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The use of steelmaking slag for sewage sludge stabilization

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ABSTRACT

The objective of this work was the examination of the stabilization of sewage sludge by the addition of a steel slag (slag), and the investigation of the effect of stabilization time on the properties of the produced mixtures. The used slag was a by-product from steelmaking refining processes in ladle furnaces, the steelmaking slag that presented high calcium content. Four samples were prepared by mixing the slag and sewage sludge in various ratios (2.5–20% on a dry basis) and the mixtures were stabilized for a period of 48 d. Monitoring of the mixtures properties was carried out for the determination of the pH, the moisture content, the pathogens removal rate and the mineralogical phases present. The addition of slag resulted in the increase of mixture pH exceeding 12, the increase of total solids content and the reduction of volatile percentage; these effects were more pronounced at the highest slag dosage. In addition, effective pathogens removal was observed in mixtures containing more than 10% slag, from the early time of mixing, due to the high pH values of the mixtures. It was concluded that this method might have a high potential for the efficient management of two solid waste streams.

Keywords: Sewage sludge; Slag; Stabilization; Solid waste management

1. Introduction

The efficient sewage sludge management is a key objective during the development of an integrated strategy for wastewater management. The beneficial use of sludge produced from municipal wastewater treatment units is a complex challenge for governmental and private organizations. Sewage sludge has been utilized for agriculture and horticulture for several years and represents a good source of nutrients for plant growth and soil conditioner to improve soil physical properties. Sewage sludge is a useful source of organic matter and also a pool of slow-release of essential nutrients (nitrogen, phosphorus, sulphur and magnesium) and micro-organisms [1–3]. This approach becomes very important especially when sludge land application is based on the appropriate conditions of the site in question, and when sludge is produced by small or medium treatment plants, given its lower contents of pollutants and probably the treatment plant is

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close to the disposal site [4]. As a result, in European Union more than one-third of the total sludge produced is recycled in farms [5]. However, sewage sludge may contain pathogenic organisms and pollutants, a range of toxic metals and high amounts of soluble salts, which may affect soil properties.

Composting followed by land application represents one of the most economical ways for the treatment and final disposal of sewage sludge because it combines material recycling and sludge disposal at the same time [6]. Unfortunately, the presence of high levels of heavy metals often hinders agricultural land application of the composted sludge. The total heavy metal content in sewage sludge is about 0.5–2% on a dry weight basis and in some cases, it may reach to about 4% [7]. Uptake of heavy metals by plants and subsequent accumulation along the food chain represent a potential threat to animal and human health. Government agencies in both the US and EU have issued regulations on the land application of sewage sludge, seeking to limit the risks from the pathogens and pollutants [8,9]. Despite these regulations, public opposition to sewage sludge land application is growing, and wastewater treatment facilities face increasing difficulty in sewage sludge management options. This is particularly important as the amount of sewage is projected to significantly increase over the next few years due to a growing population, more treatment plants transforming to full secondary treatment and requirements for higher levels of treatment that go beyond that of secondary treatment [10]. At the same time, regulations on sludge stabilization methods are revised and become more complex and stringent, hence putting more pressure on wastewater treatment plants to ensure compliance [9].

As a result, the improvement of the composting process to minimize the mobility of heavy metals using various additives is receiving great attention, in addition great interest is paid towards sludge stabilization for pathogens and odour potential reduction [6,11,12]. In the revised Sewage Sludge Directive 86/278/EEC, one of the alternative methods for sludge hygienization is chemical stabilization with lime at a pH value equal or above 12 for 3 months [9]. Lime is able to maintain high pH values of the mixtures throughout time, resulting in the removal of microbial communities in sludge; changes in pH values may imply consequent changes in metal bioavailability [13]. However, the application of lime for the stabilization of sewage sludge depends on a number of parameters such as the availability of lime with appropriate properties, the associated costs, the required period of stabilization, etc.; thus, alternative materials other than lime should be considered for sludge stabilization. Efforts are given to the examination of alternative materials, which are produced as residues from various industrial processes, and are considered as solid wastes; fly ash from thermal power plants has been already thoroughly studied for its beneficial properties for sludge hygienization [14,15].

An alternative alkaline agent is the slag produced during steelmaking which contains calcium [16] and thus a noticeable pH buffering potential.

