Aim and Scope

The objective of the *Journal of Residuals Science & Technology* (JRS&T) is to provide a forum for technical research on the management and disposal of residuals from pollution control activities. The Journal publishes papers that examine the characteristics, effects, and management principles of various residuals from such sources as wastewater treatment, water treatment, air pollution control, hazardous waste treatment, solid waste, industrial waste treatment, and other pollution control activities. Papers on health and the environmental effects of residuals production, management, and disposal are also welcome.

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CONTENTS

Research

Impacts of Municipal Sewage Sludge on Dynamics of Organic Matter and Biological Activities in Clay Loam Brown Forest Soil

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ABSTRACT: The application of municipal sewage sludge (MSS) increases soil organic matter (SOM) and improves soil structure. MSS of high heavy metal (HHM) content significantly decreased soil bioproductivity, reduced its biochemical properties, and lowered the microbial contents in comparison with MSS of low heavy metal (LHM) content. Total alfalfa dry matter yield and nitrogen increased linearly with increasing MSS application rates. Soil amended with MSS rates of 40 and 60% exhibit higher in crop dry matter, microbial contents and enzymatic activities than the control. Overall, our results demonstrated that soil amended with LHMs content can improve soil quality and soil biological and biochemical properties.

INTRODUCTION

SOIL is a dynamic system in which physical, chemical and biological components interact. Within this system, microorganisms perform an important task in the decomposition and transformation of soil materials, and are involved in the biogeochemical cycles of carbon (C), nitrogen (N), sulphur (S), phosphorus (P), etc. However, the interest in microbial functionality has grown in recent years to understand the relationship between microbial communities and their surrounding environment. Municipal sewage sludges (MSSs) can be used as an organic fertilizer. Application of MSSs in agricultural soils can directly improve soil physico-chemical properties. In relation to soil biological properties, numerous researchers have reported different effects of MSSs on soil microbial biomass and activity (e.g., Barral et al., 2009; Roca-Perez et al., 2009). It has been demonstrated that HMs adversely affect biological functions in soil, including the size, activity and diversity of the soil microbial community (Chander et al., 2001), and the activity of enzymes involved in biotransformation (Belyaeva et al., 2005). Heavy metals in MSS seemed interesting to determine their total effect on OM mineralization and microbial activities in the soil. Depending on this, our objectives are to evaluate the changes in biochemical and microbial properties of the clay loam brown forest soil when amended with various MSSs and application rates with regarding to different HM levels at plant growth.

MATERIALS AND METHODS

Soil Characterization, Sampling, and Amendment

The soil used in pot experiment was clay loam brown forest collected from farmland surface layer (0–200 mm) of an agricultural area of Gödöllő, Hungary in May 2007. Two different MSSs were selected depending on their HMs content. One is characterized as low (L) and the second is high (H) HMs content. The main physico-chemical parameters of soil and MSSs are shown in Table 1. Fresh soil was sieved through a 4 mm sieve and mixed with MSSs to form 0, 20, 40, 60 and 100% (soil:sludge; w/w), and then placed into pots with 42 cm in height and 23 cm in diameter. All treatments were designed in triplicates and submitted for statistical analysis.

Pots were incubated in greenhouse at Szent István University (Gödöllő), with 22–25°C average temperature. Distilled water was added to each pot to bring the moisture content of 45% water holding capacity throughout the plantation period. Pots were seeded with 3 alfalfa (*Medicago sativa* L.) seedlings of 15 days old. All experiments were done on three replicates. After 84 days of plantation, soil sub-samples were assayed for the following investigations.

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Table 1. The Physico-chemical Properties of Used Soil and Municipal Sewage Sludge Samples.

Parameters	Clay Loam Brown Forest Soil, Gödöllő	Municipal Sewage Sludge, Nyiregyháza	
		LHM—NySzv III	HHM—NySzv IV
pH(H_2O)	4.72	7.99	7.17
Dry matter content%	–	74	70
Organic matter %	–	25.6	48.2
Humus content %	1.24	–	–
Total N content mg·kg^{-1}	8.411	75,700	98.900
NO_3-N, mg·kg^{-1}	133.08	–	–
NH_4-N, mg·kg^{-1}	410.69	–	–
Ca, mg·kg^{-1}	856	5707	29724
Mg, mg·kg^{-1}	203	2810	5072
Na, mg·kg^{-1}	21	1290	1349
P_2O_5, mg·kg^{-1}	121.31	9700	9100
K_2O, mg·kg^{-1}	107	3120	3596
Zn, mg·kg^{-1}	38.1	453	134
Cu, mg·kg^{-1}	22.9	100	161
Mn, mg·kg^{-1}	136	309	497
Fe, mg·kg^{-1}	1187	11153	14802
Cd, mg·kg^{-1}	0.18	1	2.4
Cr, mg·kg^{-1}	–	34	46.4
Ni, mg·kg^{-1}	–	15	39.2
Pb, mg·kg^{-1}	15.1	30	83
As, mg·kg^{-1}	7.4	0.6	6.8
Hg, mg·kg^{-1}	–	0.04	2.8

Dynamics of Organic Carbon

Total organic carbon (TOC) was analyzed by dichromate ($K_2Cr_2O_7$) oxidation and titration with ferrous ammonium sulphate (Walkley and Black, 1934). The water soluble C (WSC) extraction content of the liquid fraction was determined spectrophotometrically at 590 nm after addition of $K_2Cr_2O_7$ and H_2SO_4 (digestion at 150°C for 15 min) according to Sims and Haby's method (1971). The hot-water soluble C extraction (HWSC) in fraction of SOM can be determined quickly by simple analytical method. Soil samples were dried at 40°C and extracted with water (1:5, w/v). Soil suspensions were boiled for 60 min under reflux. The contents of HWSC were determined according to Schulz and Korschens (1998).

Evaluation of Soil Respiration

To determine the soil respiration rates, 50 g of soil samples were placed in hermetically sealed glass bottle moistened at 45% of water holding capacity and incubated in the dark at 28°C for 10 days. The amount of organic carbon (OC) released as CO_2 and absorbed in vials containing 10 ml of 0.5 M NaOH placed inside bottle. The emitted CO_2 formed Na_2CO_3 which was measured by titration with 0.1 M HCl.

Measurement of Microbial Biomass Carbon

Microbial biomass carbon (MBC) content was determined by the method of Vance et al. (1987), which is based on fumigation of the sample with ethanol-free chloroform and subsequent extraction with 0.5 M K_2SO_4 of both fumigated and unfumigated samples, using a K_{EC} (conversion factor: extractable part of microbial biomass C after fumigation) = 0.45 (Wu et al., 1990; Jörgensen, 1996) to convert the measured flush of C to MBC (Yao et al., 2003). So, MBC was calculated as follows: MBC = E_C/K_{EC}, where E_C = (OC extracted from fumigated soil)—(OC extracted from non-fumigated soil).

Determination of Enzymatic Activities

Fluorescein diacetate (FDA) hydrolyzing activity of the soil sub-samples were determined by measuring the released fluorescein at 490 nm according to ALEF (1995). Dehydrogenase activity was determined by the method of García et al. (1993). Urease activity was determined in 0.1 M phosphate buffer at pH 7; 1 M urea and 0.03 M N α-benzoylargininamide (BAA) was used as substrate. The activity was determined by the NH_4^+ released (Nannipieri et al., 1980). Phosphatase and β-glucosidase activities were determined using p-nitrophenyl phosphate disodium (PNPD, 0.115 M) or *p*-nitrophenyl-β-D-glucopyranoside (PNG, 0.05 M) as substrates, respectively (Masciandaro et al., 1994). Similarly, aryl-sulphatase activity was determined as proposed by Tabatabai and Bremmer (1970), after the soil incubation with p-nitrophenyl sulphate and measured at 400 nm.

Enumeration of Some Microbial Population Densities

The enumeration of soil microbiota was done by the serial dilution plate method. The total colony forming units (CFU) of bacteria and fungi were recorded on Ken Knight and Munaier's agar (Allen, 1959) and Martin's Rose Bengal agar (Martin, 1950) media, respectively. Enumeration of cellulose decomposers was determined according to Hendricks et al. (1995). For phosphate solubilized microorganisms, method of Goldstein (1986) was applied. The plates were incubated at 28°C and microbial population densities were calculated and expressed as $\log_{10}$ of CFU × 10^n g^{-1} air dried soil, where 10^n was dilution factor.

Plant Biomass and Total Nitrogen Content

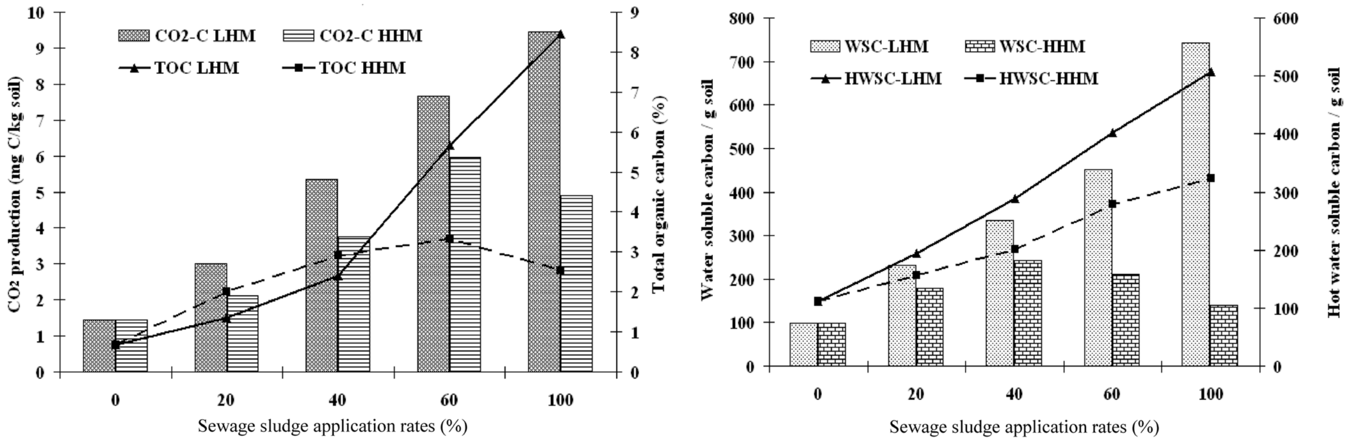
At harvest, plants were dried at 75°C and ground in a stainless steel wiley mill. Total nitrogen content in soil was determined by Kjeldahl digestion–distillation procedure (Keeney and Nelson, 1982).

RESULTS AND DISCUSSION

Utilization of MSSs on agriculture increases the concentration of HMs in soil and HMs–rich MSS drastically reduced the yield of some crops after a critical amount of MSS applied to the soil. These critical limits depend on the source, MSS application rate and frequency. Phyto- and rhizobioremediation using plants and related microorganisms are the promising approach to clean up the contaminated environment. Soil pollution by HMs is a serious worldwide problem and can be potentially harmful to human health via the food chain. The results of pot experiment illustrated the followings.

Dynamics of TOC, CO_2–C and MBC

There were great variations within the soil treated with different MSS types and concentrations regarding to the dynamics of TOC, CO_2–C and MBC. Due to these, the stability of OC in soil samples was different. The results showed that CO_2–C and TOC content of the soil increased with the addition of MSS [Figure 1(a)]; especially at higher rates of LHMs-MSS. So, soil respiration (expressed as mg CO_2–C released kg^{-1} soil) is a useful index for measuring soil microbial activity. The CO_2–C values ranged from 1.45 to 9.45 mg CO_2–C kg^{-1} soil. The WSC ranged from 99 to 743 and HWSC ranged from 111 to 507 mg kg^{-1} soil [Figure 1(b)]. The TOC values were suffered great variations during the plantation period. The addition of the MSS, regardless of their HM concentrations, increased the WSC and HWSC content in the soil [Figure 1(b)]. A higher WSC fractional value was detected in the soil amended with higher rates [Figure 1(b)]. The C content in the HWSC fraction of SOM is a simple determin-



(a) (b)

Figure 1. *Effects of sewage sludge applications on (a) soil respiration and total organic carbon and (b) water and hot water soluble carbon.*

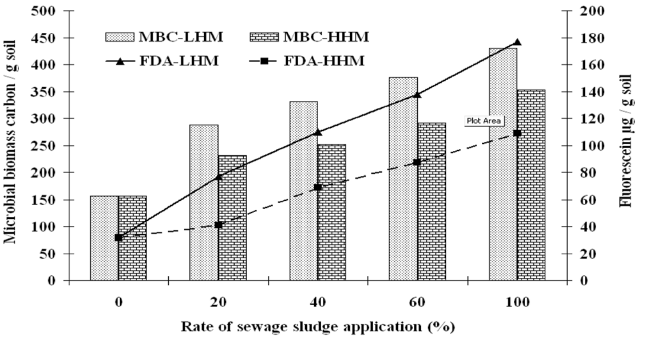


Figure 2. *Impacts of sewage sludge application on the microbial biomass carbon (MBC) and the total biological activity detected by FDA method.*

able and suitable parameter for estimating the supply of soil with decomposable SOM. The immediate and significant increases in TOC and CO_2 release were due to the presence of SOM in the amendments. However, these parameters return quickly to background level, as soil microorganisms rapidly mineralize the added OM in the form of MSS. The results indicated that LHMs-MSS application to soil stimulates the growth of soil microorganisms, probably due to the OC and other nutrients which are present in higher concentration than in the control soil.

According to a close, linear and positive relationship exists between the OC and MBC contents, the results indicated that MBC (values ranged from 156.1 to 430.1 mg kg^{-1}) was lower in HHMs-MSS content than in LHMs-MSS content (Figure 2). Soil microbial diversity is a crucial measure of sustainable soil ecosystems. Microorganisms in a soil form part of the biomass and contribute to the reserve of soil nutrients and are generally referred to as the microbial biomass (Insam, 1990). The results obtained in the present study are similar to those by Banerjee et al. (1997), who verified that the application of MSS favored an increase in microbial biomass, as well as the activity of soil microbiota, probably by the presence of OM in MSS. Soil respiration mainly comes from microbial respiration, which is the major product of aerobic catabolic processes in the C cycle, and is used as an indicator of total soil microbial activity.

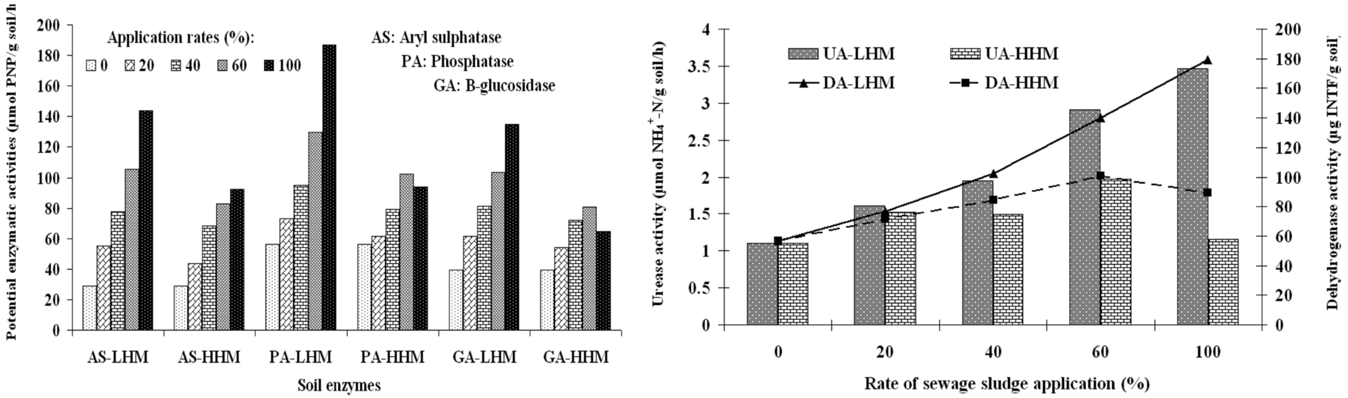
The MBC and FDA hydrolyzing activity (Figure 2) illustrated more accurate indicators of variations in soil quality than other soil C fractions. The MSS application to the soil of increased soil MBC, which can be attributed to the incorporation of easily increase the biological activities indicated by the high values of FDA hydrolyzing activity and then increases the biodegradable OM and to the MB contained in the MSS.

Our results are in agreement with Chander et al. (1995) who worked with metal-enriched SS and found that the total metal concentration at permitted limits in a soil did not decrease the amounts of MBC, indicating that the high level of HMs content affected MBC. Bhattacharyya et al. (2005) showed that HMs in municipal solid waste compost did not detrimentally influence MBC, urease and acid phosphatase activities of soil. It seems that at low rate, the positive effects of the OM added did not counterbalance the significant effect produced by the higher MSS rates. The subsequent slight recovery in MBC values was probably due to the microorganisms (mainly bacteria) becoming adapted to the high OM concentrations. In comparatively, soil amended with HHM-MSS reduced significantly the values of MBC.

Changes in Soil Enzymatic Activities

The increase of enzymatic activities with the MSS rate is probably due to the addition of labile C supplied by MSS, indicating that the MB is active and potentially mineralized OM. Soil enzyme activities are used as indicators of microbial activity and react quickly to environment change. Figure 3(a) and 3(b) show the evolution of five enzymatic activities measured during the experimental period. The results showed that elevated MSS mixing rate differently impacted on soil enzyme activities. Increases of FDA (Figure 2), phosphatase, β-glucosidase and aryl-sulphatase activities [Figure 3(a)], urease and dehydrogenase [Figure 3(b)] under addition of MSS occurred with increasing the application rate. These increases were more significant in soil amended with LHM than with HHM content compared to control.

Dehydrogenase activity has been proposed as an indicator of the total metabolic activity of soil microorganisms (Skujins, 1976). In our experiment, this enzymatic activity increased by the addition of MSS to the soil and remained stable throughout the subsequent incubation time [Figure 3(b)]. It is important to mention that the dehydrogenase activity increased with the addition of more MSS; however, this stimulation was lower in case of the MSS of HHM content, suggesting that MSS had a positive effect on the synthesis of this endocellular enzyme, similar to its effect on the MBC. The high level of MSS significantly increased, soil urease activity and the values of which remained higher in the amended soils than in the control throughout the plantation period [Figure 3(b)], probably due to the formation of urease-humus complexes that stabi-



(a) (b)

Figure 3. *Enzymatic activities (a) aryl-sulphatase, phosphatase, β-glucosidase, (b) urease and dehydrogenase activities in low (L) and high (H) heavy metal (HM) contents sewage sludge amended soil.*

lize this enzyme in the soil. This result is in agreement with the observation of Nannipieri et al. (1996). The fact that the activity of urease was always higher in the soil amended with MSS shows that higher rates of LHM content have a positive effect on this enzyme's activity. All treatments led to a significant increase in soil phosphatase activity with respect to the control [Figure 3(a)]. At the end of the plantation time, higher phosphatase values than those of the control soil were detected in all the soils amended with a high rate of either MSS. Our results are confirmed by Cook and Allan (1992) when β-glucosidase is an enzyme involved in the C cycle and hydrolyses β-glucosidic bonds of the carbohydrate chains. The activity of this enzyme reflects variations in the more biodegradable C fraction, and is therefore very useful for following the mineralization of OM. However, the activity detected at the end of the plantation period was significantly higher in amended soils with LHM content than in amended soils with HHM content and the control soil, particularly when MSS had been applied at the higher rate. Carbonell et al. (2009) mentioned that application of MSS increased the activities of dehydrogenase, phosphatase, respiration rate and soil microbial content. These results are in agreement with our results as it is present in Figures 3(a) and 3(b). From this study it can be concluded that the addition of MSS, independently of their degree of HM contamination increased the TOC. In this respect, the enzymatic activities studied helped us to follow the changes occurring in the OM during the experiment. In general, the OM added as MSS had a positive effect on the enzymatic activities. More studies are needed to deeper our knowledge of the effect of HM contamination on enzymatic activities. However, our results indicated that there are positively related correlation between the investigated enzymes and OM in the applied MSS. This indicates that an aggregate of multi-enzymatic activities may be better correlated with soil fertility than a single enzyme. Particularly, the enzymatic activities in soil amended with MSS-LHM content were markedly higher than those in the soil amended with MSS-HHM content.

Density of Soil Microbical Population

The results indicated that the metal-resistant fungi isolated from MSS amended soil belonged to genera *Aspergillus* (10.3%), *Penicillium* (9.2%), *Alternaria* (3.7%), *Geotrichum* (9.7%), *Fusarium* (13.2%), *Rhizopus* (12.3%), *Monilia* (2.5%) and *Trichoderma* (39.1%). This results are in agreement with Zafar et al. (2007). Population size and community structure of soil microorganisms are sensitive to changes in soil contaminated MSS with high concentration of HMs. The results of quantitative analysis of soil microbial (bacterial and fungal) populations were shown in Figure 4.

The soil microbial populations were far higher under MSS application than in case of the control treatments. Bacteria showed a marked increase in population size with increasing MSS mixing rate levels, other soil microbes; fungi in population size responded similarly to bacteria, although all treatments showed significant difference on population size in comparison between the MSSs of LHM and HHM contents compared to control except the fungal population and phosphate solubilizers at MSS of HHM. According to our observation, we are in agreement with Bosatta and Ĺgren (1993) on the basis of soil microbial biomass (C_{mic}) is both a labile nutrient pool and an agent of transformation and cycling of OM and plant nutrients in soils; so, it is one of the most important microbiological properties. Several

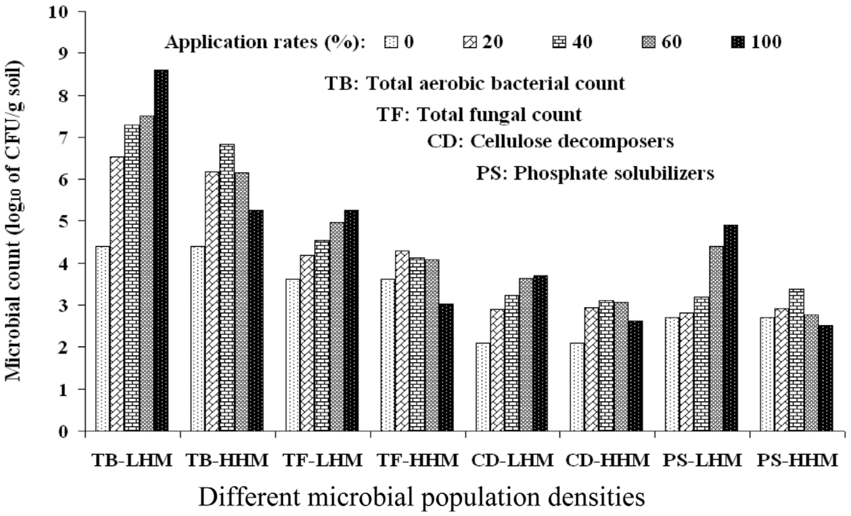


Figure 4. *Some soil microbial contents influenced by the application of low (L) and high (H) heavy metal (HM) contents sewage sludge in clay loam brown forest soil.*

studies indicated that the C_{mic} responds more rapidly to changes resulting from soil management activities than SOM and, consequently, may be an early and sensitive indicator of soil quality change.

Plant Biomass and Total Nitrogen Content

Total dry matter yield and total N increased linearly with increasing MSS application rates (Figure 5). Soils amended with MSS rates of 40 and 60% exhibit higher in plant dry matter than the control soil. The increase in dry matter and N content of alfalfa growing in MSS-amended soils may be attributed to high OM content and high macro- and micro-nutrient concentrations. This enhancement confirms the increase in shoot weight of legumes grown in MSS-amended soil, as previously reported by Ibekwe et al. (1995). The tendency observed of alfalfa cultivated in soils amended with MSS rates from 40 to 60% show maximal growth, dry weight. The increase of both shoot dry weight and the N content in alfalfa was mainly due to the plant establishment. The result illustrated that the beneficial effect of MSS increased by increasing the application rate to be at maximum at 60% and then decreased but also, they were higher than the controls.

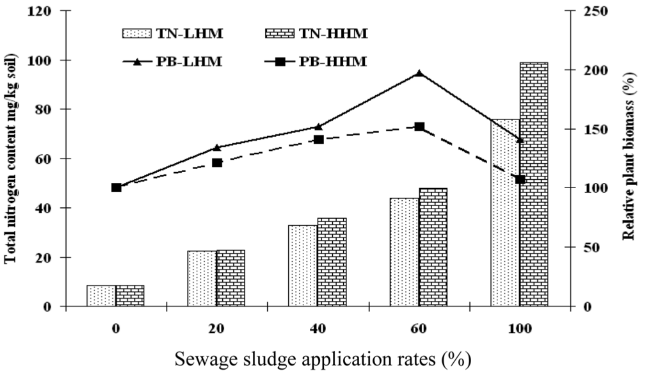


Figure 5. *Effects of sewage sludge applications on the relative plant biomass and total nitrogen content.*

According to this, our results are in good agreemant with the results of Singh and Agrawal (2008) who established that the mature municipal solid waste compost might be used as conditioner for clay soil, but not for sandy soil. Monitoring soil quality by means of bioindicators can be helpful for the management and sustainability of soils that received MSS application. It should be concluded that the accumulative concentration of HMs in MSS amended soil should be calculated after every application of MSS.

CONCLUSION

The MSS used, contained appreciable amount of HMs. The parameters like MBC, soil enzymes and microbial content are sensitive markers to detect soil pollution. Present work revealed no apparent detrimental influence on the studied soil quality indicators due to MSS application in realistic doses, to plant biomass. Addition to clay loam brown forest soil increased the values of dissolved organic C, C mineralization, MBC, and CO_2 release. Results of this study provided evidences that the addition of MSS enhanced the enzymatic activities, and indicated that MSS of HHMs content decreased soil biochemical properties, and lowered the microbial contents in soil in comparison with MSS of LHMs content. Addition of MSS induces a reactivation of soil quality and activity, indicated by plant dry matter, microbial content and enzymatic activities. However, HMs entering the soil can persist for a long time. Regular monitoring of soil quality changes should be carefully carried out in the event of long-term application of MSS. The problem is still with the accumulation of HMs in the plant dry matter.

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Adsorption Behaviors of Organic Substances on Sewage Sludge-Based Adsorbent

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ABSTRACT: Adsorption characteristics of organic substances on sewage sludge-based adsorbent (SBA) were tested comparing with those on powder activated carbon (PAC). The removal efficiencies of carbohydrate, lipid and protein on SBA with the adsorbent dosage of 4g L^{-1} are 82.09%, 97.10% and 52.24%, which are 1.07, 1.10 and 1.81 times those of PAC, respectively. The maximal total Chemical Oxygen Demand (COD) adsorption capacity on SBA from carbohydrate-lipid-protein-ternary solution is 94.83 mg g^{-1}, which is 1.19 times that of PAC. X-ray photoelectron spectroscope (XPS) analyses show that O, Si, Ca and Fe elements, etc. on SBA surface promote the adsorption of organic substances.

