zeolites are materials in which $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedra are linked by sharing oxygen atoms to give ring structures, which, in turn, are linked to give an overall three-dimensional structure which contains regular channels and cavities (like honeycomb) of sizes similar to those of small to medium-sized molecules [4,5]. As such, they are ideal molecular sieves, and, in view of the AlO_4^- acid sites they contain, a high level of selectivity can be achieved in catalysis and ion-exchange. In many zeolites these frameworks are open, so cations and water molecules, contained in cavities and channels within the frameworks, have freedom of movement. The unique structure of channels, cavities and cages results in large internal surface available for a variety of reactions, and this surface controls most of the useful properties of zeolites.

The most widely used natural zeolite is clinoptilolite (Clin) due to its occurrence in many countries worldwide, its abundance and low cost. Clin has numerous uses and benefits in maintaining and improving the quality of air, water, solid waste and wastewater. Improving drinking water filtration rate when added to bed over traditional sand filters, softening of industrial and potable water, reducing NH_4^+ to potable water standards, catalysis of numerous reactions, adsorption of benzene, toluene and xylene from water and hydrocarbons; wastewater and sludge treatment; cleanup of nuclear waste, are a few examples [7,8].

In literature there are many published research works relative to the application of zeolites to soil remediation, however, the most of them concern laboratory experiments (mainly pots, batch and column experiments) or small scale applications. There is very little evidence in the literature to support the long-term use of natural zeolites in real remediation projects. Regardless the limited application of the research results, the conclusions are particularly important and they could potentially be applied in real scale. As zeolites tend to have a high CEC, they have been identified to be good candidates for the remediation of metals in soils and effluents. For example, Li et al. [9] studied the remediation of a garden soil from Pb by using a zeolitic tuff from China, which was consisted of clinoptilolite (34.93 wt%) and heulandites

* Corresponding author. Tel.: +30 210 2832031; fax: +30 210 2842129.
E-mail address: mdoula@otenet.gr (M.K. Doula).

(34.90 wt%). The zeolite was added to artificially polluted garden soil, while the immobilization of Pb and the reduction of its uptake by rape through changing soil physical and chemical properties in pot experiment under greenhouse conditions were investigated. Results indicated that the addition of natural zeolite could increase soil pH, cation exchange capacity (CEC), organic matter content and promote formation of soil aggregate. The authors concluded that the application of zeolite decreased the available fraction of Pb in the garden soil by adjusting soil pH to higher values than pH values with no zeolite addition, rather than CEC, and restrained Pb uptake by rape. Data obtained suggested that the application of 10 g zeolite kg^{-1} soil, or higher, was adequate to reduce soluble Pb significantly, even if Pd pollution is severe in garden soil ($\geq$1000 mg Pb kg^{-1} soil), while the addition of 20 g zeolite kg^{-1} soil, could reduce lead concentration in the edible part (shoots) of rape up to 30% in the seriously polluted soil (2000 mg Pb kg^{-1} soil). Similarly, Ponizovsky and Tsadilas [10] studied the effect of clinoptilolite presence as amendment in a sandy loam soil from Greece and concluded that 1% (w/w) zeolite addition could retain 750 mg Pb kg^{-1} soil. Moirou et al. [11] investigated the stabilization of Pb, Zn, and Cd by clinoptilolite. The contaminated area selected was a former lead–zinc mining district and the metal concentrations of the area were Pb (120–11,350 ppm), Zn (140–11,400 ppm) and Cd (18–1180 ppm). Batch experiments were conducted for one-month using pot experiments with varying soil–zeolite mixtures. US EPA leaching tests were followed for evaluation purposes, mainly TCLP, EPT test (extraction procedure toxicity) and SPLP (synthetic preparation leaching procedure). According to the TCLP procedures followed, moderate solubility reductions were observed for Pb 38%, Zn 33% and Cd 32%. The EPT test, however, showed a 55%, 74% and 46% reduction in Pb, Zn and Cd, respectively. The SPLP did not produce any measurable values for Pb, which was probably due to the use of inorganic acids and test pH value of 5. For Zn, the reduction in solubility was significant for all three leaching tests (74, 81 and 33% in the EPT, SPLP and TCLP tests respectively). In all three instances, a significant decrease was observed with a 10% zeolite addition. In the case of Cd, zeolite addition improved soil by immobilizing 32% and 46% of leachable Cd from the TCLP and EPT test results, respectively. In addition, the researchers conducted also column studies that showed that 50–60% of Pb was immobilized with the 20% (w/w) zeolite amendment.

Studies have been also carried to identify the role of clinoptilolite in organozeolitic–soil systems for phytoremediation. Leggo et al. [12] used composting crushed zeolitic tuff with animal waste (patented formula) as amendment to heavily contaminated soils. They succeeded to grow various plants that have a range of metal tolerance, from low tolerant grasses (*Triticum aestivum*, *Lolium perenne*) to highly metal tolerant species such as the Zn and Cd accumulator, *Arabidopsis halleri*, on contaminated land containing, in some cases, extreme concentrations of heavy metals (up to 9.2 wt% Pb, 6.8 wt% Zn, 0.5 wt% Cd). The researchers based on the results believe that, in many cases, crops such as oil seed rape, sunflower, willow, sugar beet etc., could be grown on contaminated land and used for such purposes as biofuel and lubrication fluid while, at the same time, cleaning the rhizosphere of toxic metals. Based on their findings, the authors supported that clinoptilolite provides a natural source of plant nutrients by greatly increasing the nitrifying bacterial population of the soil substrate without any toxic effect. By composting zeolitic tuff with animal manure, ammoniation of the zeolitic component occurs. When introduced into a moist soil environment, ammonium ions are back exchanged into the soil. The crystal surfaces becomes susceptible to biofilm formation which encloses and protects a population of microorganisms which remain fully functional in the most extreme conditions of metal pollution extending to weight percent con-

centrations. So, they suggested that organozeolitic–soil systems could be applied for re-vegetating land made barren by metal pollution.

