

**Original Article****Characterization of an Industrial Sewage Sludge and Its Evaluation for Land Application**Mohsen Mohammadi Galangash<sup>\*1</sup>, Mostafa Mahdavianpour<sup>2</sup>, Samira Ghafouri Safa<sup>3</sup>

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**ABSTRACT**

**Background:** Sewage treatment leads to the production of large amount of sludge, containing organic matter and nutrients and considering requirements for recycling could be used as fertilizer. The sludge may also contain various pollutants that pose serious harm to human health and the environment. This study aimed at characterizing the industrial sewage sludge and evaluating its capability as fertilizer with no or a minor pretreatment.

**Methods:** The sludge's organic matter and nutrient contents, heavy metals, organic and microbial contaminants were determined and compared to literature data and international guidelines.

**Results:** The organic matter, nutrients, phosphorous, and exchangeable potassium contents of the sludge samples were significantly high as follows:  $33.6 \pm 2.85$  %,  $6.29 \pm 0.16$  %,  $1.41 \pm 0.01$  % and  $1.236$  g/kg, respectively. The concentration of heavy metals was  $94.3 \pm 59.5$  mg/kg. The concentration of heavy metals, organic contaminants, such as PCBs, BTEX, and PAHs, and microbial contents (coliforms & *E. coli*) were lower than those reported by other studies. Toluene concentration was high.

**Conclusions:** All characteristics of the sludge samples, except for the toluene and microbial contaminations, were acceptable for its use as land fertilizer. Both toluene and microbial contaminants can be removed, using thermal conditioning as a pretreatment.

**Keywords:** *E. coli*, Heavy Metals, Land Application, Industrial Sewage Sludge, PCBs.

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**INTRODUCTION**

Sewage treatment leads to the production of large amounts of sludge, and the treatment and disposal of sewage sludge are the most expensive steps [1-4]. Further, sewage sludge contains much organic materials and nutrients that could potentially be used as enriched source of plant nutrients, i.e., fertilizer. However, the sludge may contain various pollutants with serious and harmful effects to human health and environment. Heavy metals, organic contaminants such as, PCBs, BTEX and PAHs, and pathogens are the main groups of sludge pollutants [5-8]. The quantities of these pollutants vary depending on the sewage source and the treatment processes. Land application is the most common and beneficial option for the disposal of sewage sludge worldwide. Studies have been conducted on the application of urban raw and digested sludge samples on land, but only few have focused on other capabilities of industrial sludge [9-11]. The sewage sludge treatment consists of thickening, stabilization, conditioning, and dewatering processes [12]. Depending on the type of sludge, one or more steps may be removed from the treatment.

This study was conducted to assess the characteristics of raw and dried industrial sewage sludge and if a complete sludge treatment is necessary for all types of

sludge before they are considered as fertilizers. For these purposes, the contents in nutrients, heavy metals, organic materials, such as PCBs, BTEX, and PAHs, and microbial contaminants were analyzed. The data were then compared to those reported in the literature. Further, we have proposed a helpful sludge pretreatment step to remove the toluene content.

**MATERIALS AND METHODS****Wastewater Sources and Treatment Chain**

Wastewater sources were 15 industrial units, including food processing (9 units), metal industry (3 units), cellulose industry (1 unit), window and door manufacturer (1 unit) and electrical industry (1 unit) located in Lahijan Industrial Complex (Guilan, Iran). The influent (incoming) wastewater was treated at a treatment plant in the following order: screening, cyclone grit removal, API grease and oil separator, equalization tank, anaerobic fixed bed reactor (AFBR), moving bed biological reactor (MBBR), settling tank and chlorination. The treatment components are shown in Figure 1.

The wastewater flow was  $106$  m<sup>3</sup>/d and influent COD, BOD and TSS concentrations were in the range of 1400-2200, 800-1200 and 1500-2500 mg/L, respectively. Also, effluent (outgoing) COD, BOD and TSS