INTRODUCTION

THE organic constituents of municipal wastewater are more important than the lumped parameters (such as chemical oxygen demand, total phosphorus, total nitrogen, etc.) when investigating the removal mechanisms of organic substances in the municipal wastewater treatment process. Major organic constituents in municipal wastewater are proteins, carbohydrates and lipids derived from human activities [1,2]. So, it is necessary to monitor their contents in municipal wastewater, both in the influent and effluent of various municipal wastewater treatment processes.

Biological treatments, such as conventional activated sludge process and membrane bioreactor, are commonly adopted for domestic wastewater. These biological treatments have strict operating conditions which are hard to control [3]. Adsorption is another convenient and expeditious technique for domestic wastewater treatment. Powder activated carbon (PAC) has already been combined with biological reactor for municipal wastewater treatment [4]. This process is seldom applied in wastewater treatment plants due to high cost of PAC. Economical and efficient adsorbent which could replace PAC and be applied to wastewater treatment process should be selected.

Adsorbent can be produced from sewage sludge which is a by-product from municipal wastewater treatment plant. Sewage sludge-based adsorbent (SBA) which is an economic resource can be widely used to absorb pollutants in water and gas. The adsorptions of dyes [5–7], metals [8] and phenols [7, 9], etc. on SBA have been reported with satisfactory results. The adsorption capacities of organic substances on SBA from wastewaters were evaluated by lumped parameter COD [10,11] and favorable results obtained. COD is obtained by measuring the equivalent quantity of an oxidizing agent, usually permanganate or dichromate in acid solution, necessary for oxidation of the organic constituents; the amount of oxidant consumed is customarily expressed in equivalents of oxygen. However, the utilization of SBA for the specific removal of carbohydrate, lipid and protein has not been investigated. The adsorption behaviors of these typical organic substances on SBA should be studied before applying SBA to municipal wastewater treatment process.

Purpose of this study is to establish the ability of SBA to absorb carbohydrate, lipid and protein. Batch adsorption assays were done on SBA in pure, binary and ternary solutions of carbohydrate, lipid and protein, and compared with PAC. Adsorption behaviors of carbohydrate, lipid and protein on SBA and PAC were characterized by X-ray photoelectron spectroscope (XPS) analysis.

MATERIALS AND METHODS

Adsorbent

The raw material used for adsorbent preparation

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was sewage sludge from municipal wastewater treatment plant in Harbin (China). Water, volatile solids, organic carbon and ash contents of the sewage sludge range between 78.4–82.5%, 65.3–67.5%, 35.6–37.0% and 38.2–39.9%, respectively. The sludge was dried at room temperature (25°C) to reduce water to less than 5% before making the adsorbent.

The raw sludge was mixed with H_2SO_4 and dried in oven at 105°C for 24h. The mixture was pyrolyzed in a muffle furnace without any inert atmosphere by increasing the temperature to 650°C at a rate of 30°C min^{-1}. The final temperature was maintained for 30 min. Then the product was ground to powder ($d < 100$ μm). 1M HCl was used to wash the powder one time, after that distilled water was used to wash the powder three times. Finally, the sample was dried in oven at 105°C for 24h, and was ground to powder ($d < 100$ μm). PAC (China, $d < 100$ μm) made from coconut shell was chosen as a comparative adsorbent.

Sample porosity was characterized by N_2 adsorption measurements at 77K (Micromeritics ASAP2020, USA). Sample microstructure was observed with S-570 scanning electron microscope (SEM, USA). XPS was employed to determine the surface chemical properties of the samples. The analysis was done by using a PHI 5700 ESCA system (USA) with Al Kα X-ray source (1486.6 eV of photons). The peaks of C1s XPS after deconvolution can be ascribed to carbon atoms which are bonded to many different function groups. The separate peaks represent C–C (284.5 eV), C–N (285.5 eV), C–O–R/C–OH (286.1 eV), C=O (287.3 eV) and O–C=O (288.5 eV), respectively [12,13].

Adsorbates

Three typical organic components of municipal wastewater which are carbohydrate, lipid and protein were selected to characterize the adsorption behaviors of organic substances on SBA. Starch was chosen to simulate carbohydrate in municipal wastewater. Lipid in this study was mixed of bean oil, lard and Tween 80 (Polysorbate 80, as a kind of surface active agent, makes the lipid dissolve in water) at a mass ratio of 2:1:6. Bovine serum albumin (BSA) was chosen to represent protein in municipal wastewater.

Adsorption Assays

Batch adsorption assays were conducted to study the effect of contact time, adsorbent dosage, initial pH and initial concentration on the adsorptions of carbohydrate, lipid and protein on SBA and PAC. First, 0.20 g SBA or PAC was added to 50 mL of 100 mg L^{-1} carbohydrate, lipid or protein solution in closed flasks to avoid evaporation. The solution-containing flasks were shaken at 150 rpm at 25±2°C in a water-bath. The contact time was between 0.5–6.0 h. The pH values of 100 mg L^{-1} starch, lipid and protein solutions without pH adjusting were 6.77, 6.29 and 6.66 respectively. Adsorbent dosage study was conducted with 0.2–10.0 g L^{-1} adsorbents by the same procedure for an equilibrium time. Initial pH study was conducted by using HCl or NaOH to adjust initial pH values of organic substance solutions between 2 and 10. Carbohydrate and protein were determined by Anthrone method and modified Lowry method, respectively [1, 2]. Lipid was determined by COD method, which was tested at 620 nm by spectrophotometer (TU1901, China) after 2 h heating reaction in COD reactor (HACH drb 200, USA).

RESULTS AND DISCUSSION

Properties of SBA and PAC

SEM of dried sewage sludge, SBA and PAC are given in Figure 1. SEM of SBA shows the existence of pores in different shapes as well as scattering of salt particles. Comparing SEM of raw sewage sludge and SBA, it can be seen that pyrolysis process greatly changes the surface structure of the material. Pyrolysis process leads to the formation of plenty pores on SBA surface. But the pore walls of SBA are rougher than those of PAC. BET surface area ($m^2\ g^{-1}$), total pore volume ($cm^3\ g^{-1}$) and micropore volume ($cm^3\ g^{-1}$) of SBA are 272.81, 0.27 and 0.05, respectively, while for PAC are 1178.39, 0.67 and 0.33, respectively.

Elemental compositions (Atomic %) of SBA and PAC are summarized in Table 1. It can be seen that there are C, O, N, Si, S, P, Ca and Fe elements on the surface of SBA. Contents of these elements have the following order: C > O > N > Si > S > P > Fe > Ca. There are only C and O elements on the surface of PAC.

Table 1. Elemental Compositions (Atomic %) of SBA and PAC Estimated by XPS.

Sample	C	O	N	Si	S	P	Ca	Fe
SBA	59.31	26.45	5.94	5.18	1.66	0.56	0.28	0.62
PAC	94.44	5.56	–	–	–	–	–	–

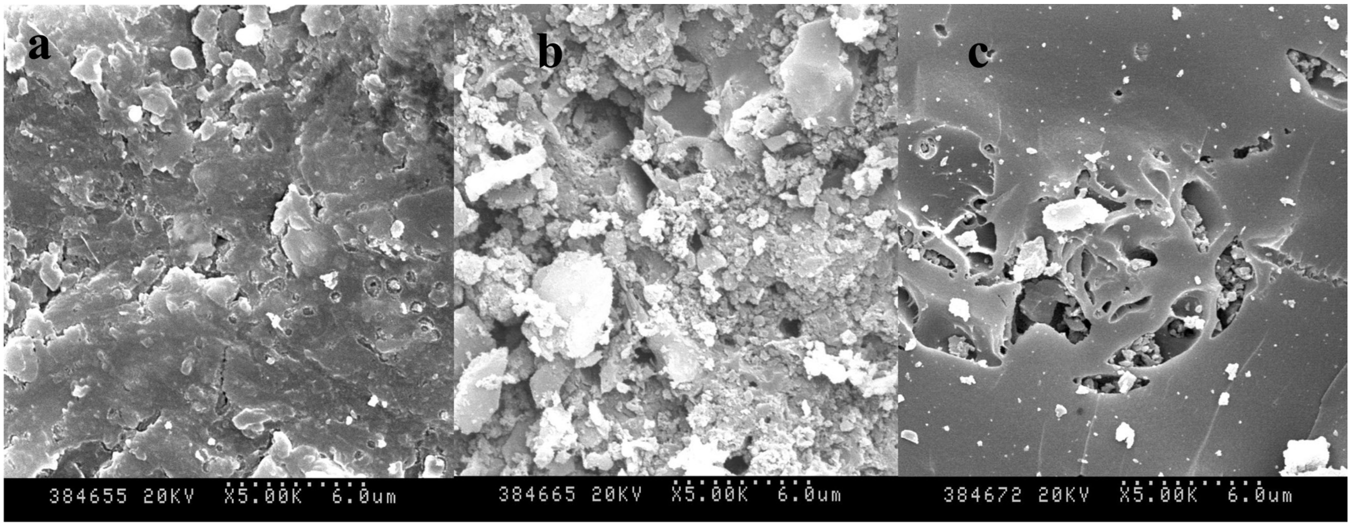

Figure 1. *SEM of (a) dried sewage sludge, (b) SBA and (c) PAC.*

Effect of Initial pH on Carbohydrate, Lipid and Protein Adsorptions

Figure 2 shows the effect of initial pH on the removal efficiencies of carbohydrate, lipid and protein on SBA and PAC. The authors chose the range of pH between 2 and 10, in order to take into account all types of conditions encountered in municipal wastewater treatment plants. It can be seen that the removal efficiencies of carbohydrate, lipid and protein on SBA are between 77.36–87.57%, 84.62–96.47% and 54.08–61.91%, when the initial pH values of carbohydrate, lipid and protein solutions are all from 2 to 10, thus indicating that initial pH values of the organic substance solutions have slight influences on the adsorption of organic substances on SBA.

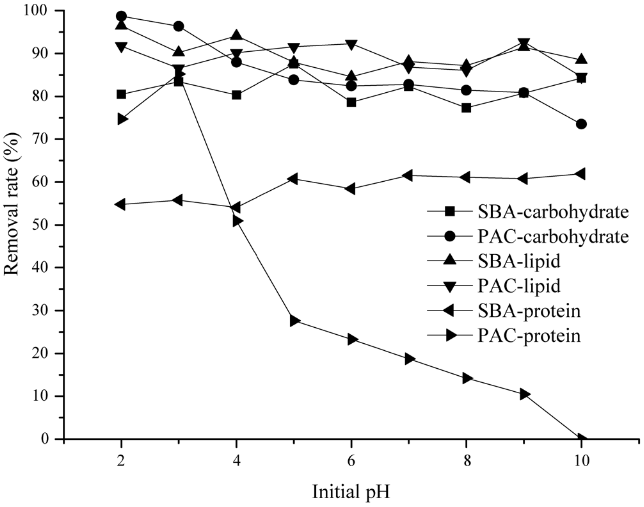

Figure 2. *Effect of initial pH on the removal of carbohydrate, lipid and protein on SBA and PAC (Concentrations are all 100 mg L^{-1}; adsorbent dosage: 4 g L^{-1}; contact time: 2 h; shaking rate: 150 rpm).*

The removal efficiency of carbohydrate on PAC decreases from 98.70% to 73.54% as the initial pH of carbohydrate solution increases from 2 to 10, while the removal efficiency of lipid on PAC is between 86.05–92.68% in the same pH range. So, the initial pH has small effect on carbohydrate adsorption on PAC and almost no effect on lipid adsorption on PAC. But the removal efficiencies of protein on PAC are seriously affected by initial pH. The maximum removal efficiency of protein on PAC is obtained when the initial pH value of protein solution is 3. The removal efficiency of protein decreases from 85.20% to zero when the initial pH of protein solution increases from 3 to 10. It has been reported that adsorption of BSA on carbon materials is the consequence of electrostatic and hydrophobic interactions [14].

Effect of Adsorbent Dosage on Carbohydrate, Lipid and Protein Adsorptions

Figure 3 shows the effect of adsorbent dosage on the removal efficiencies of carbohydrate, lipid and protein on SBA and PAC.

The removal efficiencies of carbohydrate, lipid and protein on SBA and PAC all increase as the adsorbent dosage increases from 0.2 g L^{-1} to 4 g L^{-1}. When the adsorbent dosage is 4 g L^{-1}, the removal efficiencies of carbohydrate, lipid and protein on SBA are 82.09%, 97.10% and 52.24%, respectively; on PAC are 76.56%, 88.41% and 28.83%, respectively. It follows that the removal efficiencies of carbohydrate, lipid and protein

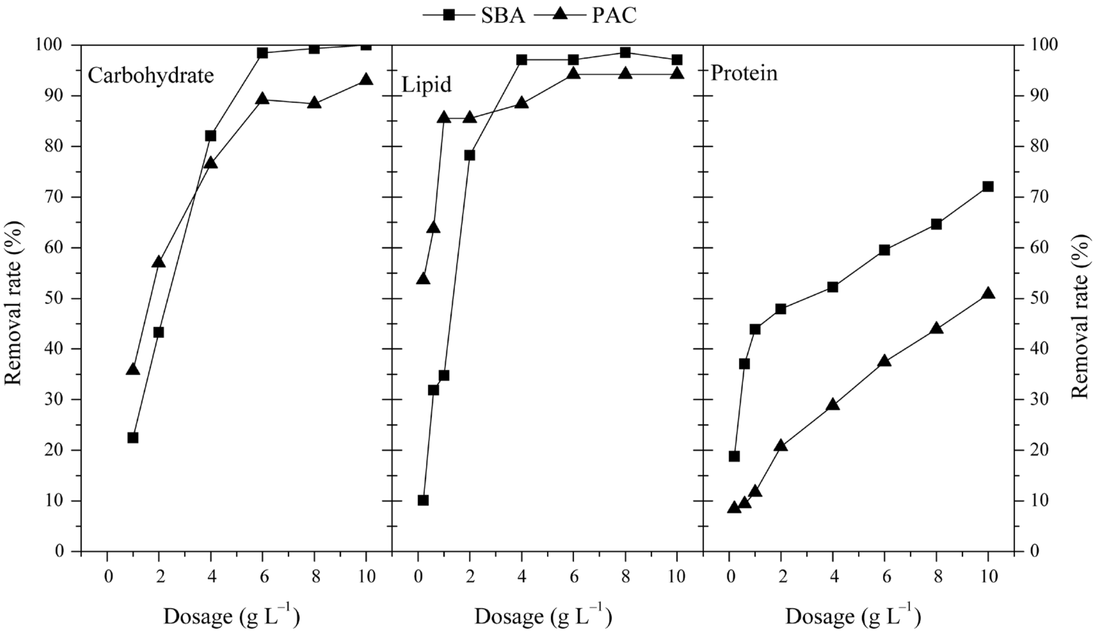

Figure 3. Effect of adsorbent dosage on the removal of carbohydrate, lipid and protein on SBA and PAC (Carbohydrate, lipid and protein concentrations: 100 mg L^{-1}; contact time: 2 h; shaking rate: 150 rpm).

on SBA are 1.07, 1.10 and 1.81 times those of PAC, when the adsorbent dosage is 4 g L^{-1}. When the adsorbent dosage is 10 g L^{-1}, the removal efficiencies of carbohydrate, lipid and protein on SBA are 100%, 97.10% and 72.09%, respectively, while on PAC are 93.03%, 94.20% and 50.79%, respectively. So, the removal efficiencies of carbohydrate, lipid and protein on SBA are 1.07, 1.03 and 1.42 times of PAC, at adsorbent dosage of 10 g L^{-1}. The removal efficiencies of carbohydrate, lipid and protein on SBA are higher than those on PAC, when the adsorbent dosages are 4–10g L^{-1}, 4–10g L^{-1} and 0.2–10g L^{-1}.

Effect of Initial Concentration on Carbohydrate, Lipid and Protein Adsorptions from Pure and Ternary Solutions

Effects of initial concentration on carbohydrate, lipid and protein adsorptions on SBA and PAC from carbohydrate-pure, lipid-pure, protein-pure and carbohydrate-lipid-protein-ternary solutions are given in Figure 4. In the preparation of experiments it was found that carbohydrate, lipid and protein can be calculated in COD units through the following conversion coefficients: 1 mg Carbohydrate (Starch) = 1.06 mg COD; 1 mg Lipid = 2.16 mg COD; 1 mg Protein (BSA) = 1.58 mg COD. Total COD removal efficiencies on SBA and PAC from carbohydrate-lipid-protein-ternary solution can be calculated by these conversion equations. As shown in Figure 4, all the adsorptions increase (or at least do not decrease) as the initial concentration increases from 25 mg L^{-1} to 200 mg L^{-1}. The maximal adsorption capacities of carbohydrate, lipid and protein on SBA from pure solutions are 26.51 mg g^{-1}, 33.88 mg g^{-1} and 17.45 mg g^{-1}, respectively, and 32.88 mg g^{-1}, 40.52 mg g^{-1} and 7.50 mg g^{-1} on PAC, respectively. It appears clearly that the adsorption capacity of carbohydrate, lipid and protein on SBA from pure solutions are 0.81, 0.84 and 2.30 times those of PAC. It also can be calculated from Figure 4 that the maximal adsorption capacities of carbohydrate, lipid and protein on SBA from carbohydrate-lipid-protein-ternary solution are 0.66, 1.32 and 1.64 times those of PAC. Although the adsorption capacities of carbohydrate and lipid on SBA from pure solutions are lower than those on PAC, only the adsorption capacity of carbohydrate on SBA from ternary solution is lower than that on PAC. The maximal total COD adsorption capacities on SBA and PAC from ternary solution are 94.83 mg g^{-1} and 79.74 mg g^{-1}, respectively. It means that the maximal total COD adsorption capacity on SBA is higher than that on PAC.

Adsorption Properties of Carbohydrate, Lipid and Protein on SBA Detected by XPS

Adsorption Properties of Carbohydrate on SBA

Relative contents of surface functional groups determined by fitting C1s XPS spectra and oxygen to

Table 2. Relative Contents of Surface Functional Groups in C1s XPS Fitting Curves (percent of total peak area, %) and Oxygen to Carbon Atomic Ratios.

Sample	O–C=O	C=O	C–OR, C–OH	C–N	C–C	O/C	Revised O/C[a]
SBA	6.78	6.34	15.03	7.53	64.32	0.45	0.27
Carbohydrate-adsorbed SBA	5.86	10.86	15.16	6.02	62.10	0.47	0.33
Lipid-adsorbed SBA	2.46	6.59	6.45	4.91	79.59	0.36	0.23
Protein-adsorbed SBA	6.96	7.87	18.06	6.57	60.54	0.49	0.34

[a] The revised O/C stands for (O-2Si)/C [20].

carbon atomic ratios of SBA before and after organic substances adsorptions are summarized in Table 2. It shows that the content of C=O on SBA surface increase from 6.34% to 10.86% after carbohydrate adsorption which is the biggest change among the oxygen-containing groups on SBA. Possible reason for this phenomenon is that O–C–O in carbohydrate molecule has the same binding energy with C=O in XPS C1s fitting curve [15]. C–OH is also one segment of the polymeric polysaccharide. But after adsorption, C–OH content on SBA surface only has a small change from 15.03% to 15.16%. It is presumed to be caused by the interaction between O–C=O on SBA surface and C–OH in polysaccharide molecule. Possible reaction is

$$\text{SBA-COOH} + \text{OH-carbohydrate} \rightarrow \text{SBA-COO-carbohydrate} \quad (1)$$

The other hypotheses regarding carbohydrate adsorption mechanism are hydrogen bonding formed between carbohydrate hydroxyl groups and SBA surface hydroxyls [16], and hydrogen bonding formed between the ether group and SBA surface silanol groups [17,18]. Besides, the ability of the hydroxyl groups in carbohydrate molecule to form an intramolecular hydrogen bond suggests that these hydroxyl groups would be equally able to complex with surface iron atoms [19]. As a result, Ca and Fe elements on SBA surface can form complex with carbohydrate molecule to promote the adsorption of carbohydrate.

Adsorption Properties of Lipid on SBA

As shown in Table 2, the surface content of C–C on SBA increases from 64.32% to 79.59% after lipid adsorption, while O–C=O decreases from 6.78% to 2.46%, and C–O–R/C–OH from 15.03% to 6.45%. The increase of C–C content is caused by hydrocarbon chains of the lipid; the decrease of O–C=O and

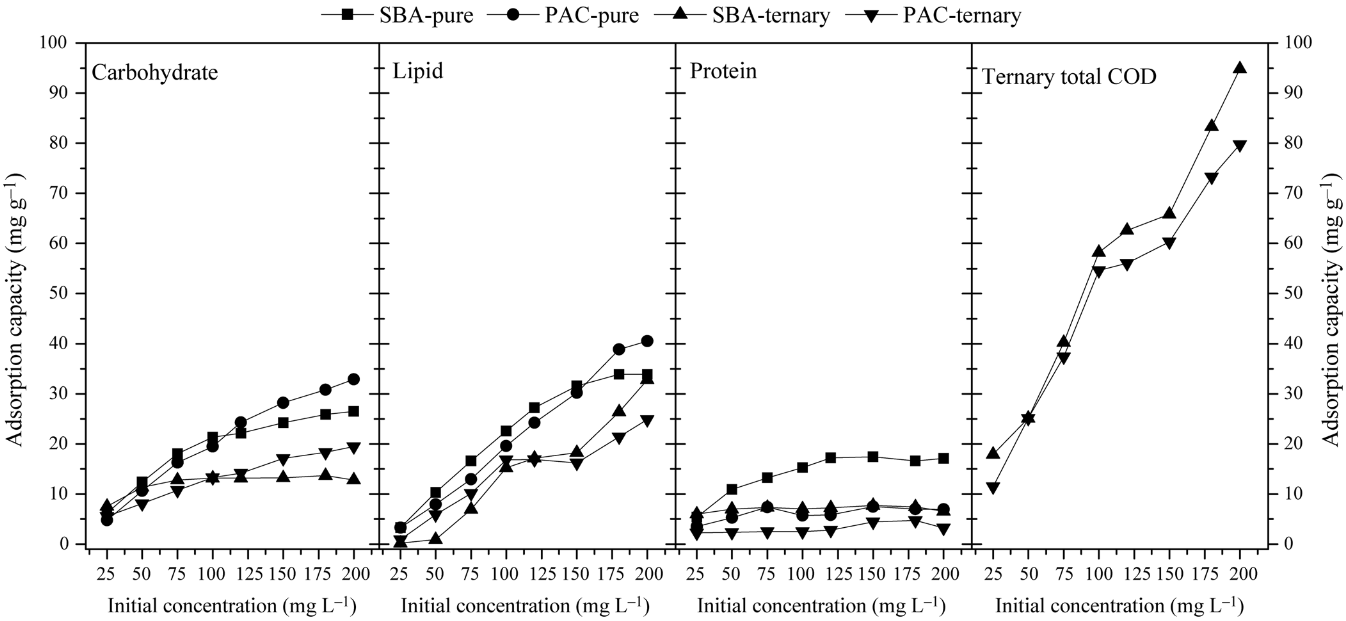

Figure 4. *Effect of initial concentration on the adsorptions of carbohydrate, lipid and protein on SBA and PAC from carbohydrate-pure, lipid-pure, protein-pure and carbohydrate-lipid-protein-ternary solutions (Adsorbent dosage: 4 g L^{-1}; contact time: 2 h; shaking rate: 150 rpm; weight ratio of carbohydrate, lipid and protein in the ternary solution: 1:1:1; initial concentration of ternary solution just stands for separate organic substance).*

C–O–R/C–OH contents are probably caused by the interaction of lipids groups and oxygen-containing groups on SBA. Small content of Si, S, P, Ca and Fe elements on SBA (Table 1) may also promote the interaction between lipid and SBA surface. After lipid adsorption, revised O/C ratio of SBA decreases from 0.27 to 0.23. This phenomenon also indicates the decrease of oxygen-containing groups on the lipid-adsorbed SBA. Maybe this is caused by low O/C ratio of the lipid.

Adsorption Properties of Protein on SBA

As shown in Table 2, the surface content of C=O on SBA increases from 6.34% to 7.87% after protein adsorption, and C–O–R/C–OH increases from 15.03% to 18.06%. They are presumably caused by NH–C=O segments in the adsorbed protein molecules on SBA surface. Protein molecule and SBA surface are both amphoteric, thus plenty of oxygen-containing and nitrogen-containing groups on SBA surface are favorable to the protein adsorption. O–C=O on SBA surface will also impulse protein adsorption process [21]. As shown in Table 1 the contents of Si, Ca, Fe elements on SBA are 5.18%, 0.28%, 0.62%, respectively. These elements can improve the adsorption of protein on SBA. These are the ligand exchange reaction of a carboxyl group with an iron hydroxyl group and the interaction of an amino group with the silica hydroxyl group at pH 7 [22]:

$$\begin{aligned}&\text{SBA-FeOH}_2^+ + \text{protein-COO}^- \rightarrow \\ &\quad \text{SBA-Fe-OOC-protein} + \text{H}_2\text{O} \qquad (2)\end{aligned}$$

$$\begin{aligned}&\text{SBA-SiO}^- + \text{protein-NH}_3^+ \rightarrow \\ &\quad \text{SBA-SiO}^- + \text{H}_3\text{N-protein} \qquad (3)\end{aligned}$$

CONCLUSION

Results show that the adsorptions of organic substances on SBA and PAC are slightly affected by the initial pH of carbohydrate, lipid and protein solutions (with the exception of the adsorption of protein on PAC). The removal efficiencies of carbohydrate, lipid and protein on SBA and PAC all increase as the adsorbent dosages increase from 0.2 g L^{-1} to 4 g L^{-1}. The removal efficiencies of carbohydrate, lipid and protein on SBA are higher than those on PAC when the adsorbent dosage is 4–10 g L^{-1}. Adsorptions of organic substances on SBA and PAC from carbohydrate-pure, lipid-pure, protein-pure and carbohydrate-lipid-protein-ternary solutions all increase as the initial concentrations increase from 25 mg L^{-1} to 200 mg L^{-1}. The maximal total COD adsorption capacity on SBA (94.83 mg g^{-1}) from ternary solution is higher than that on PAC (79.74 mg g^{-1}). XPS analyses show that the adsorptions of carbohydrate, lipid and protein on SBA are all promoted by the oxygen-containing function groups, Si, Ca and Fe elements, etc. on SBA surface.