Clinoptilolite could also be effective in radionuclides retention [13–15]. During the Chernobyl disaster, thirty to forty times the radioactivity of the atomic bombs dropped on Hirosihima and Nagasaki were released. The main radioactive isotopes from the Chernobyl accident were ^{137}Cs, [134]Cs, ^{90}Sr and [89]Sr. It is known that almost 500,000 tons of zeolite rocks, mainly containing clinoptilolite, were processed at various deposits in Ukraine, Georgia and Russia. It was recorded that the majority of the zeolite amounts was used for the construction of protective barriers and for agricultural application in polluted areas [16]. One of the famous research articles regarding the application of zeolites on soils polluted after the Chernobyl disaster is that of Chelishchev [16]. Regarding the use of zeolites, especially clinoptilolite, in affected areas in the former Soviet Union, the author mentioned that the soil-cleaning techniques used at Chernobyl included an industrial cleaning process for radioactive soil and local soil deactivation by electrodialyses. This was performed by the removal and industrial treatment of radioactive soil and by cleaning extracted solutions with clinoptilolite. An electrodialysis method using zeolite electrodes was employed to clean local strips of soil and to concentrate radionuclides from irrigation water on zeolite. Moreover, zeolite-rich soil was successfully used for vegetables growing in greenhouses while the addition of zeolitic tuff (containing about 60 wt% clinoptilolite) to soil (10–50 ton/ha) decreased the radionuclide content in plant tissue by a factor of 2–3 for ^{137}Cs and by 50–70% for [90]Sr.

Capping is another new option in remedial application of clinoptilolite in managing both contaminated sediments and dredged materials. Capping denotes the placement of a cover onto potentially hazardous sediments or dredged material dumps to inhibit the transfer of contaminants into the water column. Jacobs and Waite [17] studied the retention of divalent iron and manganese cations using sandy capping layers containing clinoptilolites of different origin as reactive additives (active barrier systems, ABS). Results from batch and column experiments revealed that ABS based on these materials can efficiently demobilize iron and manganese from percolating, anoxic pore water by cation exchange under favorable conditions. The retention, however, may be reduced strongly where competitive exchange with divalent cations such as calcium prevails or where mobile colloidal pore water constituents such as clay minerals or humic substances bind fractions of the dissolved iron or manganese.

An innovative approach in the use of clinoptilolite in environmental problems and, specifically, in soil remediation was developed and applied in the framework of a LIFE project entitled "*Strategies to improve and protect soil quality from the disposal of olive oil mills wastes in Mediterranean*", concerning the use of clinoptilolite as a soil additive in order to protect (and potentially improve) soil quality from the excess disposal of polyphenols and inorganic matter due to the uncontrolled disposal of olive oil mills wastes (OOMW).

The olive oil extraction industry represents an important activity in the Mediterranean area. Worldwide, Spain and Italy are the two leaders in olive oil production, whereas Greece holds the third place. For Mediterranean countries, the disposal of OOMW is considered a major environmental problem. In general, for each ton of olive oil production about 1600 kg of organic pollutants (dry basis) are produced while the polluting load related to the disposal of 1 m^3 of OOMW is equivalent to 100–200 m^3 of urban wastes (corresponding to the ones produced by 100,000 people). The annual olive oil mill wastewater production in Mediterranean countries is estimated to be over 3×10^7 m^3. OOMW is an aqueous,

dark (due to polyphenols content), foul-smelling and turbid liquid, which includes emulsified grease, is easily fermentable, has high organic content (40–165 g/l), low pH (4.5–6.0), high electrical conductivity (35,000–100,000 dS/m), high COD/BOD ratio (2.05–2.35) and high free polyphenol concentrations (3–24 g/l) due to olive pulp esters and glycoside hydrolysis, produced during oil extraction [18]. The uncontrolled disposal of OOMW on soil may cause several problems, such as strong phytotoxicity and antimicrobial effects, increased hydrophobicity, decreased water retention and infiltration rate [19], and it may also affect acidity, salinity, N immobilization, microbial activity, nutrient leaching, lipids concentration, organic acids and naturally occurred phenols content [20]. On the other hand, the remaining sludge after evaporation of the liquid part of the wastes contains almost 94% organic matter and although it could be highly beneficial to agricultural soil, it has been shown that it contains also toxic compounds and oil that may increase soil hydrophobicity and decrease water retention and infiltration rate if applied directly to soil [18]. Thus, soil properties are strongly affected by the direct disposal of OOMW on soil as well as, in unprotected evaporation ponds, which is a common management practice in Mediterranean. Soils loaded with OOMW are rich in organic matter, inorganic nutrients and polyphenols. Although organic matter and nutrients could be beneficial for soil fertility and necessary for plant growth, potential serious soil degradation should always be considered due to very high concentrations of inorganic elements and polyphenols, sometimes near or above thresholds. Moreover, the addition of the insufficiently stable organic matter of wastes, although it leads to a general increase in soil organic matter, may induce a number of negative effects on soil properties and plant growth, such as increase in mineralization rate of native organic carbon, induction of anaerobic conditions and release of phytotoxic substances that may have negative effects on plant growth [18].

As mentioned, the effectiveness of natural and synthetic zeolites as soil additives has been confirmed mainly for heavy metals retention, radionuclides adsorption, organic pollution reduction and improving soil prosperity and thus improving yield in agriculture. However, and in the field of OOMW problem, clinoptilolite has been studied for its catalytic properties and its contribution to polyphenols oxidation during OOMW treatment. For instance, Giordano et al. [21] studied the wet hydrogen peroxide catalytic oxidation on olive oil mill wastewaters using Fenton-like type catalysts (Cu-Clin-1 and Cu-pillared clay). Experiments revealed that both catalysts showed a high conversion in the oxidation of poly-phenols and were able to drastically reduce the chemical oxygen demand, the biochemical oxygen demand and the non-biodegradability of the olive oil mill wastewaters. After a re-calcination treatment, the zeolite was re-used for a second reaction cycle, and they showed good results.