The aims of this work were the investigation of the potential of steelmaking slag application for the stabilization of sewage sludge, the comparison to the more conventional method of lime treatment and the study of the effect of component ratios and experimental conditions on the process efficiency.

2. Experimental

Sewage sludge samples were collected from the sewage treatment plant of Thessaloniki, in Northern Greece. In this plant, excess sludge is treated by thickening, anaerobic digestion and dehydration in a filter press. The raw materials were transferred to the laboratory and were used for the preparation of the sludge–alkaline medium mixtures. Slag as fine powder was collected from a steelmaking plant in Northern Greece. Five different sample mixtures were prepared in amounts of about 20 kg, by mixing the appropriate quantities of raw materials in various ratios:

(1) Activated sludge: control sample without addition of alkaline media (designated as sample 0);
(2) Activated sludge: with 2.5% steelmaking slag on a dry matter (sample 1);
(3) Activated sludge: with 5.0% steelmaking slag on a dry matter (sample 2);
(4) Activated sludge: with 10.0% steelmaking slag on a dry matter (sample 3);
(5) Activated sludge: with 20.0% steelmaking slag on a dry matter (sample 4); and
(6) Activated sludge: with 5.0% steelmaking slag and 5.0% lime on a dry matter (sample 5).

The samples were stored outdoors in an enclosed structure, simulating the natural environmental conditions. Small amounts were withdrawn from each sample and were analysed for the determination of pH, conductivity, moisture content and concentration of total and volatile solids. The analysis of physical parameters was made according to standard methods of analysis [17]. In addition, microbiological analysis was performed for the determination of the following parameters: total viable count or total number of mesophile bacteria (SAM), total coliforms, *E. coli*, enteric coliform bacteria (feacal coliforms) and presence/absence of *Salmonella* spp., according to standard methods of analysis [17].

The elemental microanalysis was carried out by energy dispersive X-ray analysis system, Bruker AXS and Quantax 200 (Bruker AXS, Madison, WI) with an X Flash Detector 4010 (129 eV), under the same operational parameters as for imaging. The detected elements were measured both qualitatively and quantitatively.

The crystalline structure of the samples was investigated by X-ray diffraction (XRD) measurements using a Panalytical X'Pert Pro MPD (Panalytical, Almelo, The Netherlands) powder diffractometer with Cu Ka radiation ($\lambda = 0.154$ nm) at 45 kV and 40 mA. The scanning area of 2θ was 15°–120° and the scan speed was 0.10°/s, the step size was 0.10° and the time/step was 1.00 s/°.

3. Results and discussion

The addition of an alkaline agent in sewage sludge is expected to contribute to its stabilization through the increase of pH towards highly alkaline values (>11), which results in the destruction of pathogens and the immobilization of metal content. Nevertheless, the addition of lower moisture material into the sewage sludge will decrease the overall moisture content of the mixture and increase the respective concentration of solids. Furthermore, the calcium cations may react with sulphur containing substances in the sludge, resulting simultaneously in the reduction of odour forming compounds. High calcium solubility was observed during standard TCLP runs carried out on slag sample, reaching up to 120 g/kg of solid.

The steelmaking slag used in this work represents a high calcium steel slag with the following typical composition, on a dry basis (w/w): CaO 60.2%; SiO_2 20.45%; MgO 5.1%; Al_2O_3 3.4%; MnO 2.27%; iron oxides 8.5%.

The variation of pH, total solids, total volatile solids and moisture content for the various mixtures as a function of stabilization period, are presented in Figs. 1–4, respectively. The raw sewage sludge presented high moisture content, reaching up to 83% and pH values in the neutral range.

As shown in Fig. 1, the pH values of alkaline–sewage sludge mixtures are higher than the corresponding values of raw sludge sample, throughout the whole examined period of 48 d. The highest pH values, exceeding 12, were measured for the samples with the highest content of the alkaline medium, i.e. for