The investigation further proves that SBA could be used as cost-effective and sustainable adsorbent in organic substances adsorption, and it has the potential to replace PAC and being applied to sewage treatment process. The investigation further proves that SBA is a promising sludge resource utilization methods, and it has the potential to utilized as adsorbent to improve pollutants removal in wastewater treatment.

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Socio-Political Reception of Sewage Sludge Recycling: The Hungarian Perspective

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ABSTRACT: The management of sewage sludge is facing new challenges in the early 21st century. It accounts for an ever-larger proportion of the costs of wastewater treatment. In Hungary, water utilities and land suitable for agricultural recycling have a new structure of ownership as a result of post-transition privatisation, with fundamental consequences for sludge use. A new factor, climate change, may make wastewater irrigation—particularly for energy crops—an important feature of water management in areas global warming have rendered arid. As the increasing costs of sludge treatment are passed on to the customers, service charges are expected to rise, having a potentially adverse effect on water use.

INTRODUCTION

Rising Sewage Sludge Volume and Management Costs

DEVELOPMENT in wastewater treatment technology is associated with rising sludge volumes, utilization of which is made difficult by the tightening of environmental regulations.

Efforts to reduce domestic water consumption have led to higher contaminant concentrations in wastewater. This is a general trend in Hungary. Average daily domestic water use per head has fallen from over 120 litres before the political transition (in 1990) to 83 litres nowadays. In many cases—especially in smaller towns—it is now less than the accepted minimum of 70 l/day. [1] This trend is in accordance with the level of consumption of 70 l/person/day accepted as the hygienic minimum in Western Europe.

A comparison of water service charges as a proportion of net personal income with consumption per head, however, showed that increasing family income does not reduce average consumption below 80 l/person/day. This relation is shown in Figure 1.

In the 10 years since these statistics were produced, a new phenomenon has made its appearance—non-payment of water charges. We will return to this issue later.

The steady tightening of wastewater treatment emission levels has mainly involved the nitrogen and phosphorus nutrients. In response, there have been improvements in the efficiency of wastewater treatment technology, causing an increase in the unit costs of sludge. The costs of treating communal sludge in Hungary vary between 20 and 40 € per ton of dewatered sludge with 18–25% dry matter content. This includes the cost of removal and treatment of the sludge, but not the costs of handling it within the wastewater treatment plants.

Aspects Peculiar to Hungary

Hungary's wastewater system has developed very rapidly in recent years. This shows up very clearly from the 31% increase in the number of households connected to the drainage system in the last twenty years. Starting from 41% in 1990, it has reached 72% in 2010, fulfilling the European Union requirement for every system to terminate in a wastewater works providing at least biological treatment. [3]

The construction of the necessary wastewater systems and treatment works was given a powerful boost by support from both EU and government funds. Towns and villages in Hungary are spread across a relatively wide population spectrum. Budapest stands well apart, and is followed by four large cities. Villages with less than 2000 inhabitants are very numerous but account for only 17% of the country's population. [4] Owing to the low population density in such villages, unit drain-

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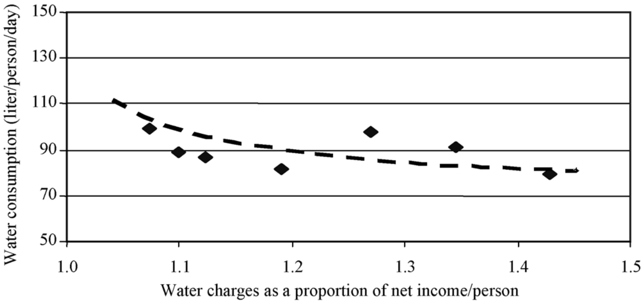

Figure 1. *Relationship between unit water consumption and service charges (water supply and waste w. treatment) as a proportion of personal net income [2] Source: Hungarian Central Statistical Office, 1999.*

age costs are very high. At the same time, the municipalities can only turn for support to national funding, which results in the choice of local treatment solutions, without a wastewater drainage system. Regulation of these treatment solutions is a current task at national level.

The EU-supported objectives of the National Wastewater Programme for 2015 are:

- By the end of 2015, level II (biological) sewage treatment must be provided in conurbations of between 10,000 and 15,000 PE, and by this time at the latest in conurbations of 2000-10,000 PE.
- By the end of 2015, artificial biological or equivalent treatment works must be set up in every wastewater drainage agglomeration smaller than 2000 PE *which lies in a designated hydrogeologically-sensitive area.*

The places where these developments have to be completed thus face crucial choices of sewage-treatment and sludge-management technology in the next five years.

Changing Reception of Sludge-Management Options

There have been major changes recently in processes and machinery for dewatering sludge. Processes which were difficult to operate or required much labour, such as sludge beds or simply spreading wet sludge on to agricultural land, have given way to mechanised technologies with high energy-consumption. Improvements in dewatering technology have achieved higher and higher levels of dry matter content, reducing the costs of transport and further treatment/recycling. The fashion for mechanised dewatering has even spread, somewhat irrationally, to the few hundred smallest-PE sites, even those serving less than 2000 PE. There are examples of this in neighbouring Austria as well as in Hungary.

Table 1. Distribution of Hungarian Population by Size of Town [4].

	Towns		Population	
Population	**Number**	**Proportion**	**Millions**	**%**
< 2,000	2,368	75.3	1.73	17
2,000–10,000	634	20.1	2.48	24
10,000–15,000	55	1.7	0.65	6
15,000–150,000	86	2.7	2.92	29
> 150,000	5	0.2	2.42	24
Total	**3,145**	**100.0**	**10.2**	**100.0**

The incineration of sludge as a primary source of energy is now widespread in Europe [5] In Hungary, despite encouraging experiments, the energetic use of sludge (in power plants or cement works) has been inhibited by factors which warrant an analysis of their own (cost factors and opposition from the energy lobby). By contrast, there are now several power-generating incineration facilities for domestic and industrial solid waste, although these have—if for different reasons—faced considerable struggles for social and political acceptance over the last two decades. An example is the waste incinerator planned at Heiligenkreuz on the Austrian side of the Austro-Hungarian border, which has become the object of protest in the Hungarian population.

Other important factors affecting the means adopted for wastewater treatment arose following the political transition in Hungary, as in other Central and East European countries.

The well-established arrangements for utilising sludge were upset by a change in agricultural land ownership. Agricultural land was divided up for compensation purposes, and this was enough in itself to inhibit the use of sludge in agricultural areas. Agricultural cooperatives cultivating several thousand hectares and employing qualified staff were capable of centralised control of sludge use. Although this was a rational use of the land, it was of no interest to most of the new owners, who mostly took possession of their small tracts for investment purposes.

Agricultural disposal offers the lowest capital-cost solution for sewage sludge [6] Sludge may be directly injected into the soil following thickening or used as a fertiliser after dewatering and appropriate storage. Composting is a more costly and higher-technology process. Production of compost is a tried and tested way of returning nutrients to the natural cycle. Aerobic thermal treatment also results in substantial disinfection, and the product is more suitable for storage and agricultural use. On the other hand, demand for compost among potential users is much lower.

There have also been developments in composting technologies. The changes have involved mechanised industrial processes in enclosed spaces—plastic sheeting or chambers—and procedures for accelerating the process. This has raised production costs. Marketing of compost has run into difficulties despite the increasing value of macro nutrients, primarily N and P, because of rising fertiliser prices. [7] The cost of nutrients which can be replaced by agricultural use of sewage sludge is over HUF 50,000 (€ 180)/ha [8]. Although the reasons for this should be investigated, the initial question is whether it is worth investing in composting technology if the final product is difficult to sell. If this solution is chosen solely because of the advantages in storage—such as smell and disinfection—the result will be higher treatment costs. The recycling of sludge could most probably be rendered economical by using it to generate biogas and using the residual decomposed sludge for agricultural purposes.

The final disposal of sludge still remains an unresolved issue despite the sudden proliferation of biogas plants. [4] The sludge left after extraction of biogas is stable and easily handled, but a means for disposing of it is still lacking. The low energy content makes incineration less economical, and there is a loss of phosphorus and other valuable macro and micro nutrients, and the recovery of phosphorous, which is otherwise transported on long distances, is essential from the resource-utilisation standpoint. [8]

In the western part of Europe, sludge is recycled for electricity generation through incineration in coal power plants or direct sludge-incineration plants [9 and 10].

Phosphorus is recovered chemically from ash remaining after mono-incineration of sludge. This yields plant nutrients after removal of heavy metals [11 and 12] The question remains, however, as to how economic this operation is. Due to the increasing phosphorus shortages, this will not be a question in 20 years' time, and it would do no harm to prepare in advance.

The process certainly has the advantage that the resulting phosphorus fertiliser has neither a chemical nor a psychological connection with sludge, and all barriers to agricultural use are removed. Could this be a potential solution? From a purely engineering standpoint, it is a safe and final means of using sludge, but its costs must be carefully assessed.

All of these factors have combined to greatly increase the cost of wastewater treatment. Sludge management costs have by now risen to the extent that, depending mainly on the size of the works, they account for nearly half the total costs of wastewater treatment. This statement is confirmed in the literature: "Sludge amounts to only a few percent by volume of processed sewage or wastewater, but its handling accounts to up to 50% of total operating costs." [13].

Climate Change and Reception of Wastewater Treatment and Sludge Management

The effect of climate change could be highly complex. Recycling of wastewater is becoming increasingly important to protect both water stocks and water quality. This has been noted by many authors. Here we quote a cogent argument:

> "One crucial climate-change issue is recycling of wastewater. This is likely to work through to be a major problem on a global scale in the foreseeable future. Sooner or later we will have to give up the idea that we just have to treat wastewater at some standard or other and then conveniently return it to the environment. Water that has been brought to the surface and distributed at great expense cannot be "thrown away" after use. Changing climatic conditions require us to "put it back into service." The form of recycling will be determined by local possibilities. Wastewater accumulates daily, whereas use for irrigation is seasonal, so that reservoirs will definitely be involved." [14].

Climate change is a new factor which could radically change the socio-political reception of sewage sludge use. Recycling of treated wastewater on agricultural land was widespread in Hungary in the 1970s and 80s, but for the reasons we have discussed it practically came to an end by the turn of the millennium. Climate change could give new momentum to this form of recycling.

Using treated wastewater for irrigation dispenses with need to remove nutrients, which are used directly in the soil before the water reaches the wider environment, and greatly reduces the quantity of sewage sludge [15].

Irrigation of traditional crops always involves restrictions for human health reasons. This problem could be avoided by use for energy crops and—to ensure reliable yields—for the production of seeds.

The antipathies to wastewater tend to evaporate in a heatwave, when water runs short. An interesting example is irrigation in Murcia in Spain, for which wastewater is transported 140 km. Irrigation for energy crops can reduce wastewater treatment costs, partly through revenue from the crops. It also contributes to CO_2 emission reductions. The procedure could usefully be subjected to lifecycle analysis (LCA). This need for LCA for both wastewater treatment and sludge management was discussed in a paper dedicated to energetic aspects [12].

Social and Political Changes

Figure 2 shows the political environmental factors affecting use of sewage sludge and how these factors interact.

The top row of the figure lists the spheres of activity where the factors take effect. Factors are grouped into those working in favour of recycling and those working against it. The diagram largely draws on experiences in Hungary, although it also incorporates wider European information in the area.

These factors are constantly varying in space and time. One side occasionally gains strength at the expense of the other, and in a way deforms the system. The conditions for finding the most appropriate solutions are when all of the factors are brought into balance.

This balance has not been achieved in the case of the new Budapest Central Wastewater Treatment Plant. Central Europe's largest wastewater treatment facility (350 000 m^3/d) was opened this year, but because of the many arguments and protests, there is still no definite solution for the disposal of sewage sludge.

One of the most striking phenomena arising from the political transition in Hungary is the disintegration of water utilities. The 33 town, county and regional utilities were split up into 400 very small entities, with an adverse effect on service quality. At the same time, foreign multinational companies have acquired various

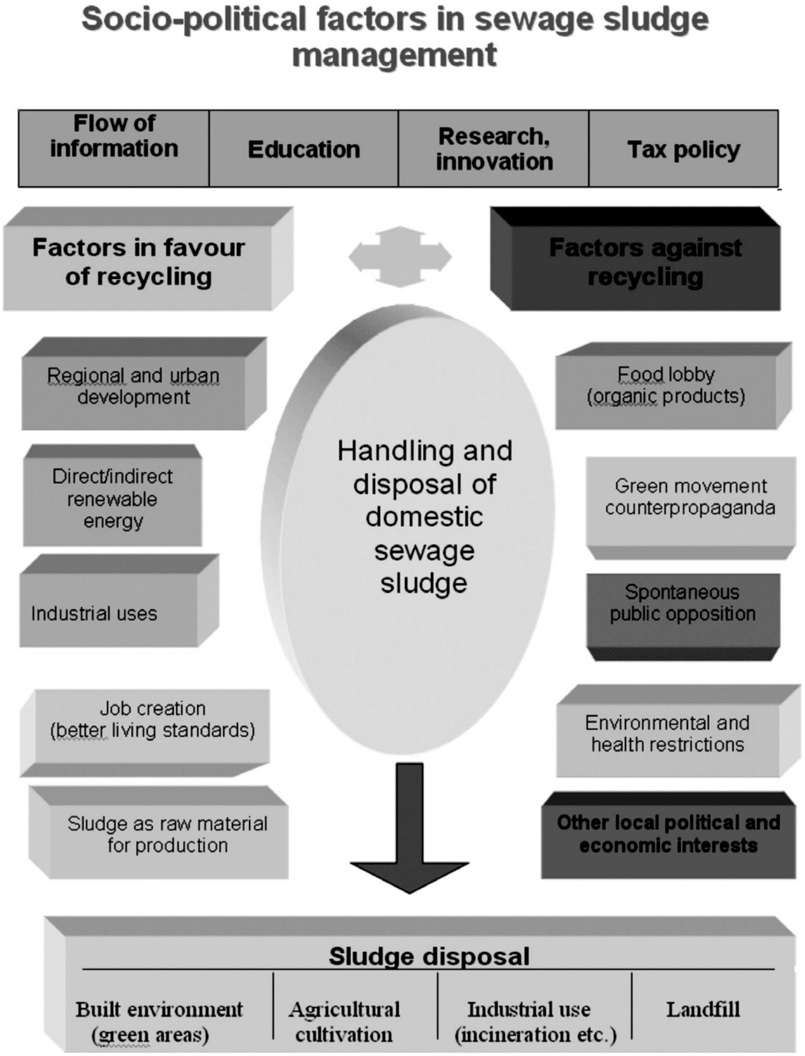

Figure 2. Socio-political factors in sewage sludge management.

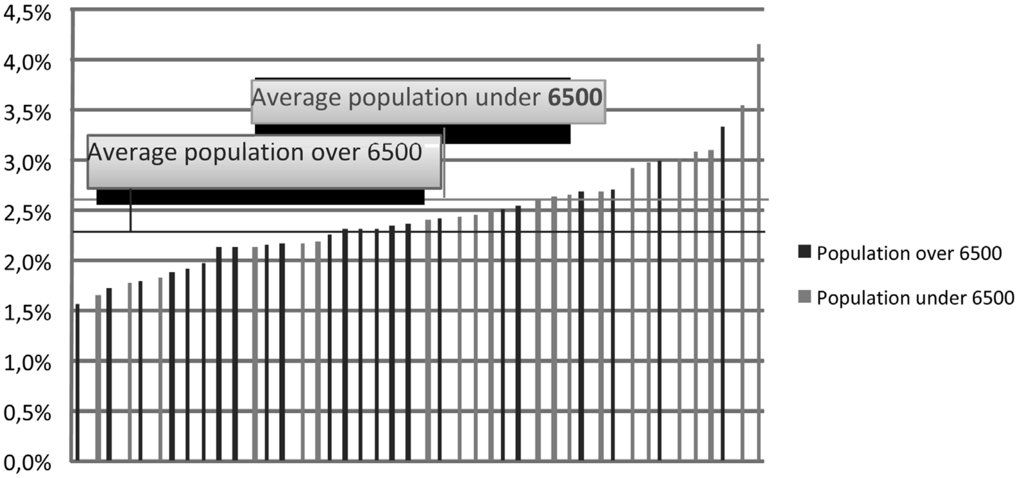

Figure 3. *Water charges as a proportion of income in towns with both services, by average population, 2009 [18].*

holdings in utilities serving Budapest and larger towns. These businesses have brought a new market-oriented outlook to the sector.

Concentration has now begun, and large utilities have in many places taken over smaller ones. There is an ongoing argument as to how far the water utility sector can go along the road to market orientation.

Some of these 400 water companies are now engaging in integration, with local authority support. Press coverage of some of these developments has reported threats to security of supply arising from political arguments [16].

Multi-stage sludge recycling procedures have now come to the forefront as perhaps the only way to implement both the energetic approach and recovery of nutrients (phosphorus).

Sludge management accounts for an ever-higher proportion of treatment costs—even up to 45–50% [17], but the setting of service charges is an increasingly political issue. The constraining factors arise from the nature of infrastructural facilities.

> "The stakes are much higher than the costs of facilities and the efficiency of their use. Facilities with long lifetimes dictate further developments after they are built. International experience shows that it is difficult to make changes to completed systems." [2].

The role of the government is to support recycling (agricultural, renewable energy, etc.) and bring environmental considerations into balance with economic and social factors (service charges, job creation).

Because of the growing costs of water supply service and sewage treatment, there was a significant growth in service charges in the last 20 years. Figure 3 shows that towns are more likely to be in the over-2.5% range if their population is less than 6500. These changes are a warning to take great care in selecting wastewater and sludge handling technology for smaller settlements, especially for villages of less than 2000 PE.

> "Figure 3 shows the average burden of charges among households connected to both the water supply and drainage in the service areas of different companies (water utilities). Each column corresponds to one company. The burden of charges for the two services together varies between 1.5% and 3.5% of income. For most companies, the figure lies between 2% and 3%, which is under the frequently-published threshold of 3–4.5%, but is considerably above the 2004 Central European average of 1.6–1.7%." [18].

CONCLUSIONS

This paper is an attempt to summarise changes in socio-political attitudes to sewage sludge management through a focus on the Hungarian situation.

Over the last 20 years, domestic water consumption has decreased, and with it the amount of wastewater to be treated. The quantity of contaminants has hardly changed, however, so that their concentration has increased and in turn resulted in higher unit quantities of sludge. This has adversely affected water utility companies, because wastewater charges in Hungary are billed on the basis of water consumption, not on the amount of wastewater. The increased costs have to be met from decreasing income.

The tightening of environmental regulations and the reduction in scope for agricultural utilisation were accompanied, or very quickly followed, by social demands which have increasingly directed public attention towards sewage sludge.

Although new technology has opened up the potential for treatment and recycling, the investment and operating costs are constantly rising. There is now no technical barrier to the exploitation of plant nutrients in the sludge; high-quality compost, for example, can be produced industrially, with a nutrient content that could enable partial replacement of artificial fertiliser. The marketing of these, however, is still very difficult.

There is a noticeable difference in the sludge recycling options taken up in the western half of Europe—the EU 12 countries—and the newer EU members. Here, thermal recycling, which is very widespread in the west of Europe, is almost totally absent. Acceptance of thermal recycling is not universal. A good example is Denmark's recent introduction of a tax on incineration of certain kinds of sludge.

Considering the potential of domestic sewage sludge as a primary energy source, and one of increasing quantity, there is a definite need to rethink its classification as "waste" (as in the EWC classification). Landfill must be regarded as a solution of last resort, to be avoided if at all possible.

The burden of regulation and restrictions have caused what is actually a useful secondary raw material to be regarded as waste to be got rid of. Climate change and energy scarcity are new challenges which could assist progress to a solution.

The role of the government is to support recycling (biogas generation, agricultural, renewable energy, etc.) and bring environmental considerations into balance with economic and social factors (service charges, job creation).

Consumers' decisions are clearly guided by both the level of charges and their own income. The response to both higher charges and lower income is lower consumption. Water consumption, however, cannot be reduced below a certain level; instead of (or as well as) holding back on water use, some consumers choose to pay their bills late or partially, if at all. [18].

We have come to the point in Hungary where service charges could hardly be further increased, this however could be a barrier to service improvements.

A positive improvement is that with EU support, biogas plants are launched for large-scale energetic valorisation of sewage sludge.

In Budapest and other large cities in Hungary, a final and satisfying solution to dealing with wastewater sludge could be co-incineration in thermal power plants or utilization in cement factories. In smaller towns and villages, valorisation in the agriculture is most promising.

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Sewage Sludge as Renewable Energy

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ABSTRACT: Organic sludge volume has been increasing since a while in European Union (EU)/Rest of the World (ROW) due to strengthened legal environment across the region, this process is specially observed in EU countries driven by major investment cycle since 1990 closing the gap in sewage treatment and supporting large foreign manufacturing capacity investments into their regions. The paper discusses different strategies for the disposal of sewage sludge, particularly the "traditional disposal/reuse" and "waste to energy" strategies. Recommends to apply full cycle for energy conversion to balance out the huge electricity usage under sewage treatment processes.

INTRODUCTION

A WASTEWATER treatment plant produces two streams, a stream containing treated wastewater and the other stream containing separated sludge from the wastewater. Both streams have requirements from authorities for discharges or uses for different purposes [1]. Requirements for wastewater discharges have successively been strengthened across the globe and more efficient treatment processes—physical, chemical, biological, novel Membrane Bio-Reactor (MBR), other—have been implemented in the past 30 years. The improved treatment efficiency also means that an increasing percentage of unwanted pollutants in the wastewater (as heavy metals, Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Bipheny (PCBs) and organic micro pollutants, pathogens like spores of Cryptosporidium and Giardia, Endocrine Disrupting Compounds (EDCs)) have been transferred into the sludge phase. Sewage sludge is the bulk of the residual material removed during the wastewater treatment process [2]. It is the solid, semi-solid or liquid residue generated during the treatment of domestic sewage, and is in fact an amalgamation of all the liquid wastes from society after aerobic biological treatment, it is not closely controlled so it may contain highly undesirable polluting trace contaminants.

Sewage sludge must be periodically wasted, removed, from a treatment works to prevent excessive biomass concentration in the system, or result in a pass through of sewage sludge to rivers or other surface waters. Sewage sludge can be composted and spread on a land. Regulations have been developed in all the developed countries to ensure that the public health and the environment are protected when sewage sludge is disposed of by each of the following accepted methods [3]:

1. application to the land as soil conditioner or fertilizer, agriculture usage
2. disposal to ocean (in the sea), (not permitted in the EU)
3. disposal on land by placing it in a surface disposal site (not permitted in the EU, to be phased out),
4. placing it in a municipal solid waste landfill unit (no longer permitted in the EU)
5. "bio-soils" production for sale in market place, composting, land reclamation, etc.
6. incineration (disposal to a certain extend in the air as consequence of incineration)
7. sludge to energy (newly applied novel technologies)

Sewage sludge is classified in different countries in different ways but for most of it falls into three categories according to application to land: unrestricted, restricted and unsuitable [2]. In many nations, sludge classified for unrestricted use may be applied in an unrestricted manner to all lands excluding sensitive sites, while those deemed unsuitable cannot be used outside the boundaries of the source sewage treatment plant. However, the rules are being tightened and it is becom-

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ing more and more difficult to spread sludge on land. The traditional sludge treatment technology is in general inefficient to remove toxic metals or micro pollutants from the sludge. Sewage sludge is produced from our wastewater plants in huge quantities day after day, year after year. Municipalities find themselves under never-ending pressure to get rid of the quantities produced. Spreading the sludge on a land is the cheapest solution, however, any wash-off during rain into watercourses is highly polluting and there are health concerns. Even if those are dealt with by, for example, injecting the sludge into the soil below the surface, there remains the danger of a slow and dangerous build-up of certain heavy metals in the injected soils.

Organic Sludge Volume Increase in the EU Region

Organic sludge volume has been steadily increasing over the past years in the EU/ROW due to strengthened legal environment across the region. This process specially observed in CEE countries driven by major investment cycle since 1990 closing the gap in sewage treatment and supporting large foreign manufacturing capacity investments into their regions. Table 1 compares the current and expected sludge production in USA and in some European countries.

Global production of sewage sludge is beyond of approximately 50M T dry solids/a, which amount enables to consider sewage sludge seriously as a special resource for conversion to renewable energy. In EU27 the current utilization of the sewage sludge is as follows: (1) Recycle to land, 42%; (2) Incineration, 27%; (3) Landfill, 14%; (4) Other, 16%; The expectation is for 2020 that the landfill ratio will be heavily decreased, Incineration will be slightly increased and other sludge to energy technologies will be promoted and get larger % of market share [5].

Table 1. Sewage Sludge Production in Different Countries [4], [5].

	Sludge Production Volume Tds/a	
Countries	**2010Estimate**	**2020 Estimate**
USA	**7,000,000**	**10,000,000**
Austria	273,000	280,000
UK	1,640,000	1,640,000
Scotland	200,000	200,000
Spain	1,280,000	1,280,000
Sweden	250,000	250,000
France	1,300,000	1,400,000
Germany	2,000,000	2,000,000
Italy	1,500,000	1,500,000
Romania	165,000	520,000
Portugal	420,000	750,000
Poland	520,000	950,000
Hungary	175,000	200,000
EU27	**11,500,000**	**13,500,000**

CURRENT STRATEGIES AND APPLIED TECHNOLOGIES TO HANDLE ORGANIC SLUDGES

Sewage sludge is a nutrient-rich organic material, about 60% of which originates from the sewers and up to 40% of which comes from the micro-organisms, or biomass, that grows during the treatment process.

The sewage sludge contains valuable nutrients essential to plant growth. In particular it contains significant amounts of nitrogen and phosphorus, typically 1–6% total nitrogen and 0.1–2% phosphorus, as well as some important trace elements such as copper and selenium [6]. Recycling sewage sludge to land is one of the most environmentally sustainable options, using it to improve land quality and diverting it from other routes, such as incineration or disposal to landfill. The practice of recycling sludge to land "The use on Land" is recognized by Governments as often being the Best Practical Environmental Option.

Generally the advanced treatment (Figure 1) includes stabilization (in order to reduce its biodegradability and its potential to cause nuisance), dewatering (in order to reduce transport cost) and includes sludge disinfection as well (in order to prevent health hazards). Environmental hazards caused by potentially toxic elements (i.e. heavy metals and specific organic compounds) are to be controlled by regulating limit values for concentrations of such compounds in the sludge to be used as well as in the soils where it shall be used.