Yet, the use of zeolites in improving and protecting soil quality from the disposal of OOMW (i.e. excess disposal of inorganic elements, other than heavy metals) has never been studied before and thus, this field is considered as highly innovative. In the present study, clinoptilolite was added at different percentages in soil samples collected from areas degraded due to disposal of OOMW, and its effectiveness in reducing inorganic elements leaching was studied through batch experiments.

2. Materials and methods

2.1. Clinoptilolite

The natural zeolite used in the present investigation was clinoptilolite, which comes from northern Greece. This material has been used for experiments by many researchers [5,22] and consequently its physicochemical properties are well known (Fig. 1 of supplementary data).

2.2. Implementation area—samples origin

Soil samples were collected from an area located in central Crete, Southern Greece (Figs. 2 and 3 of supplementary data). Geological formations of the area under study are mainly identified as limestones, dolomites and marbles. Soils are slightly alkaline to alkaline (pH between 7.3 and 8.0), rich in carbonates (up to 60%) and clay or silty clay in texture. In the framework of the project and in order to monitor soil quality, soil samples were collected from five OOMW disposal areas: three active for more than 10 years and two inactive for more than 6 years. All of them contain lagoons, which were built by excavating the superfacial materials of soil, and (for some of them) by heaping excavating materials around the lagoon to form low retaining walls (Fig. 4 of supplementary data). Protective impermeable membranes or other protective practices were not used. The disposed wastes derived from three-phase mills with continuous centrifuge extraction systems. More than 500 soil samples were collected from 46 spots in the area (Figs.3 and 5 of supplementary data) covering various depths from 0–25 cm up to 200–225 cm where possible. Sampling was conducted every two months for one year. Soil analysis was carried out using standard methodologies [23]. Particle size distribution was determined by using the Bouyoukos method [24]; pH and electrical conductivity were measured in the paste extract using pH/EC meter equipped with glass electrode; organic matter was determined by dichromate oxidation; carbonates by using Bernard calcimeter; total N by the Kjeldahl method (ISO 11261:1995); available phosphorous using sodium hydrogen carbonate extraction (ISO 11263:1994); exchangeable K, Ca and Mg using $BaCl_2$ extraction (ISO 11260:1994), while available Mn, Fe, Cu and Zn using DTPA extraction (ISO 14870:2001). Determination of water extractable NH_4^+, NO_3^-, Cl^-, PO_4^{3-}, and SO_4^{2-} was performed in 1:10 water extracts after 30 min shaking [25] using a Dionex-100 Ionic Chromatography. Soil B was extracted with boiling water using the azomethine-H method. Methanol extractable phenol compounds were quantified by means of the Folin–Ciocalteu colorimetric method [26].

From the collected soil samples, ten were selected for the experiments with clinoptilolite; eight from the active areas and two from one inactive area (Fig. 5 of the supplementary data shows the sites from where the ten soil samples were collected). Three of the selected samples were collected from the interior of disposal ponds (S2a and S2b from an inactive area and S3 from an active), while two samples were collected from clean areas and used as control samples (S5 and S8). The physicochemical properties of the samples are summarized in Table 1.

2.3. Batch experiments—use of clinoptilolite as soil additive

Samples of 10.0 g were prepared, in triplicate, by mixing soil samples and different percentage of Clin (0%, 2%, 5%, 7%, 10%, 20% and 30% w/w). 20.0 ml of deionized water was added to the samples and the mixtures were shaken for 24 h at room temperature (the sample-to-water ratio used was 2 l water kg^{-1} soil, as recommended in ISO 21268-1 [27]). After this period, the samples were centrifuged and the aqueous phase was analyzed for K, Ca, Mg, Na, Mn, Fe, Cu, Zn, polyphenols, NO_3^-, Cl^-, SO_4^{2-}, and PO_4^{3-}. The water extractable phenol compounds (total) were quantified by means of the Folin–Ciocalteu colorimetric method [26]; K, Ca, Mg, Fe, Cu, Zn and Mn were measured with a SpectrAA-220 Varian Flame Atomic Absorption Spectrometer and NO_3^-, Cl^-, SO_4^{2-}, and PO_4^{3-} by using ionic chromatography.

Table 1
Physicochemical properties of soil samples.

Parameter	S1a	S1b	S2a	S2b	S3	S4	S5	S6	S7	S8
Disposal area	A	A	I-P	I-P	A-P	A	A-S	A-S	A-S	A
Depth, cm	0–25	50–75	0–25	0–25	0.25	0–25	50–75	0–25	0–25	0–25
Texture	C/CL	C/CL	C	C	L	CL	CL	CL	CL	CL
pH	7.8	7.8	7.8	7.5	6.9	7.5	8.2	7.6	7.7	7.6
EC (mS/cm)	0.99	0.80	1.20	0.87	4.12	1.35	1.60	3.29	3.82	0.60
OM (%)	4.41	3.92	2.87	2.68	5.69	7.90	3.50	7.59	6.34	5.28
$CaCO_3$ (%)	17.6	9.70	10.5	7.60	37.8	14.3	71.4	15.5	24.4	17.2
Total N (mg/g)	3.7	2.8	2.3	3.7	8.4	5.4	1.1	5.1	5.7	3.0
P (mg/kg)	189	77	62	163	284	285	33	223	112	406
K^*, cmol/kg	4.4	5.8	8.2	8.8	17	8.6	3.9	12	11	0.63
Mg^* (cmol/kg)	1.2	1.4	2.8	3.1	2.0	3.3	1.3	4.1	4.1	2.8
Ca^* (cmol/kg)	40	35	35	47	37	31	15	45	43	51
$B^§$ (mg/kg)	1.7	1.1	0.2	2.2	1.9	3.7	0.9	0.7	0.4	0.5
Polyphenols (mg/kg)	84	104	58.2	61.5	197	147	31	148	48	19
Cl^- (mg/kg)	45	160	6.20	120	193	210	65	330	240	9.90
SO_4^{2-} (mg/kg)	175	1300	24.0	1100	27.5	1510	210	51.0	49.0	17.0
PO_4^{3-} (mg/kg)	35	15	2.90	25	110	105	10.0	15.0	12.0	1.10
NO_3^- (mg/kg)	15.0	80.0	59.0	10.0	<1.00	10.0	20.0	615	400	51.0

*Exchangeable; §water extractable; Disposal area: A – active; I – inactive; P – pond soil; S – surface disposal.