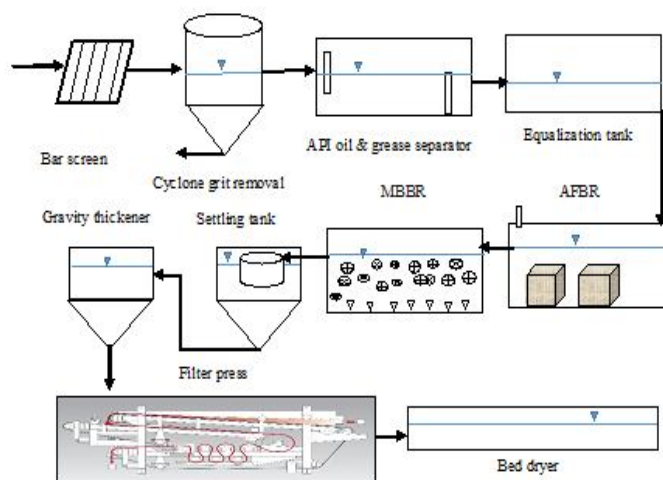
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concentrations were in the range of 40-110, 30-60 and 30-60 mg/L, respectively. Waste sludge was disposed to gravity thickening and dewatered through a filter press. Finally, dewatered sludge was transferred to bed driers for further drying.



**Figure 1.** Schematic diagram of wastewater treatment plant.

### Sampling Procedure

The samples were taken from the bed dryers based on standard procedures [13]. For this purpose, each bed dryer was divided into three parts and samples were taken from the center of each part. Then three samples were mixed to obtain a representative sample. Sampling was repeated three times and the average of three analyses for each parameter was used in this work. Sample transportation and storage were done according to standard methods for the examination of water and wastewater [13]. The samples were acidified to below pH 2, when needed, and preserved in polyethylene containers at 4°C.

### Ammonia, Nitrate and Total Nitrogen Analysis

Ammonia nitrogen was analyzed using Nessler method, modified for solid samples [14]. First, 20 g of sludge was transferred to an Erlenmeyer flask to which 50 mL  $K_2SO_3$  0.2 N was added. The mixture was shaken for 30 min and filtered with 0.45  $\mu$ m Whatman paper filter. Finally, 20 mL of the filtered solution was used for ammonia nitrogen determination, using Nessler method [14]. Nitrate was analyzed based on Brucine method [15]. In this method, the reaction between nitrate ions and brucine in acidic condition produce a yellow color. Although color intensity is not in compliance with Beer-Lambert law, adsorption light curve is proportional to nitrate concentration. First, 12.5 g of sludge and 1g of activated carbon were transferred to an Erlenmeyer flask to which 25 mL acetic acid 0.5 N (pH = 4.8) was added. Finally, 1 mL of Brucine reagent was added to the mixture and the color intensity was recorded, using a spectrophotometer at 410 nm.

Total nitrogen was analyzed using Kjeldahl method [16]. For this purpose, 1 g of dry sludge (passed through

a 0.5 mm sieve) was digested; using a prompt tablet, then 15 mL of concentrated sulfuric acid was added to the digested sludge and heated to 180 °C until the sample was decolorized. Total Kjeldahl nitrogen (TKN) was measured using Kjeldahl Digestion device (VELP CO).

### Available Phosphorous Analysis

The available phosphorous was analyzed using Olsen method [16]. In this method, 1 g of air-dried sludge was shaken along with 20 mL 0.5 N  $Na_2CO_3$  (pH = 8.5) and 0.3 g activated carbon. Then, the mixture was centrifuged at 120 RPM and the supernatant was filtered through 0.45  $\mu$ m Whatman paper filter. Finally, 5 mL of Olsen reagent was added to the filtered sample and its absorbance measured on a spectrophotometer at 880 nm.

### Organic Carbon Analysis

The organic carbon was analyzed based on the Walkley-Black method [16]. In this method, 1 g of sludge (passed through a 0.5 mm sieve) was transferred to a 250 mL Erlenmeyer flask, then 10 mL of 0.5 M  $K_2Cr_2O_7$  and 20 mL of concentrated sulfuric acid were added and reacted for 30 minutes. Finally, 100 mL distilled water was added to the mixture and titrated with 0.5 M ammonium ferrous sulfate in the presence of phenanthroline. Organic carbon was calculated using consumed ferrous sulfate.

### Heavy Metals Analysis

We analyzed 10 heavy metals contents of the samples for Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Molybdenum (Mo), Nickel (Ni), Selenium (Se) and Zinc (Zn). For volatile metals, such as As, Hg, and Se, freeze-dried samples (1 g) were digested [1]. In this method, nitric acid ( $HNO_3$ ) and hydrochloric acid (HCl) at a ratio of 1:3 were mixed with samples and heated for 1 hour at 40 °C and increased the temperature to 80 °C for 3 hours, using reflux method [1,2]. For organic metals, 6 mL of perchloric acid ( $HClO_4$ ) were added to the sample. After digestion, Tin (II) chloride was added to samples before analysis by an atomic absorption spectroscopy unit (AAS Varian 55B), equipped with cold vapor and hydride production system.