Direct use of Sludge on Land as a Fertilizer and Soil Conditioner

Use of sludge in agriculture at present seems to be the most controversial sludge disposal route. In general taken the opinion, that present sludge quality with a large marginal can be safely applied on agricultural land, authorities across the globe have strengthened the maximum limits. Agricultural use of sewage sludge has the advantages of being inexpensive and is a logical way of eco-cycling of nutrients and to be used as a soil. Future use of sewage sludge in agriculture may, however, be diminished due to: (1) Risk assessments from

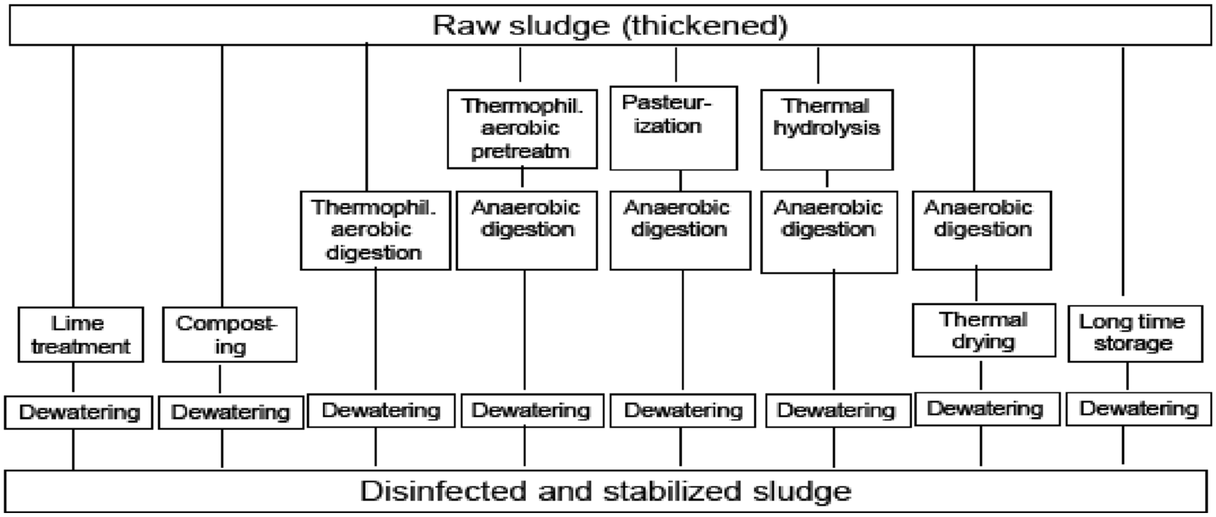

Figure 1. *Approved method for stabilization/disinfection in sludge [6].*

different organizations and researchers vary significantly indicating that scientifically based reports and evaluations should be made; (2) Many sludge analysis indicate that about 50% of the samples may have a too high concentration of at least one metal, while the concentration of the other may be significantly below the limit value; (3) Less sludge per ha will in many cases be the result of new values related to maximum metal supply as gMe/ha, year. The need to spread out sewage sludge over a larger area than before will increase the costs for sludge use in agriculture; (4) Costs for measuring limiting and guideline parameters are high; (5) Some uncertainties exist concerning the availability of phosphorus from chemically precipitated phosphorus; (6) Technical development may lead to competitive alternatives of eco-cycling to agricultural use; (7) Another sludge disposal route may be chosen by the municipality—even if the costs are higher than use in agriculture—in order to secure a safe and long range disposal of sludge; (8) The sewage sludge may—even if it has a very low concentration of pollutants—not be accepted by authorities, food industries and the public [1].

The last point is probably the most significant and the most difficult one to predict. In general, a lot of articles are published concerning emissions of organic pollutants in different fields including sewage sludge, injection agents in tightening tunnels, emissions from mobile telephones and effects on seals. Alarm from one field or finding a new organic pollutant may therefore adversely effect sewage sludge use in agriculture. It therefore seems necessary that a municipality should have at least one more route for sludge disposal than agricultural use [1].

Sludge as forest vitalizers or forest fertilizers has received a growing attention from forest companies and scientists. Sludge can be spread as dried sludge in pellet form on mineral soil to compensate for nitrogen losses due to soil acidification and intensive forestry. Pellets from ash may be used for peat land due to its phosphorus contents.

In the Member States of EU the agriculture usage of sewage sludge reaches 42% avg. and there are more than 7 countries within the EU27 where the usage is beyond 60% in agriculture [5]. New scientific evidence has been found relating to the human health and environmental impacts and the soil quality and fertility aspects of recycling sewage sludge to agricultural soil. A number of reports and risk assessments have also been published recently.

Disposal to Landfills or Special Deposits

As an alternative to the agricultural use of sewage sludge there are other practiced routes of disposal like: (1) Grinding together with solid wastes and disposal on landfill; (2) Disposal on landfill together with solid wastes; (3) Disposal on a permanent landfill of sewage sludge only. Although disposal on landfills may have increased during the last period due to recommendations to avoid sludge in agriculture, it seems reasonable to predict a decline in future due to: (1) Decisions made on forbidding to dispose any organic wastes; (2) Environmental concerns related to the release of methane gas (although a large fraction can be recovered) and possible release of phosphates into nature from the deposits; (3) Difficulties in finding new land areas or getting permits for the disposal.

Beneficial Use of Sewage Sludge in Site Restoration

Sludge based products and soil conditioners can be used on reclaimed land, parks, golf courses, green areas. Sludge can also be used as raw material for sealing and protect layers for final covering of landfills. Recycling sewage sludge to land restores derelict land to a useful purpose. The sludge can be used to stabilize spoil and other waste materials prone to erosion and to re-contour disturbed land, such as former collieries, to blend in with the surrounding landscape. Mixing sewage sludge in with colliery spoil and other materials that lack nutrients creates a growing medium capable of sustaining plant life. When applied to acidic colliery spoil, the sewage sludge provides organic matter that helps to balance the soil pH. The risk of heavy metals being mobilized and moving into groundwater or to watercourses is very low provided that the pH level is controlled.

Sewage sludge also contains major and minor nutrients, and valuable trace elements essential to animals and to plants such as boron, calcium, copper and zinc. The incorporation of sludge into other materials on derelict land produces a viable growing medium with good properties of soil structure, workability and moisture retention, all of which encourage vegetation growth.

Untreated sludge has a higher concentration of organic matter and slower release of nitrogen than treated sludge. This is valuable for after use such as forestry or short rotation coppice where slow release of nitrogen is beneficial to plant growth and more efficient than mineral fertilizers such as phosphate. It also helps to protect groundwater from leaching as the nitrogen is much less mobile or available. Organic matter may be between 15–20% and is a key component in its success as a soil conditioner [7].

The use of sewage sludge as a soil conditioner and beneficial source of nitrogen is well established in Europe and North America. It can supply nitrogen, phosphorus and some other essential elements, as well as organic matter which is useful in improving soil structure, drainage and available water capacity. All soils need these properties if they are to function effectively. Recycling sewage sludge to land has other societal values such as conserving landfill space for materials for which there are no viable alternatives and reducing the need for incinerators. It is sustainable process, allowing proper recycling of a waste material, full use of its inherent qualities and contributes to other environmental objectives such as the conservation of peat lands and mineral fertilizers.

Anaerobic Digestion, Thermal Drying and Advanced Anaerobic Digestion

This method is rapidly gaining popularity especially at medium-sized and large plants. The anaerobic step with subsequent dewatering is designed traditionally. Appropriate dryer design at right residence times combined with a temperature of 80–90°C results in compliance with the disinfection criteria. It is fair to say, however, that plant owners have experienced several operational problems, probably caused by insufficient competence at the suppliers regarding the sludge to be treated. It has also been dust problems of the very dry sludge (90% DS) connected to the handling and spreading of the dried sludge leading to the use of pelletisers in order to produce a user-friendly product. One may question whether or not sludge drying as such is a sustainable process as it is very energy consuming. Drying can only be defended when full utilization of the energy potential from the biogas production is utilized. From an energy point-of-view one may argue that incineration is more sustainable than drying since the heat value of the dry solids itself is utilized in incineration. However, the positive soil conditioning/fertilizing value of the sludge is lost through incineration. Drying/incineration is also an option even if biomethanation is not realized.

At a time of heightened concerns about waste, climate change and the need for cleaner energy, it is worth pointing out that not all the news is bad. Technologies are redressing the balance—and one of these is Advanced Anaerobic Digestion (AAD). These technologies harness natural oxygen-free decomposition by which organic materials break down to produce biogas—roughly made up of 65% methane and 35% carbon dioxide—along with a much reduced residue of stabilized organic material. The latter can be safely deployed as fertilizer. In fact, by returning it to the soil in this way, nutrient and organic matter cycles that occur naturally are completed. There are two main predigestion processes used in AAD; (1) thermal hydrolysis (the Cambi process) or (2) enzymic hydrolysis (the Monsal process) [8].

Regardless of which process is used, the key to the AAD process is a phase that significantly enhances the breakdown of organic materials by, for example, breaking down cell walls. With thermal hydrolysis this is achieved by an initial high temperature of 165°C combined with high pressure (6 Bar) for less than one hour, or with enzyme hydrolysis this is achieved by phasing an increased temperature from 42°C to 55°C over several days. The result is a far greater conversion of organic matter into biogas when the material is transferred into the anaerobic digestion phase [8]. Following this digestion phase, there is a 50% reduction in sludge volumes, combined with the additional biogas/CHP—derived energy being produced, and ultimately a better quality bio-solids fertilizer. One of the major benefits of this, of course, is that energy from biomass, including sewage sludge, is classed as renewable and therefore contribute to meeting international commitments to address climate change.

The process that the AAD plant facilitates is not only environmentally friendly, it is economically attractive too. The plant approaching energy self-sufficiency not only reduces costs, it also shields the wastewater treatment plant from the impact of volatile and unpredictable energy prices. It further offers demonstrable operational cost savings and improves the efficiency of sludge management throughout the region .In addition to the ever-important cost benefits, there are also significant operational benefits. It continues to allow the utilization of existing sludge assets where cost effectiveness has been demonstrated and the current sludge drying facilities will be retained as a strategic contingency back-up.

Addition of other organic materials such as food or abattoir wastes, to the digester can increase the volume and quality of gas yields. However, the process must then comply with additional regulation, such as the EU Animal By-products Regulation (EC 1774/2002), which may involve fitting additional units, such as pasteurization units, to existing facilities. Application of residual sludge to land may also be restricted if it contravenes the EU Sludge Directive [9].

SEWAGE SLUDGE AS RENEWABLE ENERGY

Renewable Energy

The globalization and localization of technologies and manufacturing capacities with the high speed of energy consumption growth gives foreseeable limitation for fossil based energy resources. In spite of the significant innovation results at energy efficient product launches—as per researchers—the earth possesses enough fossil resources for a maximum of couple of decades.

The strategy of the energy management of EU foresees significant changes in the near future forcing the Member States to achieve 20% of renewable energy ratio by 2020. The EU 20-20-20 Directive obliges each EU Member States to comply with directives choosing—as per local possibilities—renewables as alternatives to fossil energy in the upcoming investment cycles.

Global renewable energy distribution as per actual status, market share: (1) Wind, 40% ; (2) Hydro, 32%; (3) Biomass, 19%; (6) Sewage Sludge to Energy, < 3%; (2) Solar PV, < 1%; (3) Solar Concentrated, < 1% ; (4) Geothermal, < 1%; (5) Tidal, < 1% ; (7) Solid Waste Landfill Gas to Energy, < 1%; (8) Others, < 1%.

As an example, we should look at the Member States of EU and compare the ratio of the renewable energy in different States vs. national energy mix. Results show large discrepancies due to available natural resources and geographical & topographical positions. Countries with the largest ratio demonstrate huge "Hydro" energy investment and usage. The most beneficial users are Austria 70.4%, Sweden 46.4% Luxemburg 27.0%, Italy 19.6%, Portugal 19.5%. The most unbeneficial are England 2.4%, Belgium 1.9%.

Significant investment are under execution and the next 20 years will elevate many countries to the much higher level, as per expectations and latest estimates by 2020 the following levels will be reached by countries: Greece 18%; Germany 18%; Ireland 16%; UK 15%; The Netherland 14%; Czech Republic 13%, Slovakia 14%; Hungary 13%; Cyprus 13%; Malta 14%; Belgium 13%; [10]

Organic Sludge as Potential Source of Energy

Sewage sludge can also be used to produce renewable energy, which reduces our impact on climate change. Sewage sludge is an inevitable and unavoidable by-product of sewage treatment. The amount produced is massive and is also expected to rise rapidly in Europe in particular, mainly as a result of the higher treatment standards provided through the EU Commissions, gap closing actions in CEE past and future 20 years. Sewage sludge is a renewable, negative-cost organic material that is well suited for the energy production via different processes and methods.

The potential for renewable energy generation from sludge on a national level is approximately 50M T dry solids/a converted to energy. Access to inexpensive, renewable energy will become even more important because the cost of sewage treatment is bound to rise. Electricity from sewage sludge isn't entirely free of course, but the feedstock is free through the generous contributions of numerous small donors. With the addition of solar energy installations and other renewables at treatment plants, sewage-to-energy could at least help keep costs manageable.

There are well-established renewable energy options, such as biogas, and novel technologies, such as gasification, for sewage treatment. Many need further investment and research. Figure 2 shows how large capabilities the sewage sludge has as a renewable energy resource, focuses mostly on agriculture industry, gasification, incineration and other possible conversations are not depicted.

Applied Technologies for Energy Production

Sludge Incineration

Incineration is a technically well-proven technology that is used at many places for instance in Europe and worldwide. Treatment of exhaust gases and handling of ashes can be done in an environmentally safe way but this is complex and thereby expensive and at present mainly suitable for large plants. The use of incineration is predicted to increase in the EU-countries as it may be regarded as an "end-of-pipe"-solution [6]. Ecocycling may, however, be partly achieved if resources as phosphorus are recovered before or after the incineration process. The ashes produced after processing may be used for instance in the building industry. Incineration in air at atmospheric pressure is the most common oxidation technique currently practiced. However, incineration meets increasing opposition from the public concerned about dioxin production and toxic ash. The ash from incineration is usually treated as hazardous and therefore requires disposal at hazardous landfill. As landfill costs are increasing year on year, this places increased pressure on costs of incineration. The current level of incineration in EU27 reaches 27% and there are Member States like The Netherland or northern Belgium where 100% of the sewage sludge is taken to incineration [5].

Biogas Production

Biogas production from sewage sludge treatment,

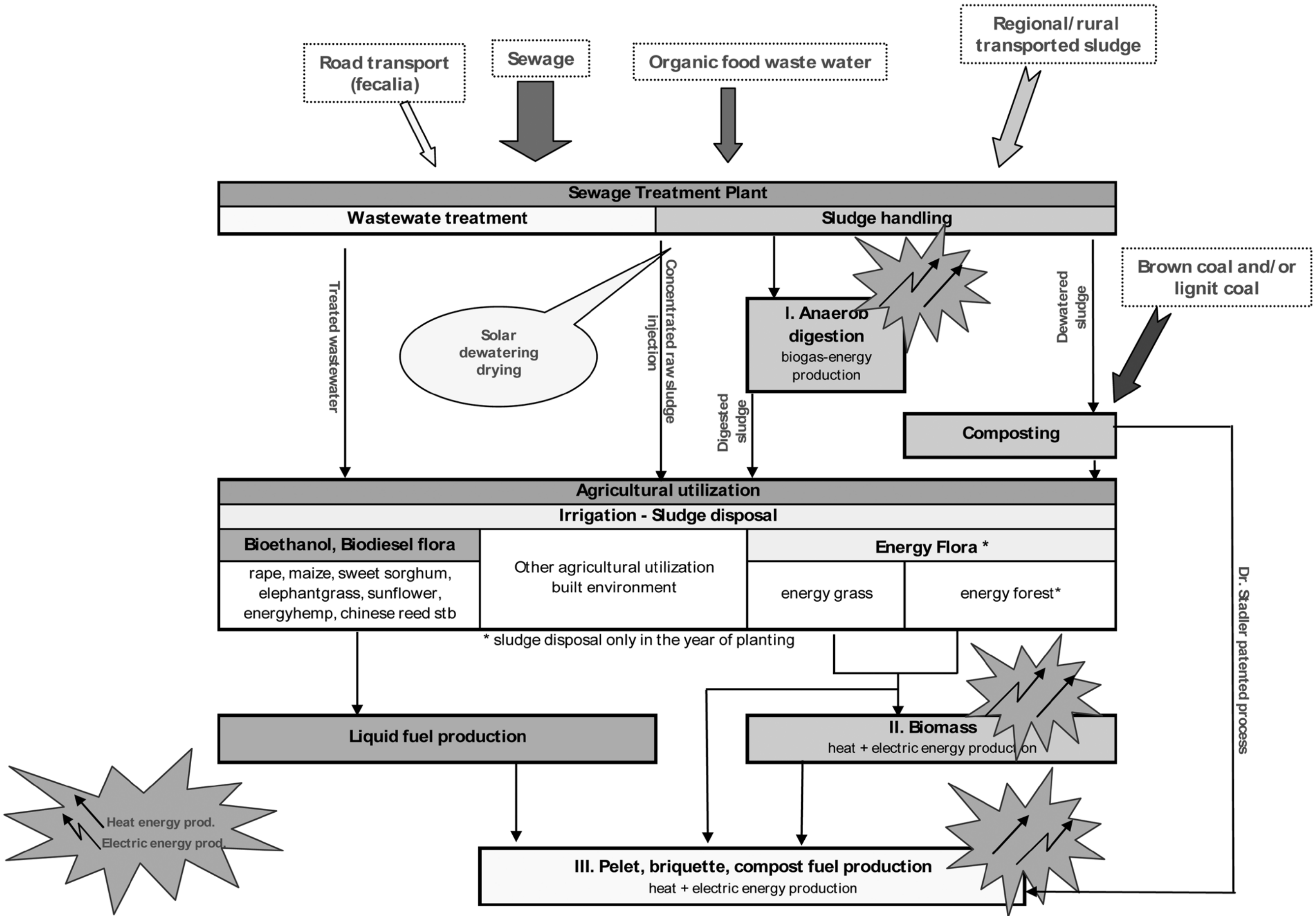

Figure 2. *Multiple-stage energy utilization of sewage and organic sludge [10]. Source: Endre Juhász dr. publication, 2007.*

via a process of anaerobic digestion, is already a well-established means of generating energy across the globe. Bacteria use organic matter in sludge to produce a mixture of methane (60–65%), carbon-dioxide (35–40%) and trace gases. Impurities, such as hydrogen sulphide and water, are removed and the resulting biogas is then commonly used in boilers or combined heat and power (CHP) systems [49]. For example, anaerobic digestion facilities are being developed at many sewage treatment plants that will provide 90% of the site's power via CHP. Biogas may also be used for other applications, such as vehicle fuel, if CO_2 is also removed. In Sweden, trains, buses, taxis and some private cars run on biogas. Anaerobic digestion also reduces the solids content of sludge by up to 30%, reducing the energy costs involved in its transport [49]. Millions of m^3 of methane in the form of swamp gas or biogas are produced every year by the decomposition of organic matter, both animal and vegetable. It is almost identical to the nature gas pumped out of the ground by the oil companies and used by many of us heating our houses and cooking our meals. Many countries have for years been steadily building anaerobic digestion facilities generating electricity from methane produced from manure, sewage and garbage.

The potential of biogas is enormous, 1 People Equivalent (PE) = 0,025 m^3/d (where CH4 app. 70% = 24 MJ/m^3). From the mezophilic digestion 1 kg DS sludge produces approximately 0.7–0.8 m^3 biogas, from the thermophilic digestion 1 kg DS produces app. 0.9–1.1 m^3 biogas. 1 m^3 biogas is app. 24 MJ energy which could generate app. 1.8–2.2 kWH/m^3 electricity. Assuming a global sludge volume at 50M T DS/a would give theoretically 121 TWh/a electrical energy via biogas production. Hungary as a country consumes annually around 40 TWh as an example, the 121 TWh would enable to serve 3 countries of the size of Hungary [10].

Innovative Technologies to Handle Sewage Sludge

There is interest in the new innovative technologies as potential alternatives to incineration of sludge and/or anaerobic digestion. However, operational costs are high, particularly those of maintaining high temperatures, and conditions must be controlled to prevent formation of harmful by-products.

Supercritical Water Oxidation of Sewage Sludge

A Super Critical Water Oxidation System (SCWO) will oxidize aqueous streams containing organic material in relatively low concentrations. SCWO is an exothermic process and is autothermal at just 3% organic content in the waste stream. When the organic content within the waste stream is in excess of 3%, the excess energy may be utilized to generate electricity and heat. The heat can be utilized to generate steam and hot water, which can find application in sludge thermal hydrolysis and or anaerobic digester heating requirements [11]. Oxidation of organic wastes to carbon dioxide, water, and other small molecules can effectively minimize waste volume and detoxify many hazardous compounds. SCWO destroys all organic wastes containing any combination of elements. Low biodegradability or high toxicity has no effect on suitability for treatment by SCWO. Technology owner have determined that organic concentrations of 3 to 10% with a total solid content not greater than 20% at 540°C is the most efficient range for treatment.

Supercritical water oxidation is an innovative, economic and effective destruction method for organic wastewater and sludge and is a realistic alternative to conventional methods. The results achieved show that the technology easily gives 99.9% destruction of the organic material in the sludge and the inorganic material left in the effluent is non-leachable and is very easily settled. The very encouraging results indicate that the sewage sludge treatment technology is ready to be commercialized.

The process offers complete mineralization of sewage sludge (Figure 3), the potential for renewable energy generation, and has the potential to significantly reduce the carbon foot print of the sewage sludge. Monitoring the market, a few technologies are available under the trademarks of e.g. AquaCritox® and Athos™. The AquaCritox® technology from SCFI offers a further benefit that there are no further toxic/hazardous residues requiring disposal and offers the option of recovering phosphorous and coagulant from the inert residue. The process is robust. Cost of sludge treatment will normally be in the region of \$39–\$78 per ton of sludge cake [11].

Athos™ is a new process combining HTO with biological treatment, which mineralizes the organic matter in the sludge under moderate conditions of temperature (235°C) and pressure (45 bar) in the presence of pure oxygen. Sludge is combined with an oxidizing gas (oxygen) which degrades its organic materials. The oxidation of sludge's organic matter produces water, carbon dioxide and easily biodegradable organic compounds. The gases released during the operation are

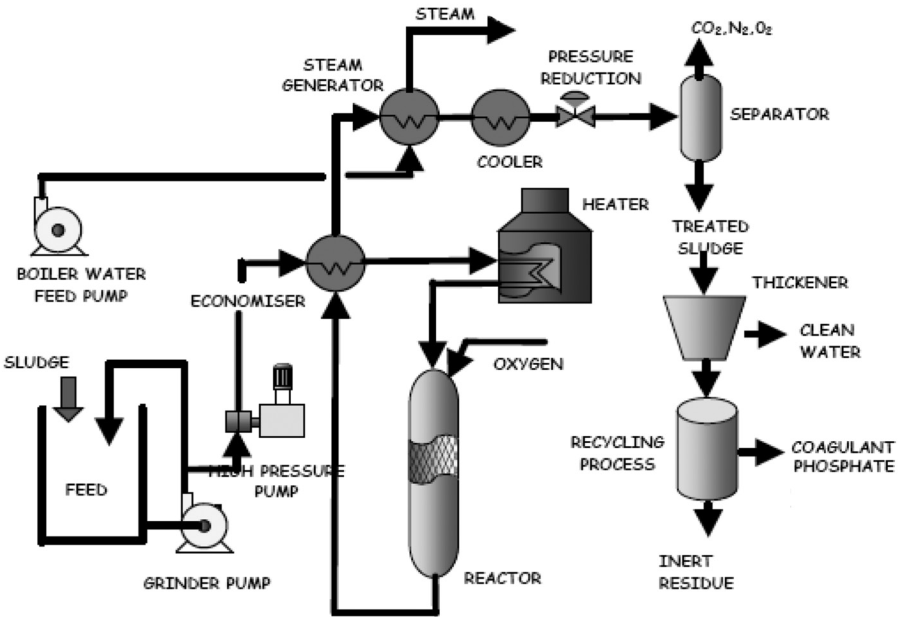

__Figure 3.__ Aqua Critox® process schematic [11]. Source: J O'Regan, S. Preston. A. Dunne: Supercritical Water Oxidation of Sewage Sludge.

released into the air following specific treatment. Thus, an ATHOS reactor adapted to a population of 30,000 does not pollute more than a big truck. In addition, the heat released by this process is recovered to pre-heat the sludge, thereby reaching a thermal balance! Oxidation residue is a solid mineral which can be recycled in ceramic production processes (roof tiles, bricks, tiles etc.).

Krepro—A Sludge Treatment Scheme Aimed at Recycling

Another innovative strategy is to recycle products from sludge that can either be used in-plant or sold to the open market. The KREPRO process outlined is one example of a treatment/recycle system. The ambition of this process is to recycle the following "products"/components; (1) biofuel for energy production based on incineration; (2) precipitant to be recycled within the treatment works; (3) phosphorous to be recycled in agriculture; (4) carbon source for N-removal recycled within the treatment works [6].