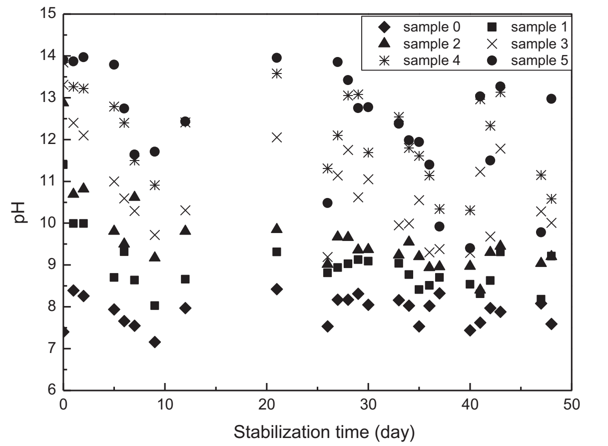

Fig. 1. The effect of stabilization time on pH values of alkaline medium–sewage sludge mixtures.

samples containing 10 and 20% slag, and for sample containing both lime and slag. Lower pH values, ranging from 7.5 to 11, were measured for the samples with the lower content of steel slag. In addition, the pH values presented slight reduction with the stabilization time for all the samples, possibly due to the reaction of calcium ions with atmospheric carbon dioxide.

Dewatering of the sludge is an important issue in sludge treatment and management, since removal of the water content may decrease the total volume of sludge; additionally the concentration of total solids, especially the volatile solids content, represents an indication of the concentration of micro-organism in the sludge and the potential for odour nuisance during sludge application. Thus, the measurement of total dissolved solids and volatile solids is essential for the assessment of the efficiency of the stabilization process. As shown in Fig. 2, the moisture content reduced by the time to values as low as 30%, and the corresponding total solids concentration increased reaching up to 70%. The increase of solids content was attributed mainly to the addition of alkaline agents, and the formation of calcium carbonate, through the atmospheric carbon dioxide.

The total volatile solids content (as percentage of total solids) is presented in Fig. 3 as a function of ageing time. Volatiles ranged between 30 and 70% of the total solids, while the highest value, about 77%, was observed for the sample 0 (control sample). The lowest solids volatile content was observed in the mixtures with the highest alkaline medium. The reduction of volatile content might be attributed to the increase of inert material, due to the addition of alkaline agents, to the deactivation of microbial load, caused by the

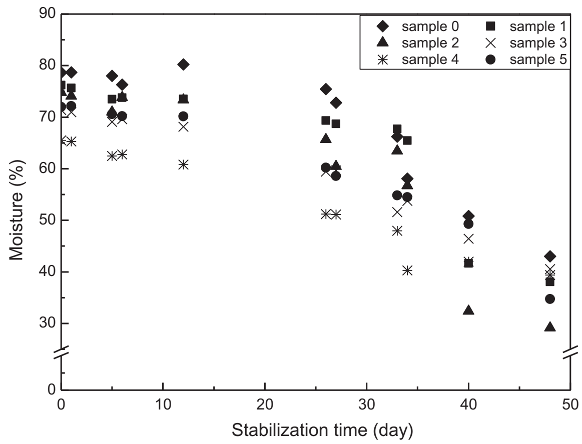

Fig. 2. The effect of stabilization time on moisture content of alkaline medium–sewage sludge mixtures.

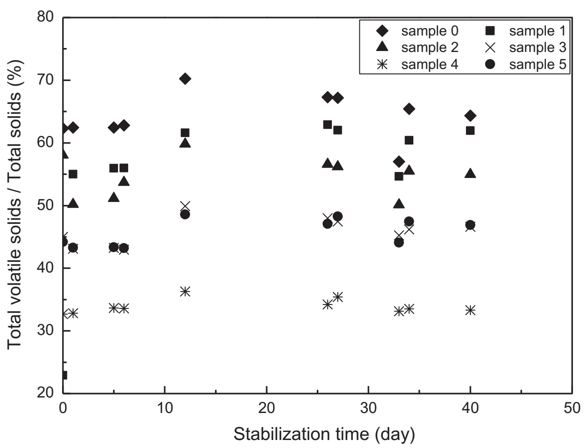

Fig. 3. The effect of stabilization time on the volatile solids content of alkaline medium–sewage sludge mixtures.

high alkaline pH values and to the stabilization reactions of steel slag with the sludge compounds resulting to the entrapment of the corresponding substances into the cement-like structures formed during the ageing period.