3. Results and discussion

The general conclusion from the evaluation of the soil analysis results of all the collected soil samples during the lifetime of the project (i.e. 500 samples), was that the most of the soil properties were affected by the direct or the indirect disposal of OOMW [18,28]. In particular, soil samples collected from waste disposal areas were characterized by increased electrical conductivity (EC), increased organic load, high content of total nitrogen, available P, water soluble Cl^-, PO_4^{3-} and SO_4^{2-}, exchangeable K, and DTPA-extractable metals (Cu, Fe, Mn, Zn). Moreover, it was observed that for the inactive OOMW disposal areas, residual levels of total phenols, P, K, SO_4^{2-}, Cl^-, B, Cu, Mn, Fe and Zn in surface soil were still noticeable [18,28].

The periodical soil sampling at the wastes disposal areas in the pilot area revealed that the K-content was for most soil samples extremely high and thus, incidents of phytotoxicity may be anticipated. High levels of exchangeable K were found also in inactive pond soils, especially in the upper soil layers (0–25 and 25–50 cm), being 13–18 times higher than the control samples. Thus, potassium concentration is an issue of concern as far as potential soil degradation is concerned. According to literature, although the research concerning the fate of potassium under waste application is limited [29], disposal of waste rich in K on soil with low content of selective adsorbing minerals will create very high K concentrations in solution with potential effects on soil structure and K mobility. As the results of the present study revealed, the addition of Clin in soil samples decreased the leached K concentrations significantly (Fig. 1). The reduction was very high and ranged from 8%, for the lowest zeolite percentage, up to 97% for the highest. Initial loading affects the released K amounts, i.e. the samples with the higher K concentration (S2a, S2b, S4, S6 and S7) released the higher K amounts and the retention of K by Clinoptilolite was more effective. On the contrary, the blank sample (i.e. S8) for which the initial K loading was only 0.63 cmol/kg released the minimum K concentration and the addition of zeolite did not seem to affect the process.

Regarding Ca and Mg leaching (Figs. 2 and 3), it was observed that the addition of zeolite did not affect their leaching significantly, although a slight decrease in leached Ca concentration was observed. Moreover, the leached Ca concentrations were significantly lower than the soils' initial concentrations (Table 1) and thus, Ca leaching is not considered as a potential risk factor for the studied soil types. This result is also significant, same as for potassium leaching, since, as it was revealed after the evaluation of the

chemical analysis results for all the samples collected from the disposal areas, Ca poses not significant problem for soil quality and its concentration was not significantly affected by the waste disposal [18,28]. Thus, the addition of zeolite does not disturb Ca presence in soil and this is also a very satisfactory result. One should, however, consider, that these results are representative for this specific type of soil samples; i.e. samples with high clay content, rich in $CaCO_3$ and Ca and thus high pH values, meaning that Ca could potentially be an issue of concern for light textured soils with adequate Ca supply and lower pH. Mg remained almost unaffected by the presence of zeolite and a slight increase in leached concentration was observed for some of the soil samples (Fig. 3). However, the conclusion of the study of all the soil samples collected from the study area [18,28] was that Mg concentration is positively affected by the disposal and high concentrations were found mainly in pond soils and in soils that accept wastes by surface disposal. In this case, although Clin, is theoretically capable of retaining Mg^{2+}, the very high K^+ retention inhibits the retention of Mg or favors the exchange between solution K^+ and solid-phase exchangeable Mg^{2+}. Initial Mg concentrations affected the amounts of Mg leached, as presented in Fig. 3, and the soils that have high Mg concentration (i.e. S2b, S4, S6 and S7) released larger Mg amounts.