Conversion of Sewage Sludge to Oil and Gas

Under carefully controlled conditions and extreme

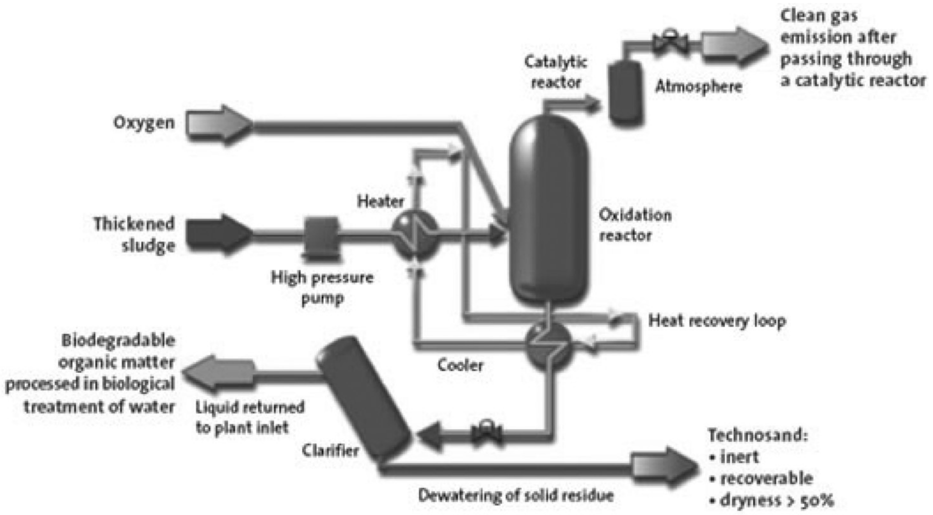

__Figure 4.__ Athos™ process schematic [12].

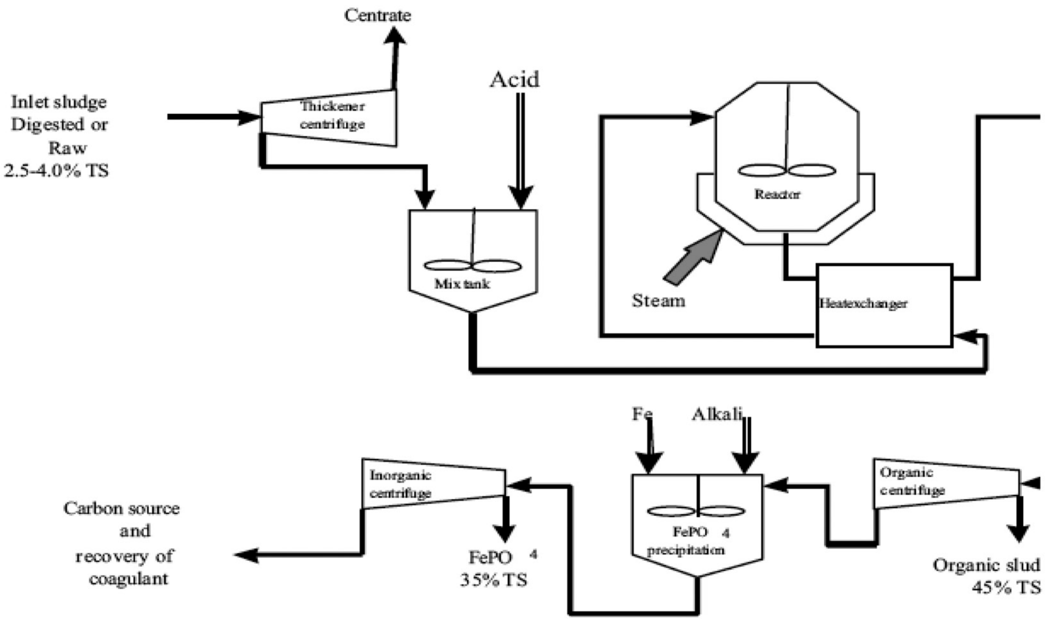

__Figure 5.__ Principle of the KREPRO-Kemwater Recycling Process [6].

temperatures (450–1000°C), sludge may undergo chemical reactions to produce fuels that may be used for energy production. The new innovative processes include gasification, which produces syngas (similar to natural gas), and pyrolysis, which produces bio-oil (similar to diesel oil).

The process of gasification is the conversion of a combustible solid into a synthesis gas [13]. The heat energy released from the sewage sludge fuel provides the dryer with the necessary heat to evaporate the water from the sludge (Figure 5). The solution for sewage sludge is to take the sludge at 25% solids into a sludge dryer, either indirect and direct dryers will work, and further reduce the moisture content of the sludge while producing a sewage sludge renewable energy fuel for a gasifier. This sewage sludge fuel will provide 100% of the thermal energy necessary to operate the sludge dryer. The only additional energy used in this whole process is the electricity needed to run the electric motors and controls. The beneficial use of dried sewage sludge as a renewable energy source destroys sewage sludge and is not just a method of disposal. This process is sustainable without the addition of supplemental fuel. This elimination of a conventional fuel source reduces the cost of operations and will compare favorably with current operational costs.

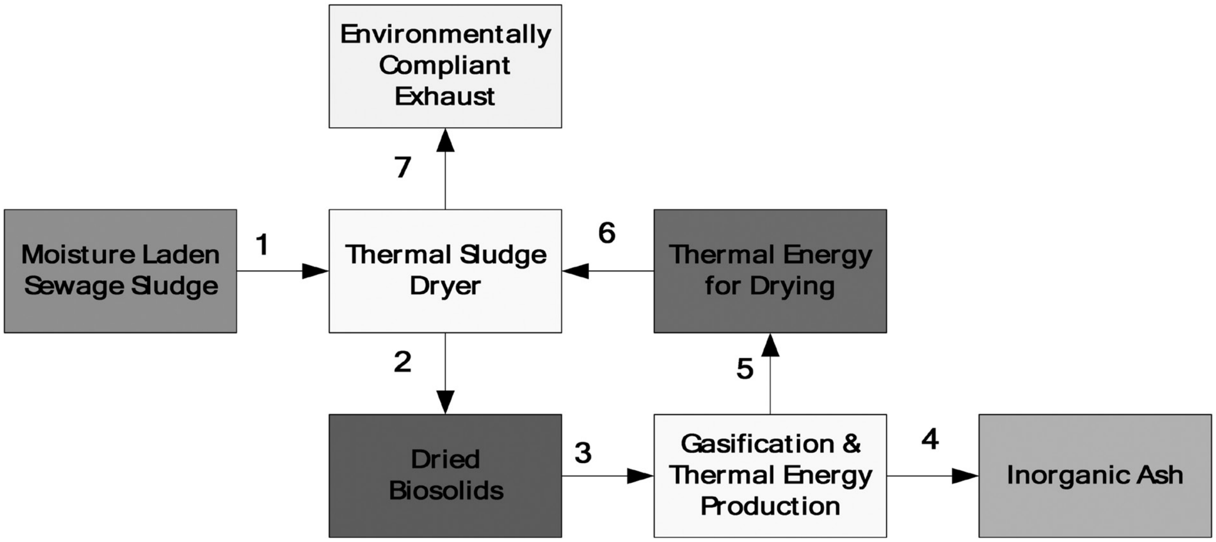

__Figure 6.__ Sludge Gasification Process [13]. Source: Primenergy, A Safe Alternative.

Gasification of sewage sludge is becoming a very popular method for disposing of the organic sludge from sewage works. Many municipalities responsible for sludge disposal have turned to the benefits of gasification, and a small but well experienced industry is starting to form to use that sludge. These new companies are developing gasification technology to generate heat and power, and from gasification will also come useful gas (syngas), which can be used as a raw material for the production of many chemicals which have until now only been produced from non-renewable carbonaceous sources [2].

Biohydrogen from Sewage Sludge

Hydrogen is now universally accepted as an environmentally safe, renewable energy carrier and an ideal alternative to fossil fuels that doesn't contribute to the greenhouse. Since, production of hydrogen from fossil fuels and by other conventional means is concurrent with CO_2 generation, biological production is considered as an efficient alternative [14]. Furthermore these techniques are well suited for decentralized energy production in small-scale installations in locations where biomass or wastes are available, thus avoiding energy expenditure and costs for transport. Renewable sewage sludge can be used as substrates for biological H_2 production facilitating both bioremediation and energy recovery. The feasibility of fermentative H_2 production from organic wastes or wastewaters has been widely demonstrated by various laboratories. Hypothetically, development of technology for conversion of waste to molecular hydrogen has the potential to address the several economic and environmental issues. Sewage sludge is an important renewable biomass energy source, which unlike others can be more harmful to the environment if not utilized or properly disposed. The high nutrient content makes it an ideal consideration as fermentative substrate especially in biological hydrogen production.

Biological hydrogen production potential of a defined microbial consortium consisting of three facultative anaerobes, *Enterobacter cloacae*, *Citrobacter freundii* and *Bacillus coagulans* was studied [14]. Through biological hydrogen production process microorganisms can recover and concentrate the energy from high water content organic resources such as waste effluents and sludge in a usable form. So, biohydrogen production in a sense is an entropy reducing process, which could not be realized by mechanical or chemical systems. The hydrogen yield from pretreated sludge obtained in one of the studies (35.54 ml H_2/g sludge) has been found to be distinctively higher than the earlier reports (8.1–16.9 ml H_2/g sludge). Biohydrogen production from renewable substrates is a promising element in the sustainable hydrogen economy. Different pretreatment techniques coupled with optimal dilution and supplementation is an attempt in this direction. However, yields to date have been low, typically less than 15% of the maximum theoretically possible. Co-digestion, whole cell immobilization and process optimization should prospectively help in attaining the critical yield value that can upgrade the process for commercial exploitation.

An experimental study was conducted using a pilot scale (5 kWe) throated downdraft gasifier [15]. Substantial amount of hydrogen gas could be produced utilizing a renewable biomass source such as dried and undigested sewage sludge pellets by applying air blown downdraft gasification technique. The product gas obtained mainly consists of H_2, N_2, CO, CO_2 and CH_4 with a maximum average gross calorific value of 4 MJ/m^3. Around 10–11% (V/V) of this product gas is hydrogen which could be utilized for fuel cells. Sewage sludge can be assumed as an alternative renewable energy carrier to the fossil fuels, and the environmental pollution originating from the disposal of sewage sludge can be partially reduced.

Conversion of Sewage Sludge to Biomass Crops

Sewage sludge is applied as fertilizer to willow plantations. The trees are periodically coppiced and the wood used for fuel [9]. Research into applying partially-treated, liquid sewage to biomass crops is also underway [16]. Passage of the sewage through the soil acts as a final polishing step for treatment, degrading organic matter, reducing nitrogen and phosphorus and producing a cleaner effluent. Little energy is required and capital/operational costs are low. Appropriate land must be available for applying the process.

Sewage Sludge Carbonization

There is an increased interest in the use of biocarbons for soil beneficiation and carbon sequestration (i.e., "Terra Preta "Application), the aim of the application is to produce of sewage sludge charcoal for land application [17]. By use of the flash carbonization process sewage sludge charcoal yields near 30 wt% and fixed-carbon yields near 18 wt% from sludge with moisture contents near 7 wt%. Low level heavy metals content sludge based charcoal was found acceptable for land application according to U.S. EPA regulation.

Simultaneous Sewage Treatment and Energy Production, Microbial Fuel Cells

These devices offer the possibility of simultaneous sewage treatment and energy production, with water, CO_2 and inorganic residue as by-products. Bacteria use organic matter to produce electricity. To date, lab-scale microbial fuel cells have been developed that are able to power small devices [9].

Biodiesel from Sewage Sludge

Existing technology can produce biodiesel fuel from municipal sewage sludge that is within a few cents a gallon (1 US gallon = 3,785 liters) of being competitive with conventional diesel refined from petroleum. Demand for biodiesel has led to the search for cost-effective biodiesel feedstocks, or raw materials. Soybeans, sunflower seeds and other food crops have been used as raw materials but are expensive [4]. Sludge is a good source of raw materials for biodiesel. To boost biodiesel production, sewage treatment plants could use microorganisms that produce higher amounts of oil. That step alone could increase biodiesel production to the 10 billion gallon mark, which is more than triple the nation's current biodiesel production capacity in US, the report indicates. To realize these commercial opportunities, huge challenges still exist, including challenges from collecting the sludge, separation of the biodiesel from other materials, maintaining biodiesel quality, soap formation during production, and regulatory concerns. With the challenges addressed, biodiesel production from sludge could be very profitable in the long run. Currently the estimated cost of production is $3.11 per gallon of biodiesel. To be competitive, this cost should be reduced to levels that are at or below (recent) petro diesel costs of $3.00 per gallon. [4]

FACTORS INFLUENCING FUTURE SLUDGE HANDLING STRATEGIES

Many of the factors that will influence future levels of sludge production and of sludge handling strategies are uncertain. The analysis identified among the key uncertainties the following factors: the development of treatment technologies for sludge; public perceptions, acceptance of sludge recycling to land; future demand and supply of mineral fertilizers; and future risk assessments related to sludge (as well as public and political reactions to their results), a broad range of EU, national and sub-national legislations, economical, environmental and social incentives being implemented by nations.

Legislation

The policy background in EU that applies to the controlled use of sewage sludge originates in European Union environmental policy. This takes effect through European Community waste legislation (the waste framework directive (WFD), Council Directive 75/442/EEC has been revised twice since 1975, firstly in 1991 and then again in 1996), which covers beneficial use of materials classified as ‘wastes’, such as compost, sewage sludge and recycled materials [7]. The waste legislation also ensures that all wastes are tracked from the point at which they are first generated to their ultimate disposal and encourages reuse and recycling. The European Union places great emphasis on the proper management of waste, in order to protect the environment, public health and the welfare of its citizens and to ensure effective functioning of the internal market of the EU. In each EU country standards are set by the environmental regulator and are informed by European directives, national legislation and local water quality objectives. The EU directives reinforces the concept of ‘waste’ being part of a cycle of use where natural resources must be used efficiently, waste minimized and properly dealt with, all as part of a sustainable natural cycle [7]. The EC Bathing Water Directive (76/160/EEC and recently revised in 2006/7/EC) aims to protect public and environmental health from faecal pollution at bathing water sites. Managing and/or processing other organic materials such as food or abattoir waste must then comply with additional regulation, such as the EU Animal By-products Regulation (EC 1774/2002), which may involve fitting additional units, such as pasteurization units, to existing facilities. Application of residual sludge to land is directed by the EU Sewage Sludge Directive.

The EU Sewage Sludge Directive was adopted more than 20 years ago with a view to encourage the application of sewage sludge in agriculture and to regulate its use as to prevent harmful effects on soil, vegetation, animals and humans. In the light of the increased production of sewage sludge across the European Union with the implementation of the Urban Wastewater Treatment Directive, and recognizing the need to assess recent scientific research on the reuse of sludge in agricultural soils, the European Commission is currently considering whether the current Directive should be revised [5].

Economic, Environmental and Social Incentives

Usually the analysis of the economic, social and environmental impacts of different sewage sludge handling strategies are a very complex task and the outcome heavily depends on detailed evaluation of costs and benefits and geographical position of the given country. Nevertheless, the major drivers for future handling strategies are the economic and environmental incentives. There is always a fine balance between the economical drivers and sustainability using the best available technology.

Public Concerns, Acceptance

It is well recognized by parties involved in the sustainable recycling of sewage sludge for beneficial use that the general public may have concerns and perceptions that cause them unease. Most of the issues causing public concern relate to matters such as the immediate and direct impact of odour and traffic movement in the vicinity of communities or to general issues such as pollution [7]. Dust and noise nuisance are also raised as matters of concern although neither odour, dust, noise nor traffic movement are normally considered to have a direct impact on public health. The issues related to sludge quality are principally those of environmental pollution, the effect of chemicals in sewage sludge and pathogen transmission. All of these are valid considerations even although they are well recognized and controlled by various methods. Proper risk assessment of specific sites is necessary ensure that the correct amount of sludge is used.

The problem of potentially toxic elements (PTEs) in sewage sludge has been recognized for many years. PTE is a generic term for the wide range of metals that originate in sewage, such as cadmium, copper (from plumbing systems), nickel, lead, zinc (from cosmetics), mercury (from dental amalgam) and chromium. Sewage sludge may also contain a number of volatile organic compounds such as benzene, tetrachloroethylene, toluene and xylenes. These originate from trade effluents and urban drainage. Other organic contaminants in sludge include phthalates, phenols and polycyclic aromatic hydrocarbons as well as surfactants from detergents. Although these compounds present a potential toxicity hazard, most of them degrade quickly in aerobic soil.

It has always been recognized that sewage sludge does contain pathogens such as bacteria and viruses. Most of the pathogens decay naturally through time. It is important to note that there are no reports in the scientific literature that link human health problems to the use of sewage sludge on land, either for agricultural purposes or land reclamation. Significant environment or health risks linked to the use of sewage sludge on land in the EU have not been documented in scientific literature since the Sludge Directive took effect.

General view of public is based on environment quality goals for a poison-free environment; (1) Pollutant levels should be near background values, (2) Pollutant levels should be near zero for substances unfamiliar under natural conditions, (3) Effective limitation of most dangerous pollutants; for metals mercury, cadmium and lead and for organic micro pollutants compounds as PCB, dioxines and dieldrin, EDC’s. (4) Systematic work to reduce other harmful substances, (5) Increase Sludge to Energy policy and strategy to move toward clean solutions.

Technology Development

The need to solve sewage sludge problems has induced different technical developments. One direction is to improve the sludge properties to facilitate further sludge handling, another direction is to find methods to diminish the produced sludge, a far- reaching technology for sludge use is fractionating of the sludge into products and with possibilities to remove toxic metals in a small stream. The general goal is to innovate and implement novel processes with sustainability concepts, to pursuit sustainability including ecocycling, critical loads, the precautionary principle, the substitution principle, best available technology and the polluter-pays principle. The goal of the poison-free society remains and drives the R&D activities.

FUTURE TRENDS

The Water-Energy Relationship

Energy is used to abstract, treat and distribute drinking water; collect, treat and discharge sewage and manage sewage sludge [9]. Data shows that in developed countries the actual energy intensity of each step of the water cycle is very high. The energy required to treat sewage to the best available technology standard is high, the water industry is in the five most energy intensive sector. Some options for EDCs removal from sewage, such as oxidation using ozone, disinfection of sewage with ultraviolet (UV) radiation, etc. are extremely energy intensive. There is no doubt that the demand for water increases in the next 30 years, so does the total amount of energy needed to complete the cycle. Therefore, the efficient use of both water by consumers and energy by the water industry can provide energy benefits. Worldwide expectation for demand increase is very high, for electricity 2 fold and for water is 3 fold till 2030.

Maximize the Value of Biogas

Many analyses proved that the use of biogas for CHP generation for on-site use would, usually, achieve the best worth for a water company. CHP is a matured technology with proved commercial benefits and the best systems can convert up to 40% of energy contained in biogas into electricity. Conversion of biogas to biomethane makes accessible all of the applications of natural gas including injection into the nation's gas grid or use as an automobile fuel. With new developments in hydrogen technology the sewage biogas will be converted economically to hydrogen. Utilization of biogas as a fuel for cars also achieves a comparatively high worth and, in some circumstances, higher than that achieved for biogas CHP. It brings ecological benefits compared to standards fossil auto fuels.

Decrease Sewage Sludge Volume by Novel Membrane Bioreactor Processes (MBR)

The term MBR simply means a connection of conventional suspended growth biological treatment and membrane filtration equipment for liquid/solid separation to retain the biomass. The commonly used membrane types in MBRs are low pressure membranes like MF or UF. In conventional sewage treatment, the final sludge separation is done in the secondary clarifier, but since the pore sizes of the membranes are below 1 μm, MBRs produce a clarified effluent without the need for secondary sedimentation (Figure 7). The elimination of final clarifiers reduces the plant footprint area; the elevated biomass concentration in the aeration tank reduces the sludge production and increases the efficiency of the biological treatment to remove organic matter, nitrogen and phosphorus [18].

Retention of biomass by the membranes allows elevated biomass concentration in the aeration tank, which means that the amount of sludge to be disposed of in the MBR process is smaller than in conventional sewage treatment plant.

CONCLUSIONS

1. Sewage sludge is an inevitable and unavoidable by-product of sewage treatment [2]. The amount

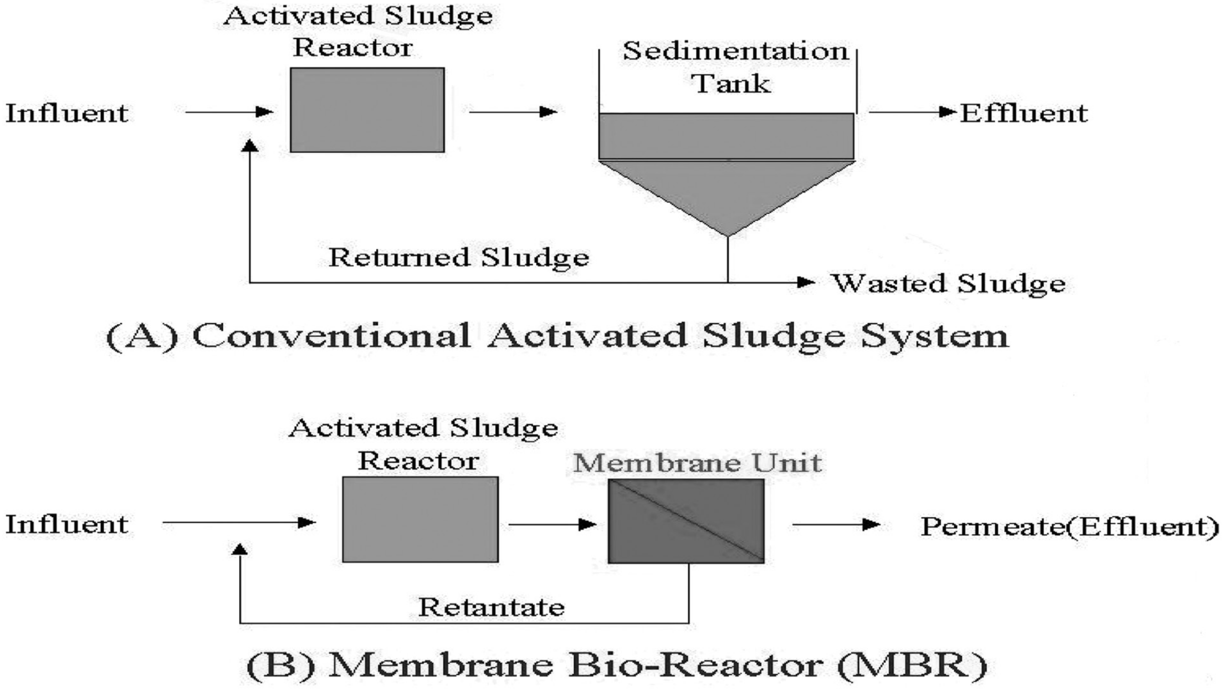

Figure 7. *Conventional Sewage Treatment and MBR process for wastewater treatment [19].*

produced is massive and is also expected to rise by rapidly in Europe in particular, mainly as a result of the higher treatment standards provided through the EU Commissions, gap closing actions in CEE past and future 20 years. Expected to reach 13,5M T DS/a volume by 2020.

2. Sewage sludge is a renewable, negative-cost organic material that is well suited for the energy production via different processes, methods.
3. Maintain appropriate balance on water-energy relationship; Choosing low-energy treatment options; Replacing machine parts, such as pumps and motors, with more efficient versions; Optimizing processes using sensor technology; Reusing water "Greywater" from bathing, laundry and washing dishes can be reused to flush WCs; Metering enables water companies to monitor input and usage and to identify leakage from the difference between the two; Incentive programs. For example, the Government's Enhanced Capital Allowance scheme enables business to recover some of the capital spent on energy saving or water conservation technologies.
4. Energy conservation is possible through the twin practices of efficient water use by consumers and efficient energy use by the water industry.
5. There are well-established renewable energy options, such as biogas, and novel technologies, such as gasification, for sewage treatment. Many need further investment and research.
6. The employment of biogas becomes more attractive as advances in technologies for biogas production, treatment and application, mixed with new financial inducements for various kinds of renewable energy progress. Optimization of biogas production and use will also bring ecological benefits, including helping the water industry mitigate its global warming impacts [20].
7. Economic and water quality considerations are key drivers for the water industry. Integration of energy related objectives into the existing regulatory framework will be necessary.
8. The potential for renewable energy generation from sludge on a national level is enormous. Access to inexpensive, renewable energy will become even more important because the cost of sewage treatment is bound to rise [21]. Electricity from sewage sludge isn't entirely free of course, but the feedstock is free through the generous contributions of numerous small donors. With the addition of solar energy installations and other renewables at treatment plants, sewage-to-energy could at least help keep costs manageable.
9. The Sewage Sludge is not a waste material, it is rather a potential source of energy, through its components is such a Raw Material, which directly or indirectly—via appropriate changeover—able to replace or complement primer materials (chemical fertilizers) and/or energy (thermal, electrical) [10].
10. Bio-energy from sewage as the main source of energy worldwide must be accepted in order to have a better and cleaner future. This means that we need to take the necessary steps to improve our technology to be able to efficiently harness the enormous potential that bio-energy could bring. It is certain that an effective R&D of the bio-energy applications/processes will provide an environmentally sustainable alternative to manage sewage sludge while producing renewable electrical energy [16].
11. Sludge to Energy: There are mature, widely-practiced technologies for generating fuels from sewage treatment and research has identified future methods for exploiting sewage as an energy resource. The amount of renewable energy which could be generated on water industry sites up to 25% of the total energy used to treat water and wastewater. A new report from Lux Research Analyst projects the global sludge-to-energy market will be around $30 billion by 2020 [22]. That includes energy recovery technologies like anaerobe digestion, gasification and biofuels production. These technologies offer utilities an immediate way to create new revenue streams.

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Effect of Organic Amendments on Metsulfuron-Methyl Dissipation in Chinese Paddy Soils

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ABSTRACT: Investigation involved soil microbial biomass carbon contents (SMBC) and dissipation of metsulfuron-methyl (MSM) in paddy soils. Results suggested organic amendments enhanced SMBC and MSM dissipation. The largest increment of SMBC was observed in treatments of decomposed pig manure (DM), followed by addition of Chinese Clover (CC) and then rice straw (RS). The shortest dissipation half-life of MSM resulted from a paddy field quaternary red clay (PRC), followed by a blue clay paddy soil (BCP) and a desalting muddy polder soil (PMP). This indicates organic materials not only effect microbial activity but also they effect fractions of extractable MSM all having an impact on MSM dissipation.

INTRODUCTION

MSM [2-(4-methoxy-6-methyl-1,3,5-triazin-2-yl-carbamoylsulfamoy) methyl benzoate], a sulfonylurea group herbicide, has high efficiency even with very low application rates and is widely used for control of most annual grasses as well as broadleaf weeds in cereal, pasture and plantation crops [1]. Previous studies revealed residues of MSM in soil can significantly damage rotation or substitution crops, [2–6], contaminate surface and ground waters, [7–9], and have unintended side effects on non-target organisms [10–14]. Therefore, there is a need to find a way to enhance dissipation of MSM in soils and to minimize residual effects of MSM in the environment.

Recent research suggests that up to 48% of applied metsulfuron-methyl is converted to bound residues and metabolites in soil [15–18]. Chemical hydrolysis and microbial breakdown are the most important pathways of sulfonylurea degradation in soil whereas photolysis and volatilization are relatively minor processes [1, 7]. Many other factors can also influence fate of pesticides such as soil moisture, temperature, soil total organic carbon content and organic and fertilizer amendments [18, 19–24]. However, effect of organic amendments on SMBC and MSM dissipation in paddy soils has rarely been reported. The purpose of this study was to understand dynamic response of SMBC to organic amendments in paddy soils and the subsequent effect on MSM dissipation kinetics. Relationships between SMBC, MSM dissipation and organic amendment in paddy soils were analyzed. The main aim was find a way to enhance MSM with in-situ remediation.