The effect on the microbiological content of mixtures due to the addition of alkaline medium to sewage sludge, in terms of concentration of total coliforms is shown in Fig. 4 as a function of stabilization time. Raw sewage sludge exhibited the highest microbial loading, as shown in Fig. 4; the addition of the alkaline agents resulted in the destruction of pathogens. The most efficient mean for microbes' removal was slag at the highest dosages. In general, the higher the slag content, the higher the pathogens removal rate and the lower the required time for stabilization; the sample prepared by the addition of 20% of slag

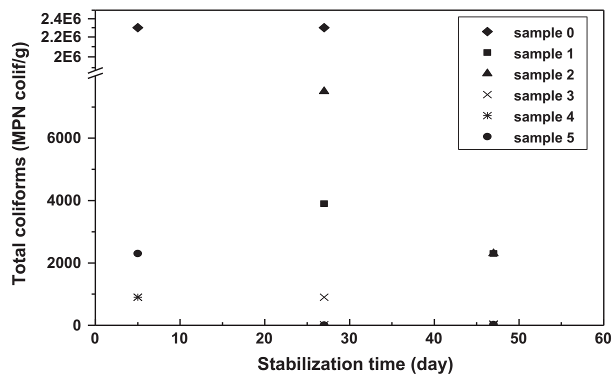

Fig. 4. The effect of stabilization time on *Total Coliforms* content of alkaline medium–sewage sludge mixtures.

presented negligible microbial content almost from the early days of stabilization. However, lower rates of stabilization were measured in the sludge mixtures containing slag in dosages lower than 5%; nevertheless, extended reaction times resulted in the efficient removal of pathogens even for the samples with a low slag content. Similar to the Total coliforms results, were the corresponding observations for *E. coli* and feacal coliforms. In addition, although the presence of *Salmonella* spp. was identified in the raw sludge sample, it was not observed in the stabilized mixtures prepared by the addition of slag at high dosages; however, slag addition at low dosages resulted in mixtures with presence of *Salmonella* spp., which was not observed at extended reaction times (up to week).

The microanalysis of the chemical elements such as calcium, (as percentage of total solids) is presented in Fig. 5 as a function of stabilization time. The main component of the alkaline medium was calcium, therefore the addition of slag for activated sludge stabilization, resulted in a high calcium content of the mixtures. As shown in Fig. 5, the calcium content in the examined samples, increased. Calcium content in the samples varied from 7 to 25%, while the corresponding value for the raw sludge did not exceed 5%. Furthermore, calcium content was not affected by the stabilization time.

The study of the crystalline structure of sample mixtures at various stabilization times has been carried out by XRD analysis in order to identify potential crystalline structures formed during the ageing process. The XRD pattern of raw materials i.e. sewage sludge, slag and lime are shown in Fig. 6. As shown, raw sludge exhibited lower crystallinity than steelmaking slag and lime. The XRD patterns of raw sludge and mixtures are shown in Fig. 7(a) and (b), for stabilization time 0 and 48 d, respectively.

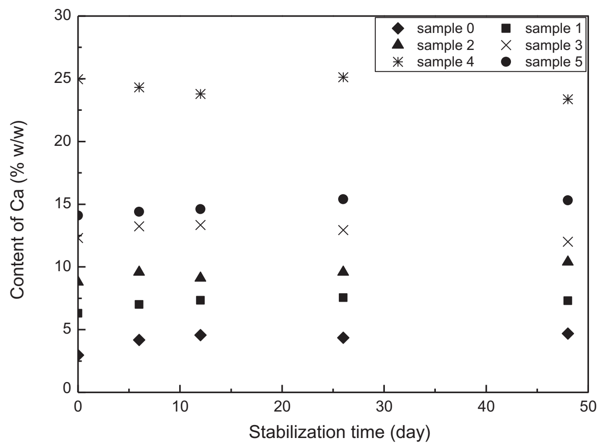

Fig. 5. Effect of stabilization time on calcium content of slag–sewage sludge mixtures.

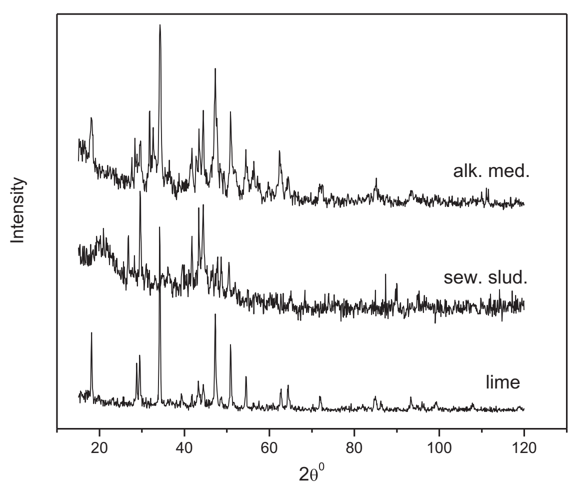

Fig. 6. XRD patterns of alkaline medium, sewage sludge and lime.