For other stable metals, first, the samples were dried at 105 °C and powdered, then filtered with 63  $\mu$ m sieve and digested, using wet digestion method [1,2]. The procedure was as described above, except for the second heating period where the temperature was increased to 120 °C. Digested samples were analyzed, using inductively coupled plasma - optical emission spectrometry (ICP-OES; Liberty RL model).

### Chlorinated Organic Compounds Analysis

For these analyses, the polychlorinated biphenyls and benzene chloride were extracted with a mixed solvent, diethyl ether/hexane or methylene chloride/hexane. The extract was concentrated by evaporation and, if necessary, it was cleaned up by column adsorption-

chromatography [13]. The individual compounds then were determined by gas chromatography – mass spectrometry (GC/MS; Agilent Technology).

### **Polynuclear Aromatic Hydrocarbons (PAHs) and Total Petroleum Hydrocarbons (TPH) Analysis**

Preparation and extraction of these compounds were similar to the method mentioned earlier for chlorinated organic compounds, based on Standard Methods [13]. Analysis of these compounds was conducted by GC/MS (Agilent Technology).

### **Microbial Analysis**

For investigation of microbial presence in the dried sludge samples, total coliforms, based on multiple-tube fermentation technique and *E. coli* (fecal coliforms) were selected as indicators. These analyses were performed based on APHA Standard Methods (9221 A and 9221 F) [13]. For total coliforms, 15 tube procedure with three steps include presumptive phase, confirmed phase and completed phase was used. For these phases, lauryl tryptose broth, brilliant green (BG) and brilliant green lactose bile broth (BGB) along with electrical conductivity (EC) were used as the Culture medium, respectively.

### **Other Analyses**

For pH determination of the samples, sludge was mixed with distilled water (ratio 1:2) and shaken for 30

minutes. Finally, the samples' pH was determined using a Metrohm pH meter (Herisau, Switzerland). The EC was analyzed using the same Metrohm device.

## **RESULTS**

### **Physico-Chemical Characteristics of Sludge**

Results of the nutrients and organic matter contents of the sludge samples in comparison with reported values in literature are shown in Table 1.

### **Heavy Metals Concentration in Sludge**

Results of heavy metal analysis in undigested sludge are shown in Table 2.

### **Organic Contaminants in Sludge**

#### **PCBs and BTEX**

The concentrations of PCB 44, 88 and total PCBs were  $7 \pm 3.1$ ,  $3.7 \pm 0.3$  and  $10.7 \pm 3.4$   $\mu\text{g}/\text{kg}$ , respectively.

Table 3 shows the mass concentration of BTEX in the studied sludge.

### **Polynuclear Aromatic Hydrocarbons (PAHs)**

The contents of individual PAHs and total PAHs documented in the present study against reported values for raw and digested sludge samples are shown in Table 4.

**Table 1.** Organic matter and nutrient contents of undigested industrial sewage sludge (mean value (SD), n=3) in comparison with urban sewage sludge reported by other studies.

<i>Parameter</i>	<b>OM (%)</b>	<b>TN</b>	<b>NH<sub>4</sub><sup>+</sup> (g/kg)</b>	<b>TP</b>	<b>K (%)</b>	<b>Exchang eable K</b>	<b>pH</b>	<b>Ref.</b>
<i>Current work</i>	33.6 (2.85)	6.29 (0.16) <sup>(a)</sup>	0.98 (0.07)	1.41 (0.01) <sup>(a)</sup>	0.31 (0.00)	1.236 (0.00)	6.06 (0.00)	
<i>Dewatered sludge anaerobically</i>	19.82	3.43	-	-	-	-	6.82	[17]
<i>digested biosolids</i>	43.4	2.5	-	1.06	0.2	0.2	8.6	[4]
<i>Dried sewage</i>	23.2	2.6	-	1.34	0.42	0.42	7.1	[4]
<i>Standards (EPA)</i>	-	0.1-3.5	-	0.3-3.5	0.1-2.8	-	6-8	[18]
<i>Dried sewage sludge</i>	36.2 (3.6)	-	-	-	-	0.25 (0.34)	9.13 (0.16)	[19]
<i>Stabilized after centrifuge</i>	-	40.61 (1.12)	0.4 (0.02)	42.54 (1.12)	-	0.41 (0.01)		[1]
<i>Stabilized with sawdust</i>	-	18.58 (0.43)	0.4 (0.02)	63.52 (2.14)	-	0.41 (0.01)		[1]
<i>sludge (compost for 4 month)</i>	-	18.95 (0.42) <sup>(b)</sup>	0.4 (0.02)	51.78 (1.89) <sup>(b)</sup>	-	0.45 (0.01)		[1]
<i>sludge (mature compost)</i>	-	11.08 (0.35) <sup>(b)</sup>	0.4 (0.03)	41.4 (2.56) <sup>(b)</sup>	-	0.45 (0.01)		[1]
<i>Sewage sludge compost</i>	-	12.2 (0.04)	-	5.4 (0.21)	-	7.3 (0.4)		[3]
<i>Anaerobic septic sludge</i>	-	32.5	-	8.7 (0.15)	-	2.5 (0.15)		[3]
<i>Aerobically- digested sludge</i>	-	53.7 (0.12)	-	16.9 (0.22)	-	5.7 (0.05)		[3]