MATERIALS AND METHODS

Soils and Amendments

Three paddy soils used in this study were collected from the surface layer (0-20 cm) of a paddy field on a desalting muddy polder (PMP) near Yuanpu, on a blue clayey paddy soil (BCP) near Pinghu and on a paddy field quaternary red clay (PRC) near Longyou. All sampling locations are in the Zhejiang Province located on the east coast of China. Soil samples were ground, sieved through a 2-mm plastic mesh, thoroughly homogenized and then stored in the dark at 4°C until used. Aliquots were air-dried, ground and sieved to pass through a 0.149 mm plastic mesh and prepared for physical and chemical properties analysis. Table 1 displays physical and chemical properties for the soils.

Three organic amendments including rice straw, decomposed pig manure and Chinese Clover (i.e., Astragalus Sinicus Linn) were used (see Table 2). Rice straw and decomposed pig manure came from a Guangxi University farm in Guangxi, China. The Chinese Clover was collected from Pinghu in the Zhejiang

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Table 1. Basic Physical-chemical Properties of Three Paddy Soils.

Property	PMP	BCP	PRC
Organic C (g kg^{-1})	20.40	23.10	7.90
Total N (g kg^{-1})	1.88	2.40	0.79
C/N	10.85	9.61	9.99
Total P (g kg^{-1})	0.74	0.93	0.26
pH (soil/water = 1/2.5)	7.38	6.10	4.96
CEC(cmol(+) kg^{-1})	9.88	18.25	8.43
Clay (%)	29.00	46.40	26.00
Silt (%)	62.70	42.10	49.50
Sand (%)	8.30	11.50	24.50

Province. All organic amendments were air-dried and ground in a "plant-blender" to a 1 mm maximum particle size.

Reagents

Metsulfuron-methyl (purity ≥ 92%) was provided by the Hormone Research Institute, Jiangsu Province, China. HPLC-grade methanol was purchased from Siyou, Tianjin, China. HPLC-grade water was obtained by purifying distilled water with a Milli-Q® water purification system (Millipore, Bedford, MA). All other chemicals were of analytical-reagent grade purity and methanol and dichloromethane were redistilled prior to use.

Incubation Experiments

Spiked soil samples were prepared by adding 0.8 ml of methanol solution containing 1000 mg kg^{-1} MSM to 80 g (oven dry weight basis) of fresh soil. After complete removal of methanol by evaporation at room temperature for 24 h, treated soil was thoroughly mixed with additional "fresh" soil to obtain an initial MSM concentration of 10 mg kg^{-1}. Amendments were individually added to MSM-spiked soil samples. Five treatments were prepared including a control (CK), an unamended MSM soil (10 mg kg^{-1} soil) (M), a M + 10 g kg^{-1} decomposed pig manure (DM), a M + 10 g kg^{-1} rice straw (RS) and a M + 10 g kg^{-1} Chinese Clover (CC). Soil moisture was adjusted to 50% of soil water-holding capacity using deionized water. Amended soil jars were then incubated at 25 ± 1°C. Loss of water from each jar was compensated daily with deionized water. All treatments were prepared in three replicates. During incubation, SMBC and concentrations of solvent-extractable MSM in soil samples were determined at 0, 7, 14, 28, 42, 56, 70 and 98 d after treatment.

Table 2. Basic Properties of the Organic Amendments.

Experiment Material	Organic C (mg kg^{-1})	Total N (mg kg^{-1})	Total P (mg kg^{-1})	C/N	C/P
Rice straw	174.4	4.8	2.0	36.3	87.2
Chinese clover	144.4	13.6	8.1	10.6	17.8
Decomposed pig manure	394.6	30.8	14.5	12.8	27.2

Microbial Biomass Measurement

SMBC was determined using chloroform fumigation and an extraction method [25–26]. Generally, soil samples were fumigated with chloroform and then extracted with a 0.5 mol L^{-1} K_2SO_4 at 1:5 soil-to-solution ratio by shaking for 2 h with an end-over-end shaker. Dissolved organic carbon content in the supernatant was measured using a Shimadzu TOC-500 automated Total Organic Carbon Analyzer (Shimadzu, Kyoto, Japan,).

Analysis of Methanol-extractable MSM

Each 10 g soil sample (oven dry weight equivalent) was extracted by ultrasonic agitation in 50 ml of methanol for 15 minutes (40 KHz, 25°C). After centrifugation at 3,000 rpm for 20 minutes the supernatant was collected. Residue was extracted repeatedly four successive times using 30 ml methanol. Combined methanol extracts were extracted using 25 ml dichloromethane three successive times. The dichloromethane layer was collected in a flask after dehydration using anhydrous sodium sulfate. Then, extracts were combined and evaporated on a rotary vacuum evaporator (RE-52A, Shanghai, China) to dryness. Residue was dissolved in methanol (5 ml) and filtered through a 0.22 μm membrane (ANPEL, Shanghai, China) and analyzed using HPLC.

Extractable MSM was analyzed on a Symmetry® C18 column (5 μm, 3.9 × 150 mm; Waters, Milford, MA, USA) together with a Symmetry® C18 guard column (5 μm, 3.9 × 20 mm) with Waters instrument (2695 Multi Solvent Delivery System, Auto Sampler) equipped with a UV detector (Waters 2487 Dualλ Absorbance Detector) at 235 nm. Mobile phases were methanol-water (Milli-Q water) 80:20 (v/v) and flow rate was set to 1.0 ml min^{-1}. Injected sample volumes used 10 μl recoveries of MSM added in soils ranging between 83.45% and 98.03%.

Statistical Analysis

Content of microbial biomass carbon was calculated using Equation (1).

$$SMBC = 2.22\,E_C \quad (1)$$

$E_C = [(K_2SO_4^-$ extracted from fumigated soil) minus ($K_2SO_4^-$ extracted from non-fumigated soil)] and the factor 2.22 is a proportionality constant to account for incomplete extraction of SMBC [27]. Dissipation kinetics of MSM in soil under laboratory conditions was accurately described using a first order model, [18, 20],

$$C = C_0 e^{-kt} \quad (2)$$

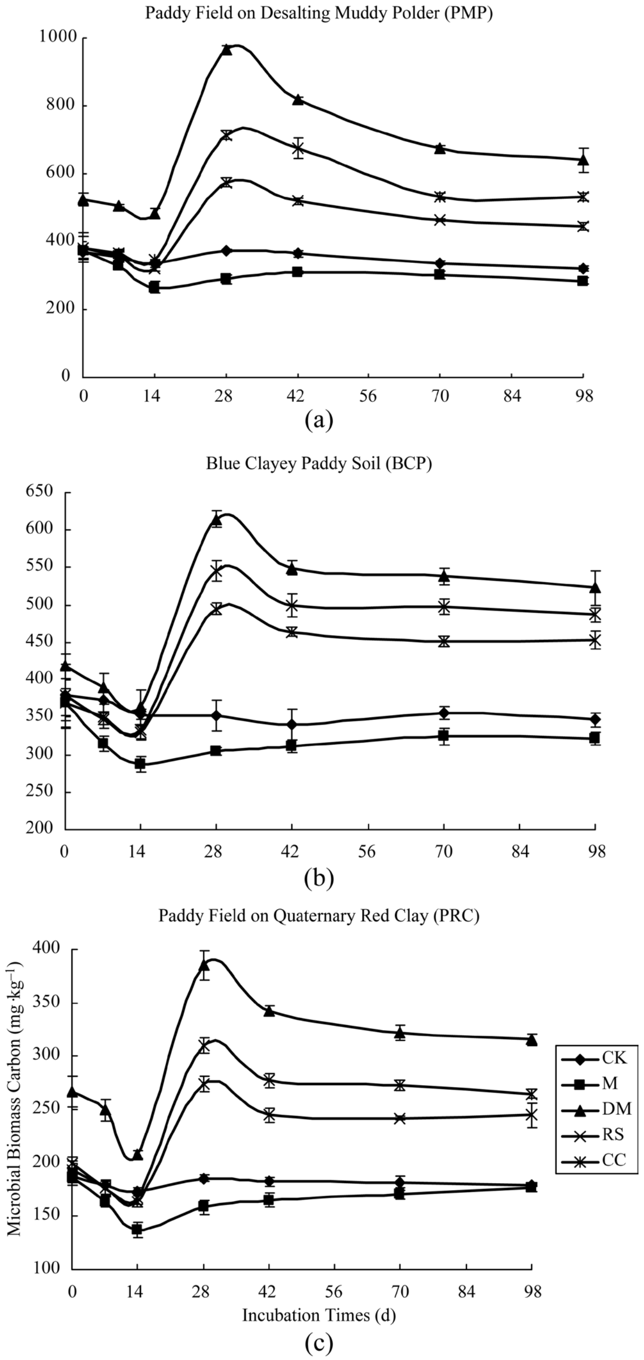
C is the amount of MSM remaining at time t, C_0 is initial amount of MSM and k is the first-order rate constant.

RESULTS

Dynamic Responses of SMBC to Organic Amendments Spiked with Metsulfuron-methyl

Contents of SMBC were noticeably different among the three soils and those without any amendment (See Figure 1). In PMP and BCP, the mean SMBC level was significantly higher ($p < 0.01$) than in PRC. Average values of SMBC were 350.94 mg kg^{-1}, 357.25 mg kg^{-1} and 181.12 mg kg^{-1} in PMP, BCP and PRC in the control, respectively. MBC significantly ($p < 0.01$) decreased in all three treatments regardless of which soil was spiked with MSM during the initial 14-d incubation period. Reduction of SMBC was less in all treatments amended with organic matter. Compared with the control, the SMBC in soils spiked with MSM were reduced an average of 12.37% in PMP, 10.70% in BCP and 8.55% in PRC at 14-d, respectively. SMBC increased rapidly from 14-d to 28-d and decreased again between 28-d and 42-d. After 42-d of incubation SMBC generally reached a plateau but it remained significantly higher in amended treatments than in non-amended and control treatments.

SMBC in all soils consistently increased after addition of organic material. The largest increase of SMBC was observed in soil treated with DM, followed by CC and RS. At the end of incubation average increase of SMBC was 87.84% in PMP, 35.88% in BCP and 64.85% in the treatment of DM in PRC. The smallest increase of SMBC was observed in the treatment of RS which was 24.60% in PMP, 16.51% in BCP and 21.52% in PRC, respectively.



(a)

(b)

(c)

Figure 1. *Dynamic of microbial biomass carbon with incubation times in three soils treated with different organic amendments in soils.*

Effect of Organic Amendments on MSM Dissipation in Paddy Soils

Dissipation rate of MSM increased with addition of organic amendments and displayed significant differences among the three paddy soils (See Figure 2). The magnitude of impact for the three amendments on MSM dissipation in each soil sample ranked in the following manner: pig manure (DM) > Chinese Clover (CC) > rice straw (RS) > control (M). Among the different soils MSM dissipation rate for DM, CC, RS and M treatments ranged from 76.59–96.71%, 74.80–96.03%, 73.76–94.30% and 63.11–92.32%, respectively and at the end of incubation (98-d).

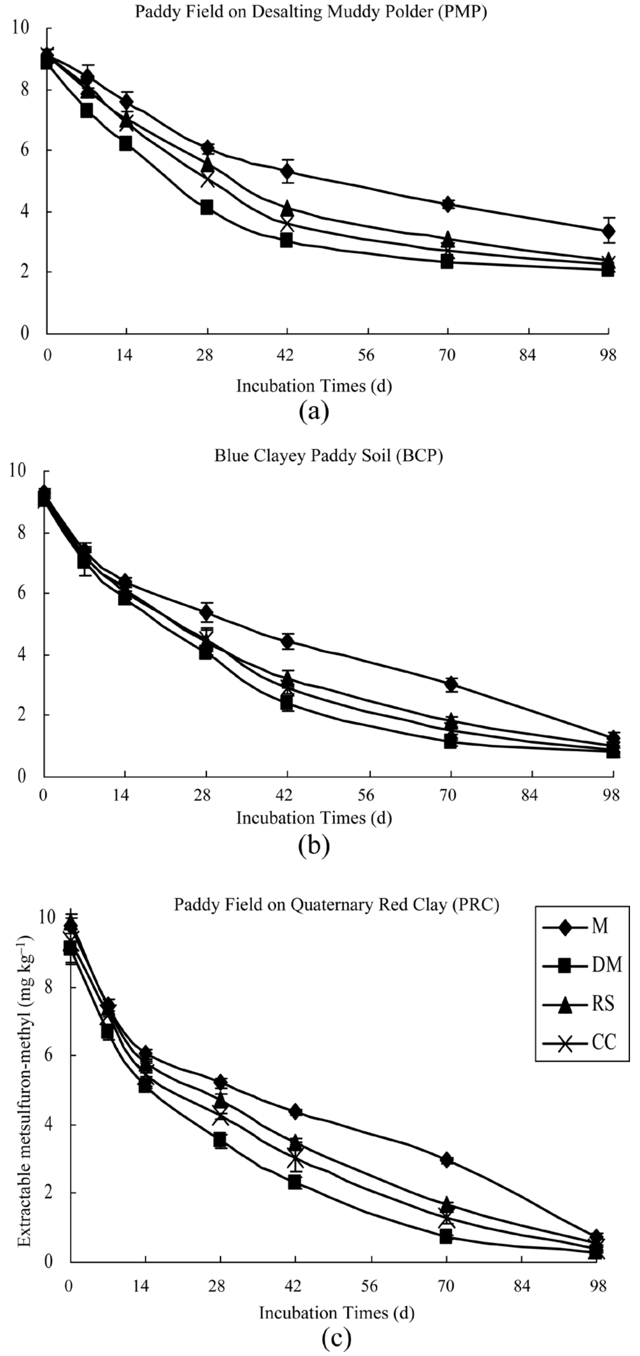


Figure 2. The effect of organic amendments on extractable metsulfuron-metyl in soils.

Kinetic Model of Effect of Organic Amendments on MSM Degradation

Among treatments the fitting equation displayed strong correlation ($r_{0.01} = 0.8745$) which suggests that such an equation can describe a relationship between MSM content and time. In each soil half-life of MSM displayed a significant difference when compared to the control. Dissipation half-life of MSM displayed a significant difference between the three paddy soils. Shortest time was in PRC, followed by BCP and then PMP. Half lives were 19.9-d~26.5-d, 28.6-d~34.5-d and 46.8-d~68.6-d for different treatments, respectively.

Displayed in Table 3 one may also observe that hydrolysis prevailed over the microbial decomposition process for MSM dissipation with time which can be explained by constant microbial mass after a period of time. Dissipation half-life of MSM in the same soil but with added organic material treatments was significantly shorter than the control. Shortest dissipation half-life of MSM was in the added decomposed pig manure treatment followed by Chinese Clover treatment and the longest was for treatment with rice straw.

Correlation Among Content of SMBC, MSM and Soil pH

There is a negative correlation between concentration of methanol-extractable MSM and content of microbial biomass carbon (See Figure 3). The higher the SMBC content the faster the dissipation rate of MSM. After incubation for 98-d, use of organic amendments increased pH of polluted soil, especially in PRC soil mixed with pig manure (DM) and Chinese Clover (CC) treatments. There is a positive correlation between soil pH and dissipation rate of MSM (See Figure 4). High soil pH accelerated decrease of MSM and this trend was more obvious in acid soil such as in the PRC and BCP soils.

DISCUSSION

The present study suggested contents of SMBC were noticeably different among the three soils without any amendment. This might be a result of differences in factors such as long-term organic C input, [28], soil texture and crop rotation systems [29–31]. SMBC decreased during the initial 14-d incubation period then increased rapidly from 14-d to 28-d and decreased again between 28-d and 42-d. For all soils spiked with

Table 3. The Kinetic Equation of Metsulfuron-methyl Degradation in Soils with Organic Amendments.

Soil[a]	Treatment[b]	Kinetic Equation of Dissipation[c]	r[d]	Variance Explained (%)	$T_{1/2}$ (d)
PMP	M	$Y = 8.6876e^{-0.0102x}$	–0.9896**	97.9	68.6
	MM	$Y = 7.4404e^{-0.0152x}$	–0.9524**	90.7	46.8
	MS	$Y = 8.4619e^{-0.0138x}$	–0.9867**	97.4	51.4
	MC	$Y = 8.2524e^{-0.0146x}$	–0.9728**	94.6	49.3
BCP	M	$Y = 8.9379e^{-0.0182x}$	–0.9862**	97.3	34.5
	MM	$Y = 8.1559e^{-0.0253x}$	–0.9874**	97.5	28.6
	MS	$Y = 8.496e^{-0.0218x}$	–0.9985**	99.7	31.2
	MC	$Y = 8.5141e^{-0.0236x}$	–0.9971**	99.4	29.6
PRC	M	$Y = 9.6821e^{-0.0227x}$	–0.9610**	92.4	26.5
	MM	$Y = 8.8851e^{-0.0347x}$	–0.9984**	99.7	19.9
	MS	$Y = 9.6696e^{-0.0274x}$	–0.9921**	98.4	23.7
	MC	$Y = 9.5646e^{-0.0312x}$	–0.9917**	98.3	21.0

[a] PMP, Paddy field on desalting muddy polder; BCP, Blue clayey paddy soil; PRC: Paddy field on quaternary red clay.

[b] M, 10 mg MSM kg^{-1} soil; MM, 10 mg MSM kg^{-1} soil + 10 g decomposed pig manure kg^{-1} soil; MS, 10 mg MSM kg^{-1} soil + 10 g rice straw kg^{-1} soil; MC, 10 mg atrazine kg^{-1} soil + 10 g Chinese Clover kg^{-1} soil.

[c] Y, the content of methanol-extractable atrazine residues in soils (mg kg^{-1}); x: incubation times.

[d] **Correlation is significant at 0.01 probability level.

MSM SMBC generally reached a plateau after 42-d of incubation. This may be caused by an addition of MSM at a relatively high rate which affected activity of indigenous soil microorganisms. Added organic material could slow or eliminate harm to the microbial community from MSM.

This observation likely reflected progress of organic matter decomposition by soil microbes and dynamic change of the soil microbial communities. During the initial 14-d period addition of MSM may have greatly affected composition and activity of soil microorganisms. From 14-d to 28-d, it is likely the readily decomposable organic matter was quickly utilized by soil microbes which resulted in increases of SMBC. After 28-d or 42-d the amount of readily decomposable organic matter became depleted and overall decomposition rate of added organic materials declined resulting in smaller populations of microorganisms in the soil.

SMBC in all soils consistently increased after addition of organic material. Differences may be partly attributed to rapid metabolism of soluble organic matter by soil microbes after organic amendments were added to soils. Organic substrates in decomposed pig manure and Chinese Clover may be more readily available than in rice straw to soil microorganisms. It is also likely introduction of organic matter into the soil increased MSM sorption by soil and thus decreased microbial toxicity by herbicide. Shen, [32], reported growth of microorganisms was closely dependent on content of available organic carbon in soil. Previous studies consistently demonstrated that soil microbial biomass increased after application of straw [32, 33–34]. Entry and Emmingham demonstrated the addition of readily decomposable organic matter and crop residues stimulated soil microbial activity [35]. Microbial biomass C and N decreased in the early culture period for paddy soils with added metsulfuron-methyl of 10 $mg.kg^{-1}$ compared with the control decreasing on average by 14.58% and 24.69% over a 7-d period [36]. Microbial biomass C and N, organic matter, total N, available P, respiration rate and cellulose-decomposing capacity in soil were all enhanced when application rate of refuse compost increased [37].

MSM degradation was mainly affected by chemical hydrolysis and microbial processes [1, 38]. Other soil properties including pH, OM, SOC and moisture also contribute to some extent to MSM dissipation. Again, magnitude of impact from three amendments on MSM dissipation in each soil sample ranked in the following manner: pig manure (DM > Chinese Clover (CC) > rice straw (RS) > control (M). This may be explained by using organic amendments that increased microbial mass thus enhancing microbial dissipation activities in contaminated soil. Amendments have similar impact on microbial mass and dissipation rate revealed that increasing microbial processes is one way to stimulate MSM dissipation. Sarmah reported microbial degradation appeared to be a major process in neutral and alkaline soils while chemical and microbial processes play important roles in acid soil for MSM [39–40]. Degradation of MSM was strongly and positively correlated to soil microbial biomass [41]. Degradation of sulfonylurea herbicide in sterile soil was slower than that in soil not sterilized where degradation products

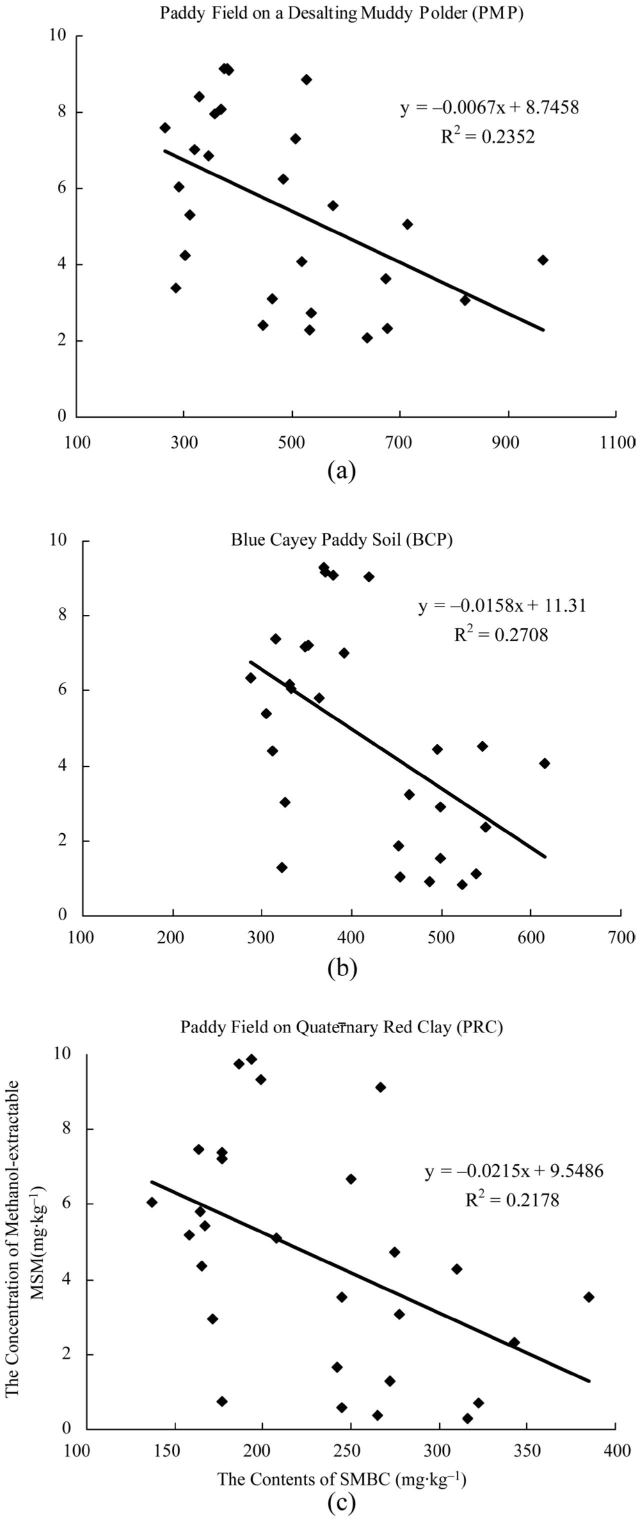


***Figure 3.** The correlation between the content of MSM and SMBC.*

were more complex [42]. Adsorption of organic matter to MSM is another reason to explain decrease of methanol-extractable MSM in soils.

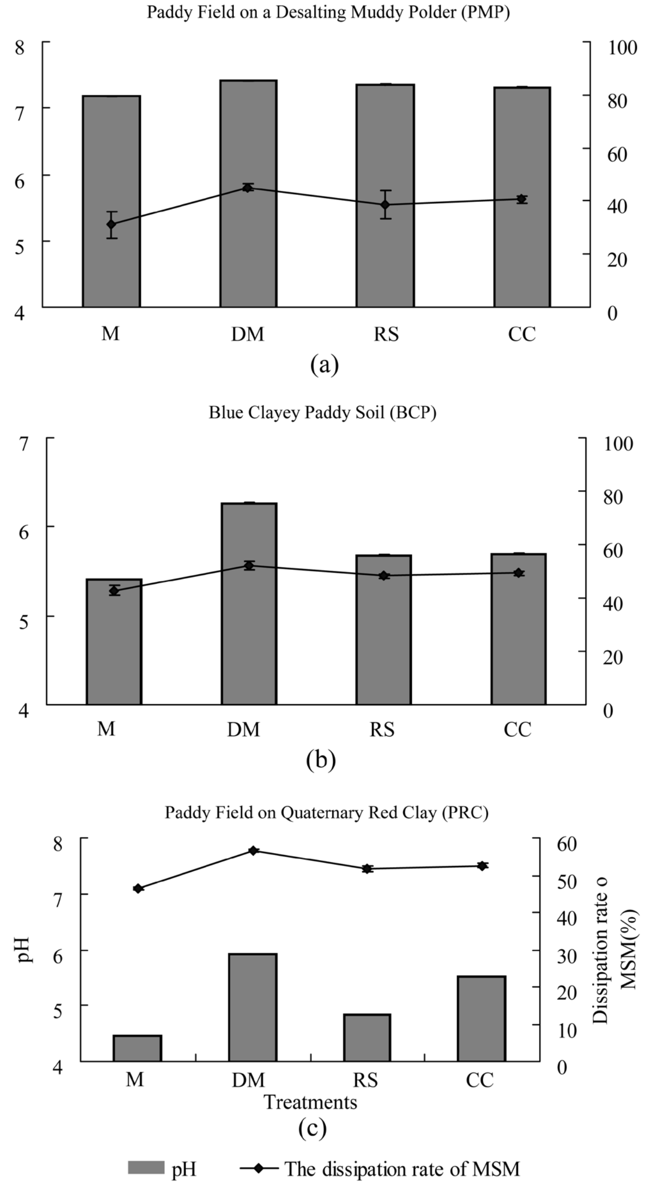


***Figure 4.** The changes of soil pH and dissipation rate of MSM in different treatments with organic amendments.*

Dissipation of sulfonylurea herbicides was greatly influenced by soil pH [42–43]. The greater the soil pH the less hydrolysis occurs. Therefore, dissipation in alkaline soil occurs mostly through microbial activity [19]. MSM retention rate in this research was positively correlated to soil pH. MSM disappears fastest in PRC soils (pH = 4.96) followed by BCP soils (pH = 6.10) while the slowest was in PMP soils (pH = 7.38) which is in agreement with the general trend observed for MSM [10, 23, 44]. Such phenomenon are often caused by changes in charges between the surface of soil particles and speciation of MSM in aqueous conditions. MSM exists as a neutral molecule and in anion form in acid soil. However, it mainly appears in anion form in alkaline soil. It is known like charges repel each other and thus the negatively charged MSM species are more likely released from soil as pH increases as a result of electrostatic repulsion. As described in Wang, the more clay there is in a soil the faster MSM dissipation rate occurs [43]. BCP has higher clay content. However, PRC has a higher MSM dissipation rate. Soil pH from this point of view is one of the main factors in the process of MSM dissipation.