In addition, it seems that stabilization time did not significantly affect the crystalline structure, as XRD patterns were similar for mixtures produced at 0 and 48 d of ageing.

Overall, it was observed that a by-product from steelmaking process, the steelmaking slag, could be used as an efficient alkaline medium, for the stabilization of sewage sludge. High dosages of slag, up to 20%, were able to produce a mixture with a high pH, and a low content of volatiles, moisture and pathogens; the higher the slag dose the shorter the required time for stabilization. As a result, the proposed method could be used for the stabilization of sludge, taking into consideration that its implementation might have an additional benefit: the exploitation of two materials, sludge and slag, which are today considered as solid wastes, that are produced in large

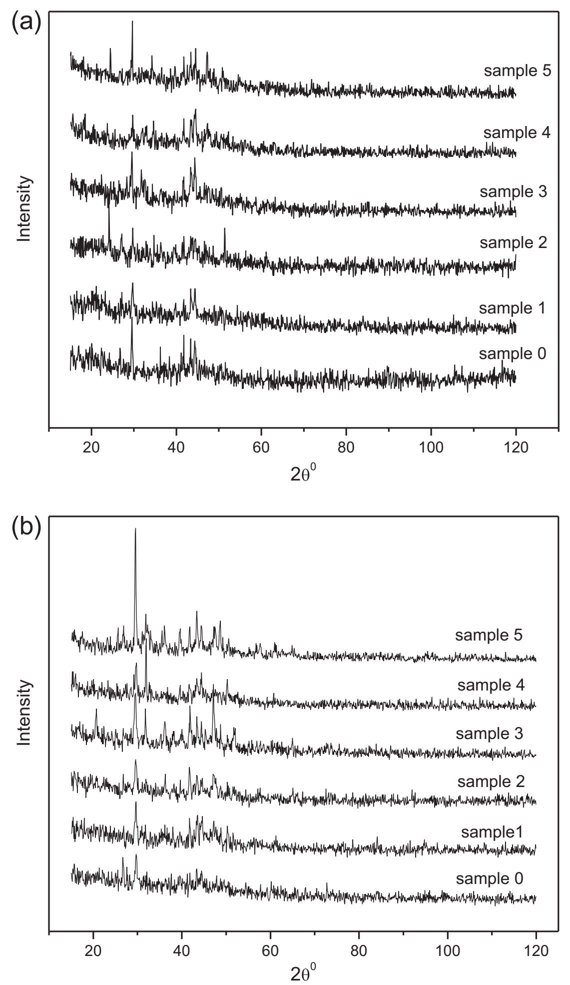

Fig. 7. XRD patterns of alkaline medium–sewage sludge mixtures (a) at the start-up of the stabilization process and (b) after 48 d of stabilization.

amounts requiring strong efforts for their management. The produced mixtures could have several applications i.e. soil amendment, daily cover in sanitary landfills, restoration of abandoned mines, etc.

4. Conclusions

The stabilization potential of sewage sludge was examined in this work, by the addition of an alkaline waste, steelmaking slag produced during steel refining, at concentrations reaching up to 20% on a dry weight basis. The produced mixtures were stabilized for a period of 48 d, and their properties were monitored for the determination of stabilization capacity. The addition of slag at the highest dosage resulted in the production of a stabilized sludge product, due to the high alkaline pH values of the mixture. The highest pH values, reaching up to 12, were observed for samples with the highest dosage of the slag. This mixture presented a low volatile content, around 30% of the total solids, a reduced moisture content lower than 50% that was reduced by the stabilization time, while pathogens were not observed from the start-up of the stabilization process. However, the addition of slag at lower dosages was not as effective as the highest dosage, resulting in mixtures with a lower pH and slower pathogen removal rate, although at extended stabilization time negligible microbes were measured. Nevertheless, the benefits of slag over the more conventional steel slag lime, such as integrated use of a solid waste, availability and low cost, indicate that steelmaking slag could become an efficient medium for sludge stabilization.

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