(a) %

(b) g/kg (DM)

**Table 2.** Concentration of heavy metals (mg/kg) compared to reported values for digested sludge samples by different methods.

Metal	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Mo (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Se (mg/kg)	Zn (mg/kg)	reference
Present work	1.6 ± 0.25	ND <sup>(a)</sup>	5.6 ± 4.8	10.3 ± 6.5	0.14 ± 0.03	0.57 ± 0.2	3.4 ± 1.7	7.4 ± 8.2	0.78 ± 0.16	94.3 ± 59.5	-
Germany (agriculture)	-	1.5	100	60	1	-	50	100	-	200	[8]
EUA (agriculture)	-	20	1500	70	8	-	210	150	-	1400	[8]
Four raw sewage sludge (mean values)	-	1.9-76	27.6- 120	156- 335	-	-	21.7- 155	37.9- 59.5	-	1015- 1385	[2]
76 days compost of 4 sewage sludge	-	1.95-76	25.7- 124.5	155- 314	-	-	17.7- 177	35.2- 52.5	-	935- 1490	[2]
Undigested dried sewage sludge	-	15.3 (2.8)	161.5 (7.5)	321.3 (6.8)	-	-	127.2 (8.1)	109.3 (6.8)	-	408 (7.0)	[19]
Stabilized after centrifuge	-	2.38 (0.21)	72 (2.04)	81.3 (2.12)	0.6 (0.09)	-	17.3 (0.34)	21.8 (0.77)	-	691.5 (11.21)	[1]
Stabilized with sawdust sludge (compost for 4 month)	-	2.12 (0.21)	40.8 (1.21)	33.3 (0.99)	0.59 (0.09)	-	16.1 (0.25)	18.5 (0.43)	-	299.1 (7.6)	[1]
sludge (mature compost)	-	0.78 (0.19)	38.5 (1.09)	39.2 (1.12)	0.58 (0.08)	-	9.6 (0.12)	7.23 (0.19)	-	160.5 (4.22)	[1]
sludge (mature compost)	-	0.56 (0.1)	33.2 (1.01)	23.7 (0.78)	0.58 (0.08)	-	8.4 (0.1)	6.38 (0.22)	-	220.9 (6.13)	[1]

(a) Nondetectable

**Table 3.** Contents of BTEX (µg/kg) in sludge samples compared to reported values.

Compound	Benzene	Toluene	Ethylbenzene	Total xylenes	Total BTEX	Reference
Current work	ND	376 (40.4)	ND	ND	376 (40.4)	-
Sewage sludge (a)	ND	0.39 (0.43)	ND	0.83 (0.37)	0.64 (0.8)	[9]
Dyeing sludge	12.81	33.98	16.85	84.27	147.91	[20]
Leather-tanning sludge	2.72	11.1	8.21	12.21	34.24	[20]
Paper mill sludge	7.9	29.52	25.66	86.07	149.15	[20]
Municipal sludge	3.91	9.02	6.18	8.4	27.51	[20]
Municipal sludge	11.12	9.66	6.2	12.12	39.1	[20]
Municipal sludge	8.51	18.88	17.73	36.3	81.42	[20]
Municipal sludge	2.55	8.47	5.73	8.37	25.12	[20]