Regarding anions leaching (Figs. 4–6), the presence of Clin in soil samples incurred different effects. The general observation is that Clin reduces anion leachability or retains it almost constant. In specific, however, this effect seems to be dependent on (1) anion content of the soil samples and (2) on the overall extent of soil quality/degradation, since soils that contain high concentration of Cl^-, NO_3^- and SO_4^{2-} (S1a, S1b, S2b, S4, S6, S7) were affected more from the presence of Clin, and anions leaching seems to be reduced, while soils that were less affected by the wastes disposal were not affected by the addition of Clin. The decrease in Cl^- concentration in the leachate could reach almost 50%, same as for NO_3^- (although there were samples with 10% and 90% nitrate reduction), while SO_4^{2-} leaching reduction does not exceed 50% and the majority of samples seem to be unaffected by the presence of Clin. From the obtained data, it is obvious that Clin is more selective for NO_3^-, while the selectivity order is $NO_3^- > Cl^- > SO_4^{2-}$ which, however, should not be considered as a general property but as an indicative behavior, specific for the present experiment. Nevertheless, according to literature, Clin is capable of sorbing Cl^- and NO_3^- ions while it is less selective for SO_4^{2-} ions [30]. Initial anion loading of soils affected only Cl^- leaching and the samples with the highest Cl^- content (i.e. S4, S6, S7) released also the highest Cl^- concentrations. For these samples the effect of zeolite was also higher.
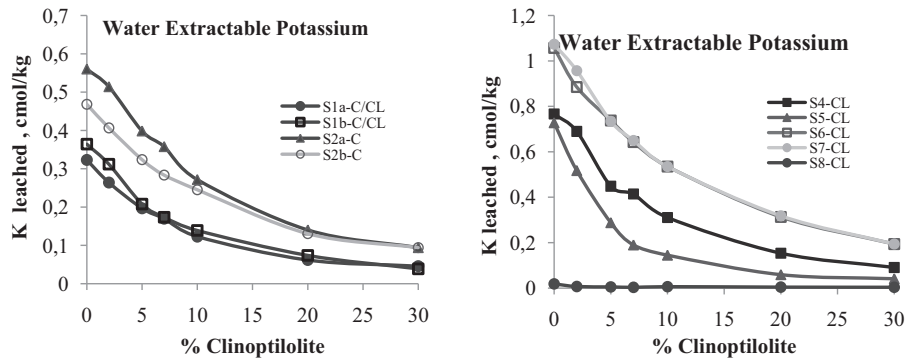
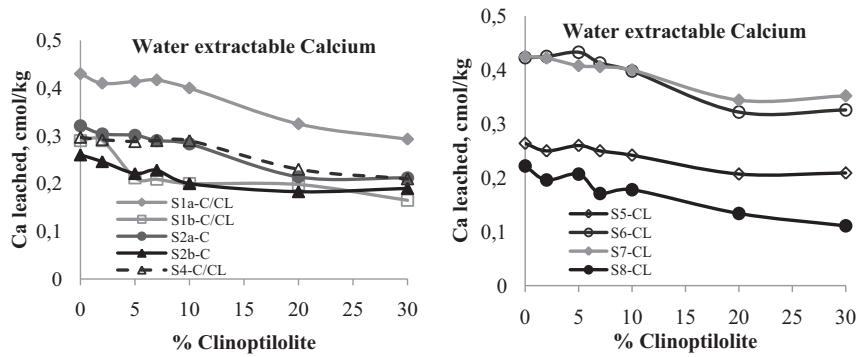**Fig. 1.** Water extractable K as a function of clinoptilolite percentage in the soil samples.

Fig. 2. Water extractable Ca as a function of clinoptilolite percentage in the soil samples.
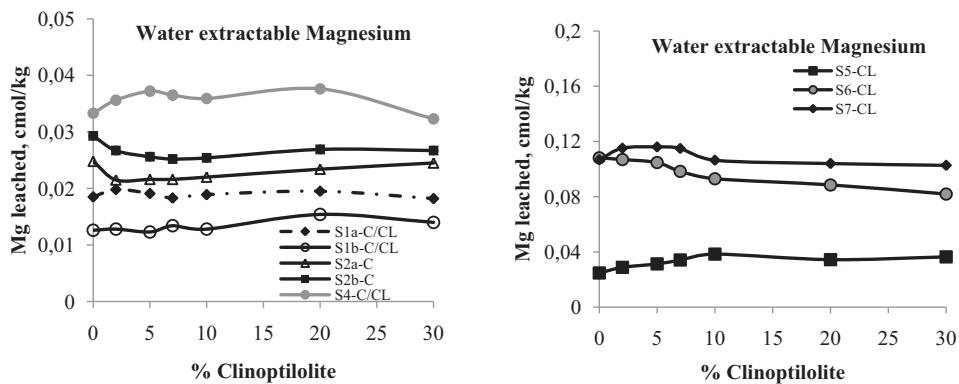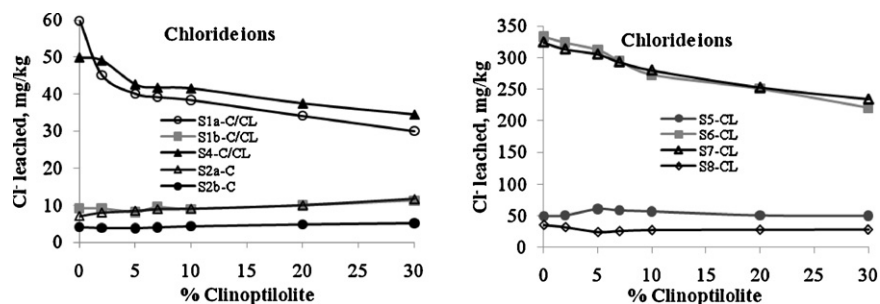

Fig. 3. Water extractable Mg as a function of clinoptilolite percentage in the soil samples.

It is also significant to highlight that the released anion concentrations after the batch experiments were significantly higher (for the most of the cases), than the measured initial soil concentrations. This is because the time during which the soil is in contact with the extractant (30 min for initial concentration determination and 24 h for the batch experiments) affects the leachability of the anions. Thus, no comparison between these two values should be attempted.