Dissipation rate of pesticide could also be affected by content of soil organic matter. Increasing soil organic carbon content promoted formation of combined MSM and reduced the extractable content [44]. Some believe the higher the clay content in soil the faster the dissipation rate of pesticide [42, 44]. Dissipation rate of MSM was faster in soil containing a high content of clay and low content of silt but dissipation rate of MSM in Purple Paddy soil which was made up of high soil organic carbon and low clay content was lower than that in the Yellow Bars Paddy soil in the study. Therefore, soil pH appears to be the most important factor in MSM dissipation.

CONCLUSIONS

Application of organic materials increased soil pH and soil microbial biomass for test soils and accelerated degradation of methanol-extractable MSM. Pig manure (DM) has the best effect on dissipation rate followed by the Chinese Clover (CC) and then rice straw (RS). Effect of organic amendment on rate and dynamic of MSM degradation in the soils varied in relation to types of organic amendment and properties of soil. Findings from this study help with understanding fate of MSM in paddy soils and relation to potential risks to the environment. Also, this study provides certain measures potentially useful for in-situ remediation of pesticide polluted soils.

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Characterization of Bottom Ash from Petrochemical Waste Incinerator

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ABSTRACT: The purpose of this study is to investigate bottom ash from a petrochemical waste incinerator in terms of its physical properties, chemical compositions and leaching behavior. Results showed that mean values for the Fineness Modulus (FM), for water absorption and for the saturated surface dry specific gravity (SSDSG) of bottom ash were 2.56, 12.82% and 3.21, respectively. Main oxides of bottom ash were Fe_3O_4, CaO, Sulfur (reported as SO_3), MgO and ZnO with weight percentages of 49.8, 16.2, 7.6, 4.0 and 3.8, respectively. Two standard leaching tests under different leaching conditions [EN 12457-2 and Toxicity Characteristic Leaching Procedure (TCLP)] were performed in order to compare results with regulatory values. Chemical analysis and leaching behavior of the studied Petrochemical Incinerator Bottom Ash (PI-BA) showed this material should be considered hazardous waste with respect to release of trace metallic elements (Cu, Cr and Zn) and should be properly managed in accordance with hazardous waste regulations.

INTRODUCTION

THE petrochemical industry is one of the most important key industries in oil producing countries. In past decades rapidly developed and new petrochemical plants in Pars Special Economic Energy Zone (PSEEZ) have caused environmental impacts because of production of hazardous wastes as well as illegal disposal and inadequate capacity of treatment/disposal facilities. Management of petrochemical sludge in the PSEEZ is an important issue due to a large variety and volume of petrochemicals production [1]. M.B. Petrochemical Complex is located in southern Iran. This complex not only produces base chemicals for five petrochemical companies (i.e., A.S. Petrochemical Co. [Olefin producer], J.P. Petrochemical Co. [Olefin producer], Z.P. Petrochemical Co. [Methanol producer], B.O. Petrochemical Co. [Aromatic producer] and P.A. Petrochemical Co. [Ethane producer]) but it also treats their liquid waste in a wastewater treatment unit. These wastes include boiler washing water and surface runoff water as well as water from column washing and other liquid waste.

Two of the most common metals found in wastewater discharge from petrochemical plants are copper and chromium [2]. Some studies have investigated reuse of copper and chromium [3] or copper and cadmium in aqueous solution [4] from petrochemical wastewater. However, various compositions of heavy metals and low-efficiency for recovery are disadvantages of methods mentioned above.

Incineration is a frequently used practice in hazardous waste management and is one option for petrochemical [1, 5] and refinery [6] waste treatment. Incinerators are used in the petrochemical industry for hazardous waste management in some developing countries such as Turkey [7] and Kuwait [8] for examples. Although, they are not very popular in developed countries due to ashes resulting from incineration processes which contain heavy metals and landfill facilities needed for final disposal [6, 9].

Waste volume reduction in the incinerator can reach

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up to 90% [10] but incineration has disadvantages of concentrating persistent pollutants in combustion residues [11]. Generally, bottom ash is less toxic than fly ash [12] but the amount of bottom ash is far more than that of fly ash and composition is more heterogeneous [13–14]. In addition, refinery and petrochemical plant incinerator bottom ash has potential to cause significant environmental pollution [9] and managing residues will become a major critical issue regarding use of these residues or landfilling them in the future.

In 2009, an incinerator facility was established to incinerate hazardous waste at the M.B. Complex in order to decrease amounts of waste volume as well as for meeting environmental regulations. Up to 2009 the petrochemical industries dumped biological and chemical residue bottom sludge without treatment resulting in environmental pollution.

During post chemical and biological treatment oily sludge and biological bed sludge were collected, dewatered, mixed and carried for burning into a rotary kiln incinerator. In addition, some barrels of specific hazardous materials are treated in the incinerator, simultaneously. Solid waste is burned in the first combustion chamber at above 850°C for about 30 minutes and the liquid waste is burned in the second combustion chamber at 1100°C for about 2 seconds. The flue gas treatment system removes NO_x and SO_x as well as fly ash from incinerator off-gas. Then, fly ash is returned to the starting point of the treatment process via a water scrubbing and circulation system. Moreover, clean gas is regularly checked by a local environmental agency. Nevertheless, a remaining problem results from the amount of generated bottom ash (i.e., about one ton per day) which will be dumped without treatment (See Figure 1).

Most residues which have been characterized originated from municipal solid waste incinerators [15–17], municipal district heating plants [18] or from refinery sludge incinerators [19] but not many studies have been found in the literature on specific type of residues from petrochemical incinerators.

Figure 1. Produced bottom ash (i.e., dumped without treatment).

In this study PI-BA is characterized in terms of physical, mineralogical, morphological and leaching characteristics.

MATERIALS AND METHODS

Bottom ash comes from the incinerator of the M.B. Petrochemical Complex. Bulk sample (i.e., approximately 200 kg) of waste in a specific barrel was taken from the incinerator bottom ash in April of 2010 and transported to a laboratory. The incinerator unit sprays water on bottom ash to avoid scattering fine particles into the environment followed by barrel storage. Therefore, PI-BA was uniformly dried in the natural environment. Nine samples were taken and mixed homogenously.

Three composite samples were prepared by homogenizing and combining every three samples. Gradation of PI-BA was obtained according to ASTM C136 standard after PI-BA had been washed in each sieve to make sure conglomerate particles were well separated. SSDSG and water absorption of samples were obtained in accordance with ASTM C128 standard test procedure. Main oxides of PI-BA samples were analyzed using X-ray Fluorescence (XRF, Philips X'UNIQUE II).

Leaching tests were performed according to standard procedures under different leaching conditions in order to compare results to currently proposed regulations. (1) TCLP was performed according to USEPA Method 1311 [20] and (2) a Single Stage Leaching Test (SSLT) was performed according to European Union leaching test EN 12457-2 [21].

A summery of extraction for both tests is presented in Table 1.

At the end of the leaching process samples were filtered and contents of major and trace elements in leachates were determined by means of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, TERMO-ICP6000 model).

Supplementary investigation by X-Ray Diffraction (XRD) measurement was performed on a SIEMENS D5000, CuKa radiation. The measured 2-θ range from 5 to 70° was scanned in steps of 0.02° with speed of 1 sec/step. Furthermore, Scanning Electron Microscopy (SEM) was performed using a Seron Technologies Inc (AIS2100) SEM for morphological investigation.

Table 1. Summary of Leaching Extraction Tests (TCLP and UNI EN 12457-2).

Leaching Test	Code	Specimen Condition and Dimension	Contact Time	Liquid-to-Solid Ratio
SSLT	EN 12457-2	Granular (< 4 mm)	24 h	10:1
Toxicity Characteristic Leaching Procedure	TCLP	Granular (< 9.5 mm)	18 h	20:1

RESULTS AND DISCUSSION

Physical Properties of Bottom Ash

Grading, FM, water absorption and SSDSG of samples are presented in Table 2. The average for FM of the PI-BA was 2.56 indicating a rather fine grading.

The SSDSG of PI-BA was 3.21 which is significantly higher than it is for fine aggregates (2.50–2.65) and most likely due to high iron content. Furthermore, water absorption was 12.8% and much higher than that of sand and crushed stone.

Data in Figure 2 display the percentage passing by mean particle size for each fraction. It also presents lowest, highest and average percentages for three samples.

Chemical composition of the PI-BA samples were determined by the XRF method. Results are presented in Table 3. Results show that magnetite, CaO, Sulfur (reported as SO_3), MgO and ZnO were main constituents of the bottom ash and present at 49.8, 16.2, 7.6, 4.0 and 3.8% by weight, respectively.

There is no quartz (SiO_2) detected in the studied bottom ash in contrast to results reported by Fujimori et al [22]. This variety of concentration values may be attributed to complex and inherent characteristics of oily sludge in petroleum industries [23] and the source of wastes combusted in an incinerator (Silicon oil and glass materials in input waste reported by Fujimori et al) [22].

Average Loss on Ignition (L.O.I) for samples was 8.27 which is a little higher compared to other studies on solid residues from MSWI [16–17]. This might be due to incomplete operation of incineration for burning organic components [5].

Percentage of Fe_2O_3 in PI-BA was higher than that observed for other studies regarding municipal solid waste incinerator residue [16, 24] and fly ash [17]. Although, it was lower than thermal power plant air heater ash [25]. The high amount of hematite in PI-BA is due to usage of ferric chloride ($FeCl_3$) as a flocculating agent in treatment procedure and formation of floc iron (III) hydroxide ($FeO(OH)^-$) that can be removed by suspended materials and confirmed by XRD analysis (See Figure 3). Main trace elements in PI-BA samples were copper, chromium and nickel with concentration values of 12,286, 6,067 and 264 $mg.Kg^{-1}$, respectively. The high concentration of Zn, Cr, Cu and Ni in the bottom ash may be related to origin of waste fuel oil, corrosion products of alloys, washing reactors and washing surface of catalysts. It is also reported for incinerated refinery sludge by Karamalidis et al [19]. In contrast to MSWI fly ash in some studies [16–17], the sum of percentage of SiO_2 and Al_2O_3 was negligible and therefore it is not expected to be considered as pozzolanic additions in a cementitious system.

Table 2. Gradation, FM, Water Absorption and Specific Gravity of PI-BA samples.

		Percent Passing (%)			
Standard Mesh	Sieve Size (mm)	Sample No. 1	Sample No. 2	Sample No. 3	Mean ± SD
4	4.760	98.84	99.60	99.68	99.37 ± 0.46
8	2.380	88.15	94.21	93.51	91.96 ± 3.32
16	1.190	67.80	70.09	71.43	69.77 ± 1.84
30	0.595	47.97	50.12	44.16	47.42 ± 3.02
40	0.420	32.77	35.75	30.84	33.12 ± 2.47
50	0.297	20.98	23.19	23.38	22.52 ± 1.33
100	0.149	11.01	15.12	13.31	13.15 ± 2.06
200	0.074	7.77	9.08	8.77	8.54 ± 0.68
FM		2.65	2.48	2.55	2.56 ± 0.09
Gs		3.12	3.29	3.21	3.21 ± 0.08
Water absorption (%)		12.40	13.12	12.95	12.82 ± 0.38

SD: standard deviation

Table 3. Chemical Composition of PI-BA Samples.

Sample Code		**1**	**2**	**3**	**Mean ± SD**	**Sample Code**		**1**	**2**	**3**	**Mean ± SD**
L.O.I	(%)	7.50	9.07	8.24	8.27 ± 0.79	Ba	($mg\cdot kg^{-1}$)	1	1	1	1
SiO_2	(%)	< 0.01	0.30	< 0.01	–	Sr	($mg\cdot kg^{-1}$)	355	101	101	186 ± 147
Al_2O_3	(%)	0.87	1.03	4.45	2.12 ± 2.02	Cu	($mg\cdot kg^{-1}$)	9474	11873	15512	12286 ± 3040
Fe_2O_3	(%)	56.40	53.40	49.80	53.20 ± 3.31	Pb	($mg\cdot kg^{-1}$)	122	61	87	90 ± 30
CaO	(%)	15.70	15.40	17.60	16.23 ± 1.19	Ni	($mg\cdot kg^{-1}$)	344	157	291	264 ± 96
Na_2O	(%)	< 0.01	0.12	0.05	0.09 ± 0.05	Cr	($mg\cdot kg^{-1}$)	4600	5879	7721	6067 ± 1568
K_2O	(%)	< 0.01	0.10	0.20	0.15 ± 0.07	V	($mg\cdot kg^{-1}$)	78	56	101	78 ± 23
MgO	(%)	4.50	3.70	3.90	4.03 ± 0.42	Mo	($mg\cdot kg^{-1}$)	127	180	113	140 ± 35
TiO_2	(%)	1.04	0.92	2.24	1.40 ± 0.73	Cd	($mg\cdot kg^{-1}$)	9	9	9	9
MnO	(%)	0.26	0.50	0.36	0.37 ± 0.12	Sn	($mg\cdot kg^{-1}$)	16	8	8	11 ± 5
P_2O_5	(%)	0.76	1.04	1.03	0.94 ± 0.16	Rb	($mg\cdot kg^{-1}$)	15	9	9	11 ± 3
SO_3	(%)	8.10	7.40	7.20	7.57± 0.47	Hg	($mg\cdot kg^{-1}$)	< 0.5	< 0.5	< 0.5	< 0.5
ZnO	(%)	2.04	4.80	3.80	3.55 ± 1.40	Ag	($mg\cdot kg^{-1}$)	1	1	1	1
Cl	(%)	0.02	0.01	0.02	0.02 ± 0.01	Co	($mg\cdot kg^{-1}$)	117	73	73	88 ± 25

SD: standard deviation

XRD patterns as displayed in Figure 3 show that crystalline compounds in ash were minerals in the form of oxides, hematite, magnetite, renierite, calcium hydroxide and brushite. Hematite was the major crystal phase viewed in XRD due to a high concentration of iron. Formation of zinc iron oxide and renietrite were because of the solid formations of copper and zinc which were also confirmed by XRF analysis.

Leaching behavior of waste may be related to its porosity, outer surface and density particle interior [26]. Therefore, morphology of bottom ash was investigated by SEM images (See Figure 4).

The SEM images of bottom ash show a wide range of particles that have various forms and highly irregular shapes. In addition, high water absorption may be related to high porosity of fine PI-BA particles.

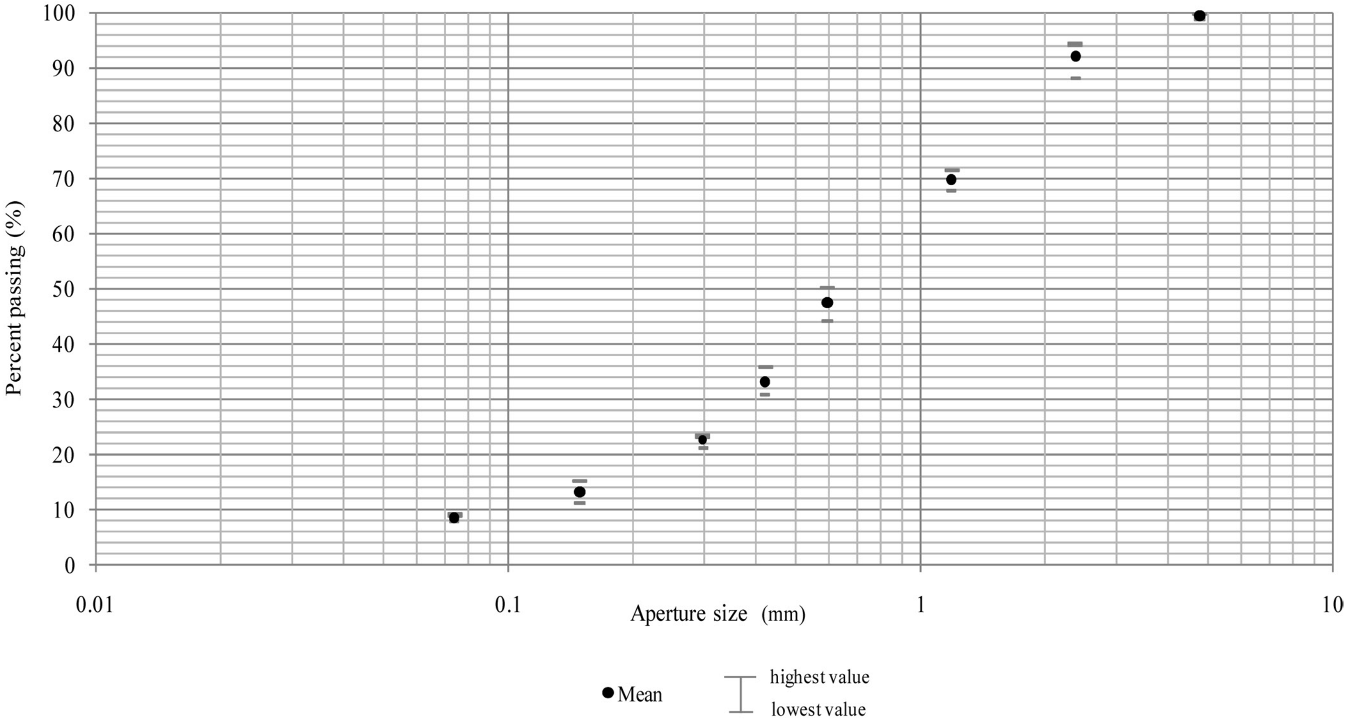


Figure 2. *Grading of washed petrochemical incinerator bottom ash (PI-BA) samples.*

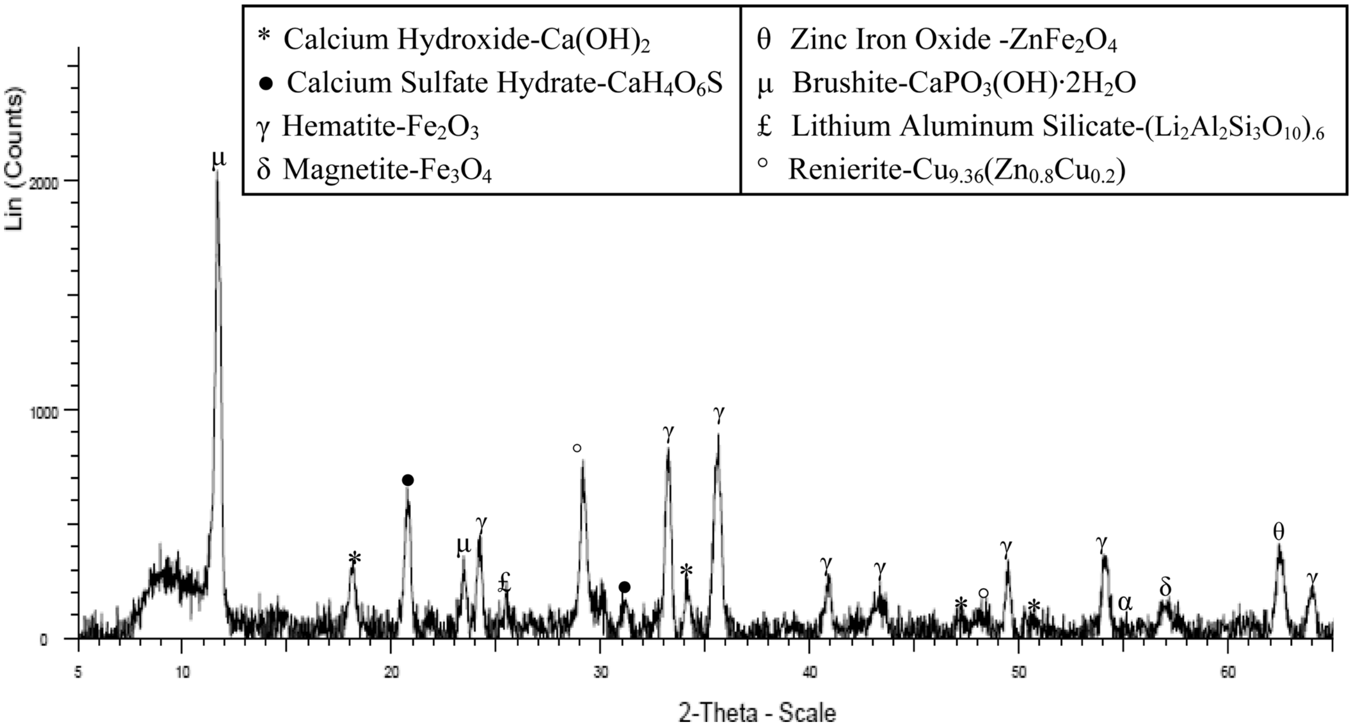


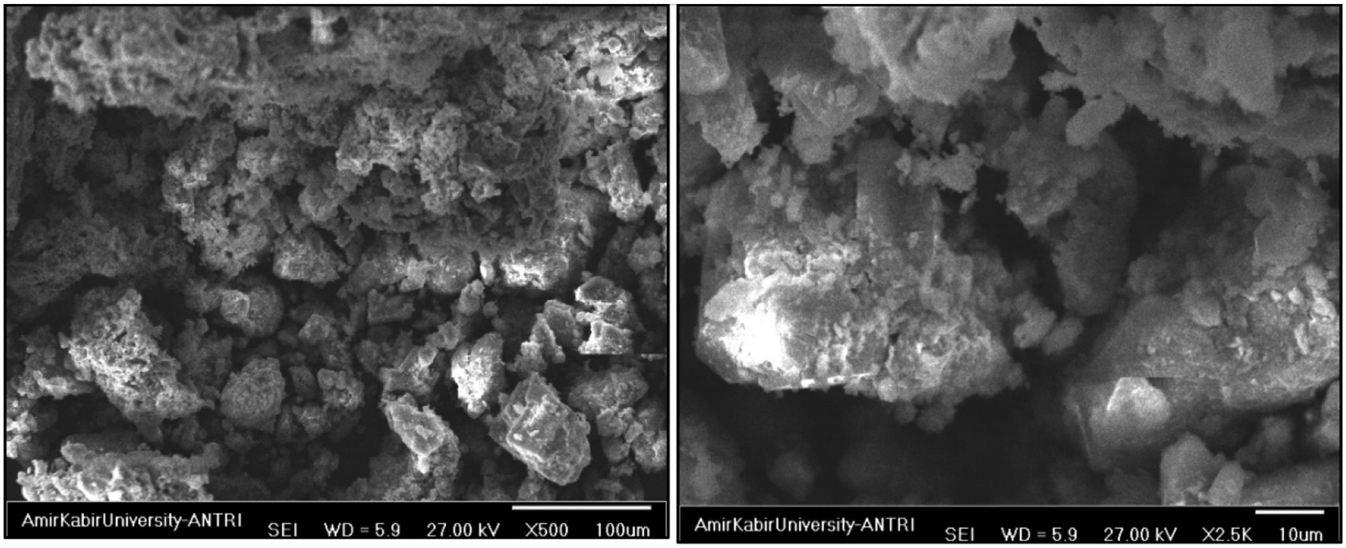
Figure 3. XRD spectra of PI-BA.

Leaching Properties

Leaching tests employed are the US method TCLP-1311 and the European method EN 12457-2. From leaching tests the elemental (Ca, Cr, Zn, Cu, Ag, As, Cd, Mn, Ni and Pb) concentrations were determined using ICP-AES (See Table 4).

The pH value ranges from TCLP eluates were in the low alkaline range varying between 7.5 and 8.1 while the same values of EN eluates were between 11.1 and 12.7. This can attributed to the lower initial pH value of the TCLP solvent.

Generally, high contaminant concentrations have been detected in TCLP in leachates compared to similar materials by the EN leaching test. It might be attributed to acidified eluate in the TCLP test procedure



(a) (b)

Figure 4. SEM photographs of bottom ash residues (a) ×500 (b) ×2500.

Table 4. Concentrations of Heavy and Other Hazardous Metals in Eluates After Leaning Tests of Waste.

TCLP Concentration (mg·lit^{-1})

					Criteria			
	Sample No. 1	**Sample No. 2**	**Sample No. 3**	**Mean ± SD**	**US EPA-1311**	**Ettler et al. [27]**	**Luo et al. [28]**	**Pereira et al. [29]**
pH	8.1	7.7	7.5	7.7 ± 0.3	–	–	–	–
Ca	2550	1550	1215	1772 ± 695	–	–	–	–
Cr	5.7	11.1	16.4	11.0 ± 5.4	5.0	–	5.0	5.0[a]
Zn	84.5	110.4	91.7	95.5 ± 13.4	–	5.0	25.0	300[b]
Cu	22.5	34.1	35.3	30.6 ± 7.0	–	1.0	15.0	–
Ag	< 0.2	< 0.2	< 0.2	< 0.2	5.0	–	–	–
As	< 0.5	< 0.5	< 0.5	< 0.5	5.0	5.0	5.0	–
Cd	< 0.01	0.04	< 0.01	–	1.0	0.5	1.0	1.0[a]
Mn	0.20	0.40	0.10	0.20 ± 0.15	–	–	–	–
Ni	< 0.05	0.15	0.10	–	–	–	–	–
Pb	< 0.2	< 0.2	0.4	–	5.0	10	5.0	5.0[a]

EN 12457-2 Concentration (mg·lit^{-1})

					Criteria		
	Sample No.1	**Sample No. 2**	**Sample No. 3**	**Mean ± SD**	**Landfill CI-inert**	**Landfill CII-not hazardous**	**Landfill CIII-hazardous**
pH	12.1	11.1	11.6	11.6 ± 0.5	–	–	–
Ca	978	533	579	697 ± 245	–	–	–
Cr	6.4	7.1	8.3	7.3 ± 1.0	0.05	1.00	7.00
Zn	5.1	6.7	5.5	5.8 ± 0.8	0.4	5.0	20.0
Cu	8.0	14.2	15.1	12.4 ± 3.9	0.2	5.0	10.0
Ag	< 0.2	< 0.2	< 0.2	< 0.2	–	–	–
As	< 0.5	< 0.5	< 0.5	< 0.5	0.05	0.20	2.50
Cd	< 0.01	< 0.01	< 0.01	< 0.01	0.004	0.100	0.500
Mn	0.05	< 0.01	< 0.01	–	–	–	–
Ni	< 0.05	< 0.05	< 0.05	< 0.05	0.04	1.00	4.00
Pb	< 0.2	< 0.2	< 0.2	< 0.2	0.05	1.00	5.00

SD: standard deviation.