(a): average values of 5 raw sewage sludge

**Table 4.** PAHs contents of industrial sewage sludge (µg/kg) compared to reported values.

Compound	Naphthalene	Acenaphthene	Phenanthrene	Benzo[k] fluoranthene	Others	Total	Ref
Present work	9.5 (1.76)	3.3 (0.46)	5.1 (0.9)	1.3 (0.26)	ND	19.2 (3.4)	-
11 raw urban sewage sludge <sup>(a)</sup>	0.49	0.15	2.2	0.4	-	16 <sup>(b)</sup>	[7]
35 raw urban sewage sludge	ND	26.25 (9.5)	63.5 (32)	68 (62) <sup>(c)</sup>	-	452.5 (149)	[6]
19 raw urban and industrial sewage sludge	80 (225)	65.9 (300)	1062 (1490)	28.7 (70) <sup>(d)</sup>	-	2420 (3000)	[11]
14 digested urban sewage sludge	3.7 (9.4)	4 (2.45)	7 (6.4)	2.2 (1.9)	-	130 (151.5)	[21]

(a) Mean value (mg/kg)

(b) Sum of 16 US EPA priority PAH concentration.

(c) Sum of 3 isomers j, k and b of benzo-fluoranthene

(d) Sum of 2 isomers j and k of benzo-fluoranthene

### **Microbial Contaminations of Sludge Samples**

The values of total coliforms, fecal coliforms and *E. coli* for studied sludge samples were  $17.8 \pm 0.5 \times 10^6/\text{gDS}$ ,  $7.3 \pm 0.7 \times 10^6/\text{gDS}$  and  $3.6 \pm 0.35 \times 10^6/\text{gDS}$ , respectively.

## **DISCUSSIONS**

### **Physico-Chemical Characteristics of Sludge**

As seen in Table 1, organic matter contents of the industrial sewage sludge ( $33.6 \pm 2.85$ ) were in the range of reported dried [17,19] and digested urban sewage sludge [4], but values of nutrients were higher than mentioned sludge samples. Both AFBR and MBBR processes employed for the treatment of industrial wastewater produced stabilized sludge, so the dried sludge samples had similar organic contents compared to the reported values in the literature. The high organic matter of the studied sludge could improve the short-term properties of soil including the microbial populations and humic contents [19]. The values of phosphorous and potassium were in the range required for land applications, based on EPA standards, but nitrogen contents were higher than the normal limits. The pH value of the undigested industrial sludge was lower than those reported by other studies. In this context, the acceptable pH range for land application is anywhere from pH 6 to 8) [22]. Although mineralization of OM in the sludge could induce metal solubilization and release into the soil solution, sludge chemical properties, such as pH buffering capacity and high levels of exchangeable cations, would suppress the release of metals into solution [17]. The low pH value may be because of non-degraded organic acids (mainly acetic and butyric acids) [23] in the undigested sludge or the characteristics of treated wastewater. The EC value of the investigated sludge samples was  $7.23 \pm 0.1$  dS/m. The high EC value of the sludge samples was because of high salinity contents of processed food and cellulose in the wastewaters [24,25].

In comparison with stabilized sludge samples obtained through different methods, the investigated sludge in this study had a very high content of total nitrogen, the ammonium content was slightly higher than 2-fold. Based on the reported value in Table 1, increased in stabilization level of the sludge samples lead to a decrease in nitrogen contents through dilution, microbial consumption, and gaseous loss. Regarding the land application as fertilizer, ammonia nitrogen is directly available for the plants, so undigested sludge has a higher fertilizing value than the stabilized sludge [26].

Phosphorous is another valuable element for recycling. The total phosphorous content was 22-33-fold higher than that found in the digested sludge. The solubility of potassium leads to its release from the treated sludge supernatant, it appears that digestion

methods lead to a loss of  $\text{K}^+$  contents [1,2]. As shown in Table 1, the potassium content found in this study was approximately 3 times higher than the reported values for the evaluated and digested sludge samples.

### **Heavy Metals in Sludge Samples**

Based on the data presented in Table 2, the concentrations of all of the heavy metals were significantly lower than the international limits for agricultural use. Except for the lead content, compared to the value in well-digested composts, the concentrations of other heavy metals found in the present study were significantly lower than those reported for raw and stabilized sludge samples [1,2,8,19]. The high concentrations of heavy metals reported by other studies could be due to variations in wastewaters and treatment processes. The order of individual heavy metals, based on their values from undigested sludge samples was:  $\text{Zn} > \text{Cu} > \text{Pb} > \text{Cr} > \text{Ni} > \text{As} > \text{Se} > \text{Mo} > \text{Hg} > \text{Cd}$ . This order was different from both undigested dry sludge ( $\text{Zn} > \text{Cu} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Cd}$ ) (19) and digested sludge by different methods (1). Shrivastava et al. [19] reported that the residual fractions of Zn, Cu, Cr, Ni, Pb, and Cd in undigested dry sludge was higher than those in available forms when measured by fractionation method. Using a similar method, Ignatowicz et al. [1] reported that the available heavy metals in digested sludge samples were significantly higher than those in the residual fractions. This suggests that the digestion of sewage sludge leads to the release of heavy metals and their harmful dissipation into the environment.