Fig. 4. Water extractable Cl⁻ as a function of clinoptilolite percentage in the soil samples.
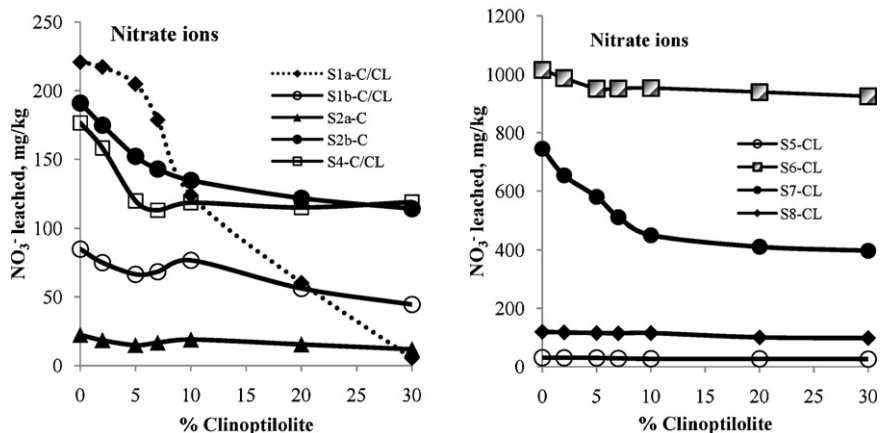
Fig. 5. Water extractable NO_3^- as a function of clinoptilolite percentage in the soil samples.
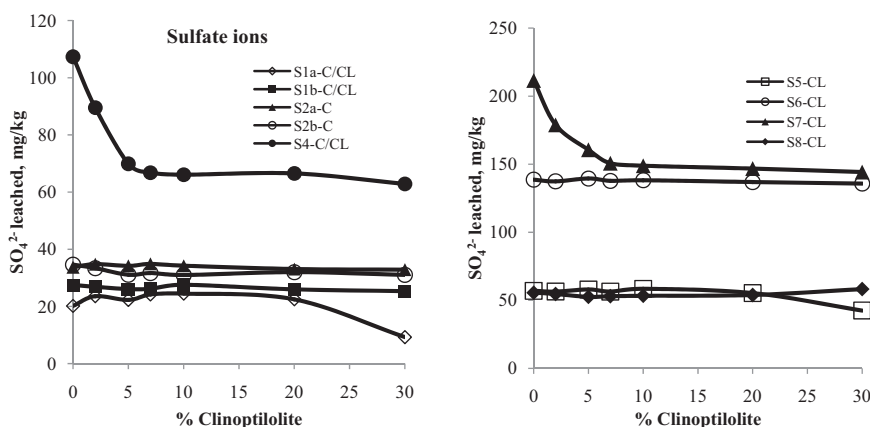

Fig. 6. Water extractable SO_4^{2-} as a function of clinoptilolite percentage in the soil samples.

In general, the concentration of leached phenols (Fig. 7) was higher for soils with high initial loading. The leached amounts were decreased, but, again, not at the same extent for all the tested samples. The maximum decrease recorded was almost 50% and the lowest no more than 10%.

Soil samples collected from inside the evaporation ponds were very degraded systems, which are characterized by high values of all parameters. A pond soil sample (S3) collected from

Fig. 7. Water extractable polyphenols as a function of clinoptilolite percentage in the soil samples.

an active disposal area was also used during experimentations and the results revealed that the presence of Clin significantly improved its chemical parameters, as far as the inorganic components and the polyphenols are concerned. Fig. 8 presents the changes caused to the concentrations of leached components as a function of Clin percentage in this soil sample. As it can be seen in Fig. 8, potassium was significantly decreased with the increase in Clin percentage. The reduction of K leaching ranged between 15% and 90% compared to the leaching with no Clin addition.

Leached polyphenols were also decreased and for the highest Clin percentage this reduction reached almost 60%. Reduction in leached concentrations was also recorded for nitrates, chlorides and sulfates. Increased leaching was observed for Ca and Mg; for Ca, the increase reached almost 17% while for Mg nearly 50%. The explanation derives from the extent to which K retention took placed for this soil sample (due to K very high concentration) as well as, the high selectivity of Clin for K.

Pond soils were found to be overloaded with K, Ca and Mg and since the cation retention mechanism on clinoptilolite involves mainly ion exchange and adsorption, the very high uptake of K inhibit the adsorption of Ca and Mg from the solid phase. Moreover, Ca and Mg cations, which are already present in the zeolite specimen, as these cations play a charge balancing role in the framework of its mineral constituents, are forced from the high concentration of K ions to leave their sites on clinoptilolite and enter soil solution.