[a] EPA criteria.

[b] Spanish guidelines for pre-potable water (3 mg.lit^{-1}) × 100.

[30]. Furthermore, variations in values from the TCLP test were more than that of EN due to the complex behavior of acetic acid and influence of leaching time on TCLP. The CaO content of solid samples is conducive to high pH and Ca concentrations.

Low concentrations of heavy metals were obtained from low alkalinity eluates compared to those resulting from high alkalinity samples which is also reported by Tsiridis [31]. Cr, Cu and Zn appeared to be predominant contaminants existing in both elute tests and other metallic elements which were under proposed regulations for hazardous landfilling.

Due to lack of national standards for hazardous waste in Iran and also for no TCLP limit for zinc and copper in the US concentrations of heavy metals in the TCLP eluate were compared to other country regulations and a publication suggestion. The Republic of China Environmental Protection Agency (ROCEPA) [28], Czech Regulations [27] and the maximum permissible concentrations for potable water multiply by one hundred heuristic which is suggested by Pereira and et al [29] were used instead.

Concentration of zinc was significantly higher in TCLP elutes and it exceeded the threshold leaching test limit according to the Czech and the ROCEPA regulations. However, it was lower than the maximum permissible concentrations for potable water multiplied by one hundred heuristic. Moreover, Zn leached from samples after the EN extraction were found to be lower than criteria for a hazardous landfill.

The Cr concentration in sample No.1 was slightly lower than for No. 2 and No. 3 probably due to lower concentrations in the original solid composition (See Table 3). This is also because of the solubility of chromium which is a minimum at a pH value near 9 [32].

Average amount of copper in leachates for both TCLP and EN tests exceeded the Czech and ROCEPA regulation limits and for a hazardous waste landfill. Results show that mean values for Cr and Cu obtained in leachates from both tests of PI-BA caused waste not to be disposed of at non-hazardous waste landfill sites.

Particle size distribution of solid waste was another reason for different results which has been studied with both TCLP [30, 33] and EN 12457-2 [30, 34] leaching tests. This should particularly be considered for the bottom ash that has a wide range of particle distributions.

The TCLP procedure often has been criticized as a conservative test due to acidic pH which is not often representative of natural environmental conditions [30]. Nevertheless, in the landfilling scenario at the M.B petrochemical plant high acidified rain may be considered because of high concentrations of sulphur compositions in the PSEEZ environment [35].

PI-BA used in this study and according to the Waste Management Act of Iran should be categorized as a hazardous waste and disposed of in an environmentally safe manner. As an alternative, stabilization and solidification techniques could be suggested because of specific speciation and concentrations of heavy metals prior to disposal.

CONCLUSION

For the first time in Iran bottom ash from a petrochemical waste incinerator was subjected to characterization studies by evaluating its physical properties, chemical composition and leaching properties. Results showed PI-BA is fine grade with the FM and SSDSG at 2.53 and 3.21, respectively. Primary chemical constituents from the waste were magnetite, CaO, Sulfur (reported as SO_3), MgO and ZnO with weight percentages of 49.8, 16.23, 7.6, 4.0 and 3.8, respectively. The TCLP and EN 12457-2 single batch leaching tests were used to examine extraction capacity of bottom ash from solid to aqueous phase under different leaching conditions.

With regard to results for Cr and Cu concentrations from the TCLP and EN 12457-2 tests, PI-BA should be classified as a hazardous waste and disposed of according to hazardous waste disposal considerations or stabilized prior to disposal. The stabilization process can be considered an appropriate and cost-effective alternative to the hazardous waste landfill disposal, especially in the PSEEZ area where hazardous waste landfills do not yet exist.

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Predicting Required Time for Salt Leaching through Laboratory Physical Modeling using Artificial Neural Networks

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ABSTRACT: Forecasting appropriate time for cultivation after salt leaching in saline soils is considered as a fundamental element in sustainable production in natural resources management. The aim of this study is to develop an artificial neural network in combination with laboratory physical model to precisely estimate required leaching time before cultivation phase. To achieve this objective, soil samples from field were ordered in to cylinders in the laboratory as same as soil profile in the field. Process of salt leaching was carried out and time series of electrical conductivity (EC) were measured in collected drainage water. Parameters in the neural network were trained and predictions were validated. The results indicate that the developed ANN is capable of predicting required time for salt leaching accurately with an error of less than 0.0001 minute from observations.

INTRODUCTION

LAND degradation is a process that decreases the capacity of land [11]. It has been one of the major global issues during the last century and continues to be important in the international agenda in the 21th century [7]. Soil salinity as one of the most important land degradation problems limits sustainable production, particularly in arid and semi-arid regions. Salinization can be created by various factors which some of them are natural and some others are human-induced. Salt contained parent materials, inappropriate drainage systems, rising ground water table, and mismanagement in irrigated lands are some important reasons for soil salinity [20, 21].

According to statistics, one billion hectares of earth's continental naturally have been affected by salts and around 77 million hectares of lands have been salinized as a consequence of human activities. On average, 20% of the world's irrigated lands have been affected by salinity which increases to more than 30% in some countries such as Egypt, Iran and Argentina [8]. Based on FAO and UNESCO reports, about half of the current world's irrigated regions are under the influence of secondary salinization. In fact, in spite of general awareness of the problem and advancements in assessment approaches, salinization continues to increase in some parts of the world [3, 25]. Due to population growth, limitation in arable lands, and fresh water, some land reclamation practices were made to increase the agricultural production during the last decades [12].

In principle, management or amendment of salt-affected areas is not impossible but land reclamation and remedial actions require reliable information to set priority considerations in each case. Decision-makers need confidence that all technical approaches and provided data are reliable and accurate enough, since over- or underestimating in the extent, magnitude, and spatial distribution of salinity extremely affect the socio-economical condition [17].

In saline areas, the first suggested remedy is to adequately drain off the affected site naturally or artificially. In fact, one of the most common and easy to use approaches for decreasing salt concentration is to leach soil profile by fresh water (low content of salts). Therefore in such areas, due to the importance of using extra water, in addition to the plant needs, amendment practices play an important role in water resource management. According to the aforementioned issues, monitoring soil salinity variation for improving water usage efficiency and predicting appropriate cultivation

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time after salt leaching is a fundamental issue in sustainable agriculture development [5, 15].

Although nowadays critical environmental problems can be modeled by sophisticated three-dimensional numerical approaches, yet a large amount of field observation and lots of efforts are required to calibrate and verify these models. Due to this reason, a simple one-dimensional model or time series models are used as a useful tool for planners to rapidly assess the environmental changes [10]. During last years, advances in computational power facilitate innovation and development of new technologies. Such is the case of artificial neural networks that have brought various solutions to design and implement intelligent systems [18].

ANN, inspired by the biological nervous system, increasingly has been used as one of the most common and valuable modeling approaches to forecast in a broad field of science, such as finance, power generation, medicine, and environmental science. Recent studies revealed that statistical principles in the design of ANN improve performance of the model [16]. Indeed, ANN modeling approaches could successfully overcome some of the difficulties associated with traditional statistical approaches [10].

MATERIALS AND METHODOLOGY

The study area was in Markazi Province, central part of Iran. Based on available geo-pedological map and previous salinity reports, the most salt-affected site was selected for collecting field data. Possibility of amendment of saline soils through laboratory physical models was examined, and relationship between amount of soil salinity and time was explored for further use in developing neural network.

Soil Sampling and Laboratory Analysis

After exploring the most salt-affected series of soil in the study area, a vertical soil profile was excavated and soil samples from 0 to 10, 10–20, 20–30, 30–40 and 40 to 50 centimeter depths were collected. Collected soil samples from different layers were air dried and ordered in to designed cylinders in the laboratory as same as soil profile in the field. Before and after leaching procedure, important physicochemical soil attributes such as EC, SAR, ESP, and pH were measured. Permanent flooding method was applied on the cylinders for leaching salts from soil. In order to simulate reality, required leaching water was provided from the nearest well in the area, which was routinely used for irrigation. Before starting leaching, chemical properties of water sample were analyzed.

Design of Cylinders and Laboratory Physical Modeling

To facilitate Laboratory Physical Modeling, the cylinders with 10.5 cm diameter, and 70 cm height were designed. As mentioned above, soil samples were placed in the cylinders with the same order of soil profile in the field. In order to understand the relationship between amount of soil salinity and time, electrical conductivity of drainage water as indicator was measured. To gather the drainage water, a pipe was placed at the end of each cylinder. Some gravel was placed in the bottom of the cylinders to prevent blockage of the pipes. The process of leaching salt from saline soil was carried out by using twice the calculated pore volume in three different cylinders. Once every 160 minutes, the electrical conductivity was measured in the collected drainage water. The average of measured EC from three different cylinders was computed to train the developed artificial neural network [19].

Network Architecture

In this study with respect to the type of required data, Feed Forward network with two layers was used (Figure 1). Feed forward networks often have one or more hidden layers of sigmoid neurons followed by an output layer of linear neurons. Multiple layers of neurons with nonlinear transfer functions allow the network to learn nonlinear and linear relationships between input and output vectors. The linear output layer lets the network produce values outside the range –1 to +1 while the output of sigmoid neurons were limited to a small range.

In the developed network in this study, the first layer (Hidden Layer) includes two neurons, with translation function, Tan Sigmoid, and outer layer is composed of one neuron with liner translation (purelin) [22, 23, 24]. Figure 2 and 3 illustrate the Tan-Sigmoid Transfer and Linear Transfer Functions respectively.

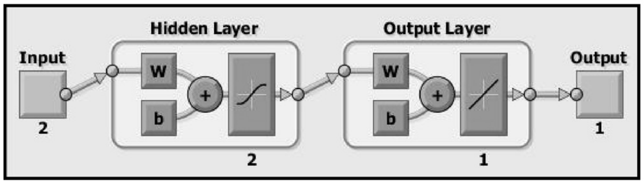

Figure 1. *A schematic diagram of the developed neural network.*

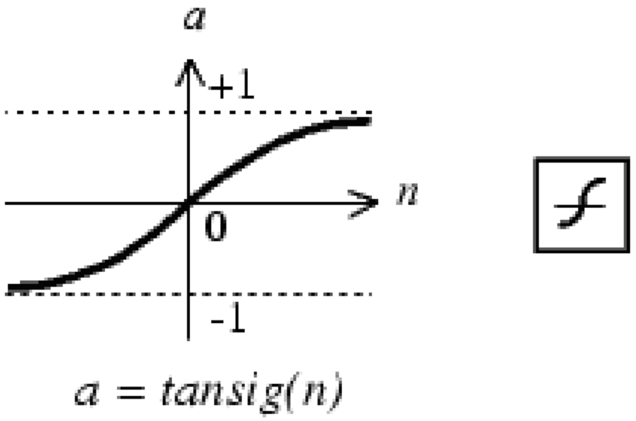

Figure 2. *Tan-sigmoid transfer function.*

ANN classifier was the Feed forward back propagation (BP) architecture trained using the Levenberg–Marquardt Algorithm.

In fact, in order to decreasing the computation time and increasing the accuracy, Levenberg–Marquardt Algorithm was used. The Levenberg–Marquardt Algorithm was designed to approach second-order training speed without having to compute the Hessian matrix. When the performance function has the form of a sum of squares (as is typical in training feed forward networks), then the Hessian matrix can be approximated as:

$$H = J^T J \tag{1}$$

and the gradient can be computed as:

$$g = J^T e \tag{2}$$

where J is the Jacobian matrix that contains first derivatives of the network errors with respect to the weights and biases, and e is a vector of network errors. The Jacobian matrix can be computed through a standard back propagation technique that is much less complex than computing the Hessian matrix. The Levenberg-Marquardt algorithm uses this approximation to the Hessian matrix in the following Newton-like update:

$$X_{k+1} = X_k - [J^T J + \mu I]^{-1} J_T e \tag{3}$$

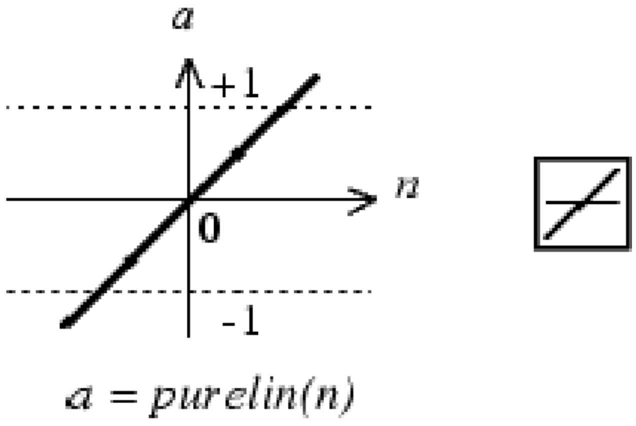

Figure 3. *Linear transfer function.*

When the scalar μ is zero, this is just Newton's method, using the approximate Hessian matrix. When μ is large, this becomes gradient descent with a small step size. Newton's method is faster and more accurate near an error minimum, so the aim is to shift towards Newton's method as quickly as possible. Thus, μ is decreased after each successful step (reduction in performance function) and is increased only when a tentative step would increase the performance function. In this way, the performance function will always be reduced in each iteration of the algorithm.

According to priori knowledge and correlation analysis [6, 13, 14] matrix EC was input and the output matrix was *T*, which is the leaching time required to achieve a specific EC. The network programming was done using Matlab software and the Neural Network Toolbox [10].

Training Feed-Forward Network and Validation

The average of recorded EC and time from three different cylinders was normalized into the range of zero to one. It was done by determining the maximum and minimum values of each variable over the whole data period using the following equation [22, 24].

$$X_{norm} = \frac{X}{X_{\max}} \tag{4}$$

Where X is the observed value for each variable and $X_{\max}$ is the Maximum observed value over the whole data period. The provided data set were divided into three groups to use in the processes of design, calibration and validation of the network development. The statistical properties of the data sets were evaluated to ensure each set can present the population [2]. The training process is affected by several parameters such as goal, the number of epochs and check validation. In training phase, the parameters were adjusted until the root-mean-square error (RMSE) between time predictions by model and the observations reduced to an acceptable level [1]. The principal of empirical regression equations and neural network are similar, in both of them after satisfactorily training the model, no itera-

Table 1. Physicochemical Properties of Soil Before Leaching.

SAR (meq/lit)$^{0.5}$	pH	EC (ds/m)	T.N.V %	Texture	Depth (cm)
49.2	8.15	40.0	38.75	Si–C	0–10
37.5	8.40	36.0	38.25	C–L	10–20
48.4	8.35	24.0	39.25	C	20–30
55.2	8.34	20.0	38.75	C	30–40
35.4	8.33	18.0	41.25	C	40–50

tive computation is required [3, 4]. As mentioned in the previous section, in order to decrease the complexity of computation and increase the accuracy, Levenberg–Marquardt Algorithm was used in the training phase of design [9, 23]. In order to evaluate the accuracy of the predictions, performance of the designed network was validated with another independent data set [4]. Regarding matrix EC as input and matrix T as out put, some following parameters were defined; learning rate of the ANN classifier = 0.1, number of epochs = 300 with the goal of 1e–5 and check validation equals 8 [22, 24].

RESUTS AND DISCUSSION

As mentioned above, some important physicochemical soil attributes which were summarized in Table 1 and Table 2 respectively, before and after leaching procedure were measured.

Results show that corresponding soil salinity parameters has been reduced after leaching.

Selected chemical properties of leaching water are also illustrated in Table 3.

Statistical analysis showed a high correlation between electrical conductivity of drainage water and time with correlation coefficient of above 0.99 (Figure 4). Based on correlation analysis and priori knowledge, EC of drainage water was considered as input and time as output in the neural network development phase.

Model predictions during the training phase fit well with observation, showing a correlation coefficient above 0.99 (Figure 5).

Table 2. Chemical Properties of Soil After Leaching.

SAR (meq/lit)$^{0.5}$	pH	EC (ds/m)	T.N.V %	Depth (cm)
29.9	6.9	9.8	34.5	0–10
28.2	7.1	11.1	34.7	10–20
28.5	7.3	10.0	35.0	20–30
30.3	8.3	10.3	38.8	30–40
30.9	7.7	10.7	41.8	40–50

Table 3. Chemical Properties of Soil After Leaching.

SAR (meq/lit)$^{0.5}$	Ca+Mg (meq/lit)	Na (meq/lit)	pH	EC (ds/m)
12.97	17.4	68	7.9	7.3

Statistical analysis showed a strong relationship between electrical conductivity of drainage water and time with correlation coefficient of above 0.99 during test phase (Figure 6).

Although 300 iterations (epochs) was initially defined for the training process, the process was stopped after 12 epochs with check validation equals 8 and Mu = 1e–005. Figure 7 demonstrates the training process for the first twelve iterations (epochs) while the model was properly trained after 4 epochs. As can be seen, there was a downward trend in RMS error for the first twelve iterations while it remained constant until the end of process.

Comparison between results of the developed artificial neural network and available data set for validation showed a strong correlation between model predictions and observations (Figure 8).

As can be seen from corresponding figures, the correlation coefficient between measured time in the libratory and time predicted by the model was above 0.99, with the RMS error less than 0.0001 minute. In fact, the performance of the model matched reasonably with the observations in both training and validation phases.

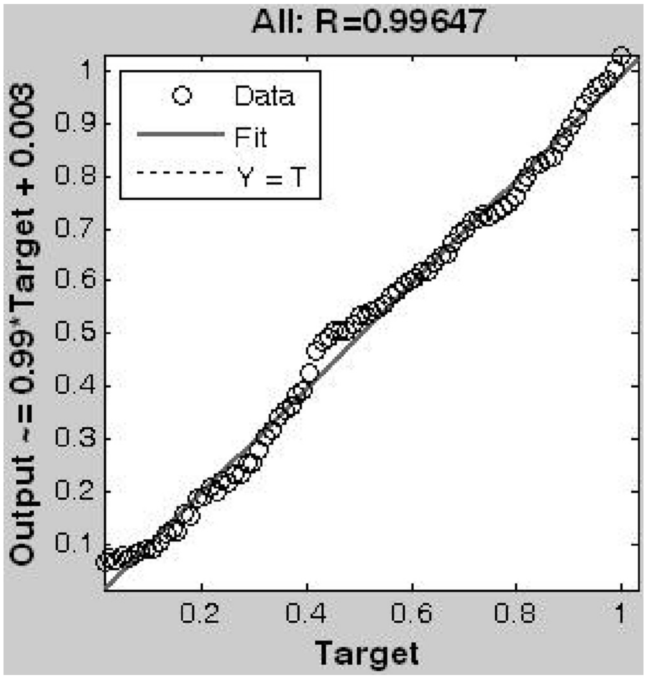

Figure 4. *Correlation between electrical conductivity of drainage water and time.*

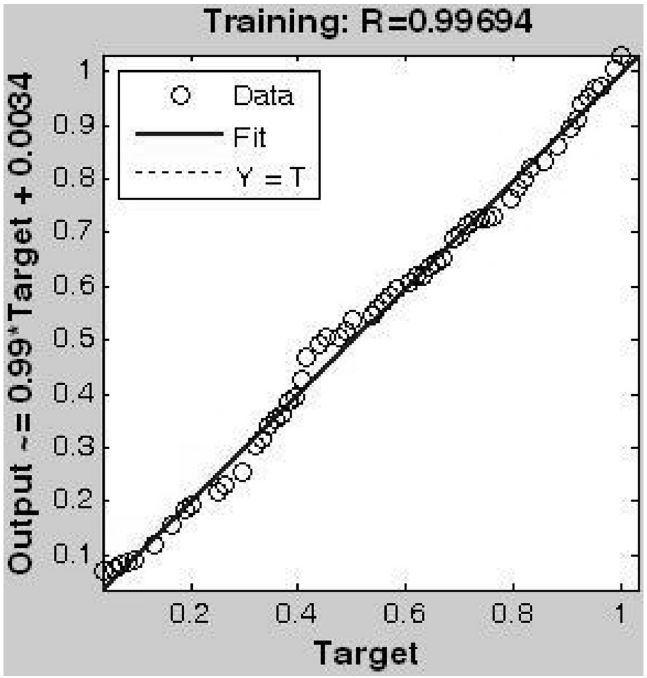

Figure 5. *Correlation between electrical conductivity of drainage water and time during training phase.*

It is necessary to mention by predicting time, corresponding Electrical Conductivity of drainage water can be driven from artificial neural network. With respect to EC of irrigation water and EC of drainage water, EC of soil saturation extract can be calculated as displayed in Equation (5).

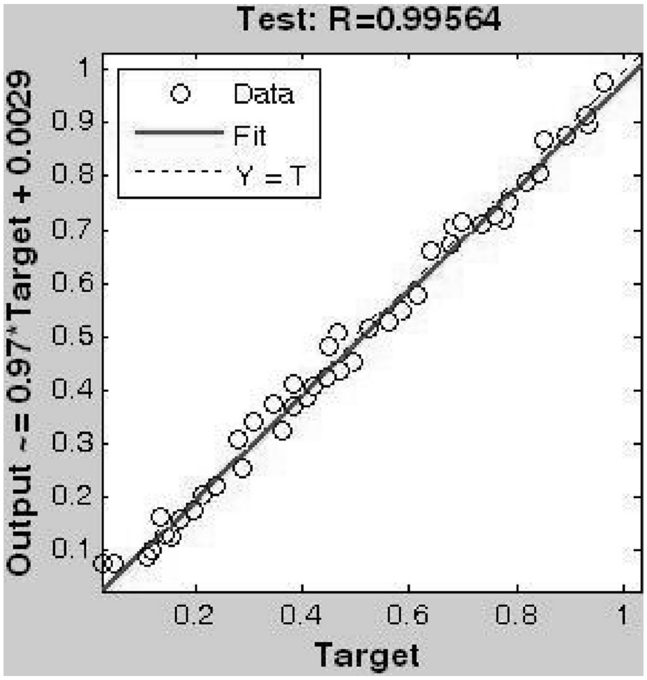

Figure 6. *Correlation between electrical conductivity of drainage water and time during test phase.*

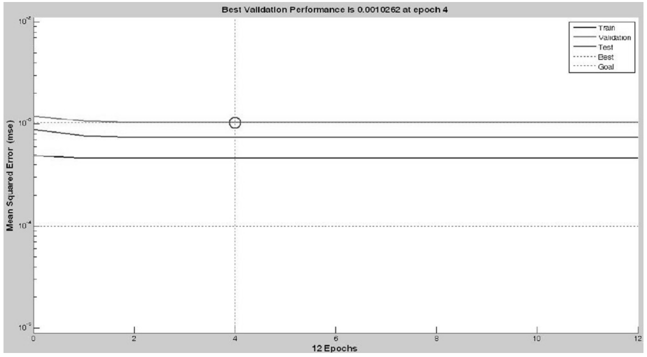

Figure 7. *Results from network training, validation during the model development period.*

$$EC_e = \frac{(EC_{dw} + EC_{iw})}{2} \tag{5}$$

According to the relation between EC_e and Electrical Conductivity in Field Capacity condition [Equation (6)], the value of EC_{fc} (suitable condition for cultivation) can be obtained.

$$EC_{fc} = 2.5EC_e \tag{6}$$

In fact, by measuring Electrical Conductivity of leaching water and tracking Electrical Conductivity of drainage water, Electrical Conductivity in Field Capacity condition (FC) can be calculated. Concerning ideal Electrical Conductivity for any type of crops and their salinity tolerance, suitable time for plantation can be identified.

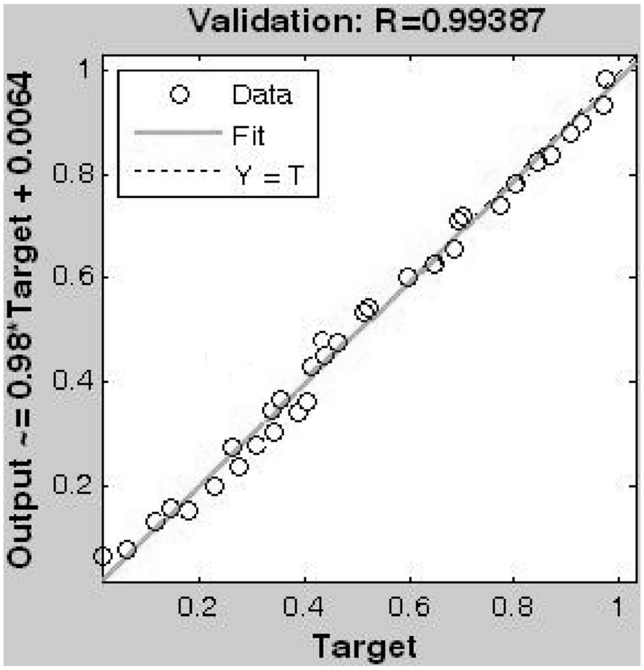

Figure 8. *Comparison between observed and predicted time.*

CONCLUSION

To make appropriate decisions for crop production, an accurate estimation of soil salinity is appreciated for both land planners and farmers. In this study, in addition to demonstrating the laboratory leaching, a successful application of ANN was presented to simulate variation of soil salinity during leaching process. Results indicate that neural network model can be trained to provide satisfactory predictions of cultivation time in saline soil regarding salinity tolerance of crops type. In fact, by considering the relation between Electrical Conductivity of leaching water and EC of drainage water, Electrical Conductivity in Field Capacity (FC) can be calculated. Evaluating temporal variation of soil salinity through laboratory physical modeling integrated with ANN algorithms can be applied in all salt affected areas. The proposed methodology can be considered as a feasible, cost-effective and easy-to-use tool for land amendment practices in saline areas.

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Table 5. Comparison of state-of-the-art matrix resins with VPSP/BMI copolymers.

Resin System	Core Temp. (DSC peak)	T_E	Char Yield, %
Epoxy (MY720)	235	250	30
Bismaleimide (H795)	282	>400	48
VPSP/Bismaleimide copolymer			
C379: H795 = 1.9	245	>400	50
C379: H795 = 1.4	285	>400	53

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