For all soil samples, the concentrations of Cu, Mn, Fe and Zn in leachates were not detectable while PO_4^{3-} ions concentrations were very low.
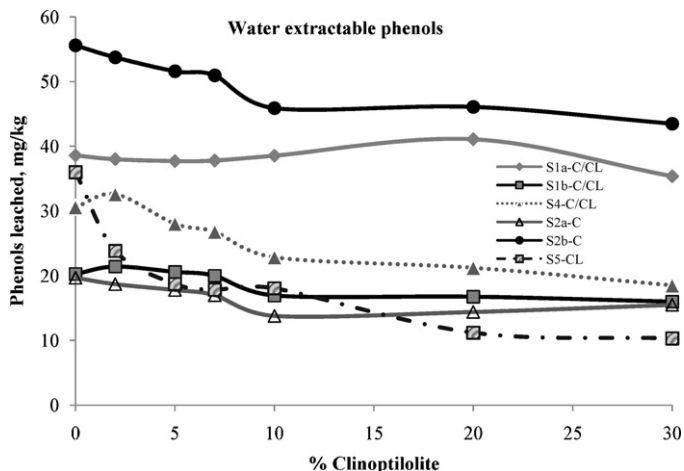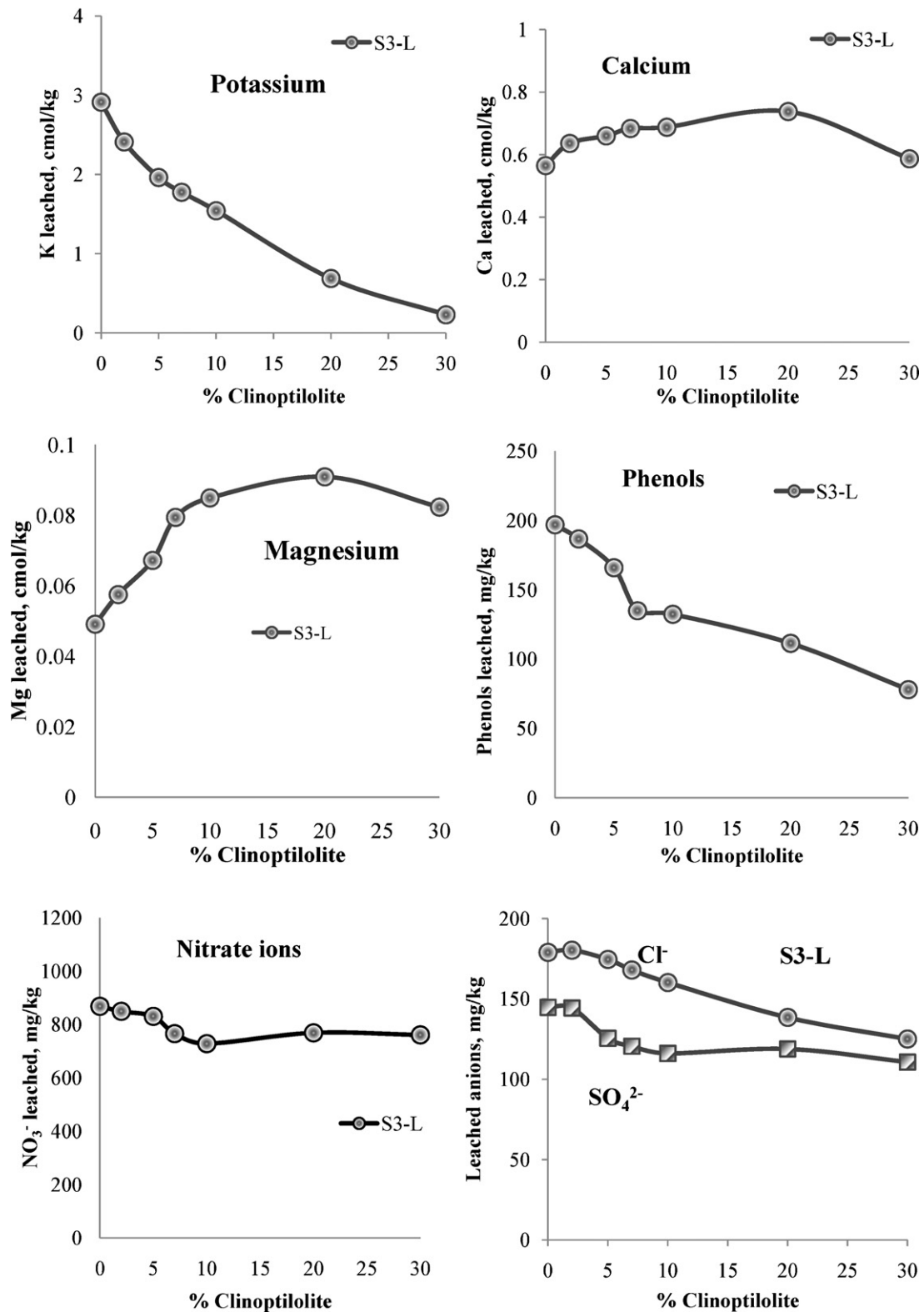
Fig. 8. Water extractable K, Ca, Mg, polyphenols, NO_3^-, SO_4^{2-} and Cl^- as a function of clinoptilolite percentage in the soil sample taken from the interior of a disposal pond.

The use of clinoptilolite as soil amendment to improve soil quality from the disposal of wastes is an easy, environment friendly and also cost effective technique that can be easily applied while it requires no specific machinery and non-skilled personnel. Considering that 1 ton of clinoptilolite costs almost 160€ or 220$, its application at a percentage of 5% for the upper 25 cm of an area of 1 ha costs nearly 26,000–30,000€ (or 36,000–41,000$). The cost includes nearly 21,000€ for zeolite (for 5% almost 130 ton are needed) and the cost for a small tillage machine to work for land configuration and application of zeolite. However, it should be also considered that an area of 1 ha is very large since usually the OOMW disposal areas are not larger than 0.1–0.2 ha.

The addition of clinoptilolite as soil amendment is a technique that has been used in the past for soil remediation, mainly from heavy metals. Although effective, this method does not permit the separation of zeolite after the treatment for its regeneration and thus, re-use. Once the zeolite is mixed with soil then the mixture's constituents cannot be separated. However this is not a disadvantage of the technique, since zeolites have the ability to participate in the natural ion-exchange processes and thus continuously retain and release elements and thus adjust the elements concentration in soil solution and in solid phase depending on their concentration. However, if a soil amended with zeolite accepts continuously waste disposal, the zeolite may progressively lose its ability to retain elements due to saturation. For such cases, it could be proposed that the use of zeolite as amendment would be more effective in combination with vegetation, to assist the uptake of elements and thus to prolong the effectiveness of zeolite.

4. Conclusions

As far as the samples' origin and soil types used for the experiments are concerned, the addition of clinoptilolite in soils, which were affected by the disposal of OOMW, seems to be beneficial and may contribute to overall balance of soil inorganic constituents. Use of Clin as soil additive may result in significant inhibition of excess K leaching, as well as in retention of excess quantities of polyphenols, nitrates, sulfates and chlorides. The release of Ca was reduced or maintained almost constant, while Mg release was hardly affected. For heavily degraded soils, increased leaching of Ca and Mg was recorded with the increase in Clin percentage in soils while, the reduction in K, polyphenols, Cl^- and SO_4^{2-} leaching was significant.

Although more data will allow a more accurate evaluation of the properties of soils treated with clinoptilolite, current data indicates that the use of clinoptilolite in soils affected by olive oil mills wastes could be a cost-effective and socially acceptable soil protective/remediation practice.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.04.014.

References

[1] S. Ouki, M. Kavannagh, Performance of natural zeolites for the treatment of mixed metal-contaminated effluents, Waste Manage. Res. 15 (1997) 383–394.
[2] M.I. Panayotova, Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite, Waste Manage. 21 (2001) 671–676.
[3] J. Perić, M. Trgo, V. Medvidović, Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms, Water Res. 38 (2004) 1893–1899.
[4] M.K Doula, Removal of Mn^{2+} ions from drinking water by using clinoptilolite and a clinoptilolite–Fe oxide system, Water Res. 40 (2006) 3167–3176.
[5] M.K. Doula, Synthesis of a clinoptilolite–Fe system with high Cu sorption capacity, Chemosphere 67 (2007) 731–740.
[6] M.E. Argun, Use of clinoptilolite for the removal of nickel ions from water: kinetics and thermodynamics, J. Hazard. Mater. 150 (2008) 587–595.
[7] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.
[8] E. Alvarez-Ayuso, A. Garcia-Sanchez, X. Querol, Purification of metal electro-plating wastewaters using zeolites, Water Res. 37 (2003) 4855–4862.
[9] H. Li, W. Shi, H. Shao, M. Shao, The remediation of the lead-polluted garden soil by natural zeolite, J. Hazard. Mater. 169 (2009) 1106–1111.
[10] A.A. Ponizovsky, C.D. Tsadilas, Lead (II) retention by alfisol and clinoptilolite: cation balance and pH effect, Geoderma 5 (2003) 303–312.
[11] A. Moirou, A. Xenidi, A. Paspaliaris, Stabilization of Pb Zn, and Cd-contaminated soils by means of natural zeolite, Soil Sediment Contam. 10 (2001) 251–267.
[12] P.J. Leggo, B. Ledesert, G. Christie, The role of clinoptilolite in organo-zeolitic–soil systems used for phytoremediation, Sci. Total Environ. 363 (2006) 1–10.
[13] M. Fuhrman, D. Aloysius, H. Zhou, Permeable, subsurface sorbent barrier for ^{90}Sr: laboratory studies of natural and synthetic materials, Waste Manage. 15 (1995) 485–493.
[14] P. Misaelides, A. Godelitsas, A. Filippidis, D. Charistos, I. Anousis, Thorium and uranium uptake by natural zeolitic minerals, Sci. Total Environ. 173 (174) (1995) 237–246.
[15] S. Akyil, M.A.A. Aslani, S.O. Aytas, Distribution of uranium on zeolite X and investigation of the thermodynamic parameters of this system, J. Alloys Compd. 271/273 (1998) 769–773.
[16] N.F. Chelishchev, Use of natural zeolites at Chernobyl, in: D.W. Ming, F.A. Mumpton (Eds.), Natural Zeolites' 93: Occurrence, Properties Use, Int. Comm. Natural Zeolites, Brockport, N.Y., 1995, pp. 525–532.
[17] P.H. Jacobs, T.D. Waite, The role of aqueous iron(II) and manganese(II) in sub-aqueous active barrier systems containing natural clinoptilolite, Chemosphere 54 (2004) 313–324.
[18] V. Kavvadias, M.K. Doula, K. Komnitsas, N. Liakopoulou, Disposal of olive oil mill wastes in evaporation ponds: effects on soil properties, J. Hazard. Mater. 182 (2010) 144–155.
[19] M. Abu-Zreig, M. Al-Widyan, Influence of olive mills solid waste on soil hydraulic properties, Commun. Soil Sci. Plant Anal. 33 (2002) 505–517.
[20] J. Sierra, E. Martí, A.M. Garau, R. Cruãnas, Effects of the agronomic use of olive oil mill wastewater: field experiment, Sci. Total Environ. 378 (2007) 90–94.
[21] G. Giordano, S. Perathoner, G. Centi, S. De Rosa, T. Granato, A. Katovic, A. Siciliano, A. Tagarelli, F. Tripicchio, Wet hydrogen peroxide catalytic oxidation of olive oil mill wastewaters using Cu-zeolite and Cu-pillared clay catalysts, Catal. Today 124 (2007) 240–246.
[22] V.J. Inglezakis, A.A. Zorpas, M.D. Loizidou, H.P. Grigoropoulou, Simultaneous removal of metals Cu^{2+}, Fe^{3+}, and Cr^{3+} with anions SO_4^{2-} and HPO_4^{2-} using clinoptilolite, Microporous Mesoporous Mater. 61 (2003) 167–171.
[23] A.L. Page, R.H. Miller, D.R. Keeney (Eds.), Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, American Society of Agronomy, Madison, Wisconsin, 1982.
[24] G.J. Bouyoucos, Hydrometer method improved for making particle and size analysis of soils, Agron. J. 54 (1962) 464–465.
[25] D.R. Keeney, D.W. Nelson, Nitrogen-inorganic forms, in: A.L. Page, R.H. Miller, D.R. Keeney (Eds.), Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties, American Society of Agronomy, Madison Wisconsin, 1982, pp. 643–698.
[26] J.D. Box, Investigation of the Folin–Ciocalteu phenol reagent for the determination of polyphenolic substances in natural waters, Water Res. 17 (1983) 511–525.
[27] ISO 21268-1, Soil quality-leaching procedures for subsequent chemical and ecotoxicological testing of soil and soil materials—Part 1: batch test using a liquid to solid ratio of 2l/kg dry matter.
[28] M. Doula, V. Kavvadias, S. Theocharopoulos, P. Kouloumbis, D. Oikonomou, D. Arapoglou, Environmental impacts relative to soil quality caused from the disposal of olive oil mills' wastes. Case study: a municipality in Crete, Greece, in: Proceedings of 3rd AMIREG International Conference: Assessing the Footprint of Resource Utilization and Hazardous Waste Manage, Athens, Greece, 2009, pp. 84–89.
[29] M. Arienzo, E.W. Christen, W. Quayle, A. Kumar, A review of the fate of potassium in the soil–plant system after land application of wastewaters, J. Hazard. Mater. 164 (2009) 415–422.
[30] M. Doula, A. Ioannou, The effect of electrolyte anion on Cu adsorption–desorption by Clinoptilolite, Microporous Mesoporous Mater. 58 (2003) 115–130.