### **Organic Contaminants of Sludge**

#### **PCBs and BTEX**

Only two PCBs marked as 44 and 88 were detected in the sludge samples, while other PCBs were undetectable. Also, 7 indicator PCB congeners for agricultural use (codes of 28, 52, 101, 118, 138, 153 and 180) were not detected in undigested sewage sludge. By comparison of these compounds with other reported values, it is obvious that the concentration of PCBs in studied sludge samples were negligible compared to the raw, digested, centrifuged and thermally dried sludge samples [5]. This is mainly because of variations in wastewater source (urban versus industrial) and the applied treatment processes. On the other hand, quantified PCBs in this work (codes of 44 and 88) were not reported by other studies [8,27]. The total PCBs concentration ( $10.7 \pm 3.4$   $\mu\text{g}/\text{kg}$ ) was by far lower than the maximum value recommended for agricultural use, i.e., 0.2 mg/kg DW [8,27]. Based on studies on PCBs biodegradation, congeners with high chlorine number (tetra and higher) could degrade simply through anaerobic dehalogenation and congeners with low chlorine number (mono, di, and tri) could degrade better

under aerobic conditions [10,28]. Therefore, the treatment processes employed in present work (AFBBR and MBBR) and their order could qualify these requirements for PCBs degradation.

In this study, the detected PCBs in the sludge samples where highly-chlorinated (2,2',3,5'-Tetrachlorobiphenyl and 2,2',3,4,6-Pentachlorobiphenyl). Therefore, the appropriate digestion process for the stabilization of current sludge is anaerobic digestion.

As shown in Table 3, toluene was detected in our sludge samples at a concentration of  $376 \pm 40.4 \mu\text{g/kg}$ . This high concentration of toluene not only makes it higher than that in typical urban and industrial sludge samples, but also makes the total BTEX concentration higher than others. Higher concentration of toluene in undigested industrial sludge compared to that of other aromatic hydrocarbons (benzene, ethylbenzene, and xylenes) is consistent with other reports [29,30]. The high concentration of toluene could be because of wastewater source (use of toluene as a dye in cellulose and paper industries) and its production in anaerobic processes, mostly acidogenic phase [20,29,30]. In addition to the high concentration of toluene in sludge, its concentration in the supernatant during the drying process is high and can be used as carbon source in enhanced biological nutrients removal processes (EBNRP) [29]. For the removal of toluene, thermal conditioning of sludge at 170-220°C and pressure of 1.2-2.5 MPa for 15-30 minutes is the best option before dewatering samples through filter press. Using this method, 75-80% of toluene is degraded, 20-25% of which is emitted into the air. Therefore, adding an appropriate air pollution control system is a necessary step for this unit. This system improves the sludge dewatering by 50-60% after filter press and eliminates the need for chemical conditioning and sterilization of the sludge [12].

### **Polynuclear Aromatic Hydrocarbons**

As seen in Table 4, only four compounds (Naphthalene, Acenaphthene, Phenanthrene, and Benzo[k]fluoranthene) were detected in the sludge samples. The total concentration of detected compounds was  $19.2 \pm 3.4 \mu\text{g/kg}$  that was significantly lower than the maximum permissible concentration (6 mg/kg) proposed by EU for sludge used as soil fertilizer and to protect the soil microbial contents [6,7]. The concentrations of individual and total PAHs were considerably lower than those for raw urban and industrial sewage sludge reported by China, Italy and Spain [6,7,11,21]. However, the concentration of individual PAHs obtained in the present study was comparable with that for digested sludge, but total PAHs for digested sludge was higher and the reported concentration of naphthalene in digested sludge was lower than that in the present work. Considering to reported values in Table 6, there is a wide fluctuation

among the reported concentrations for individual and total PAHs in the literature. This could be due to differences among wastewater characteristics and the employed treatment processes. Regarding the number of rings in the structure of PAHs, the total concentration of 2-ring PAHs (naphthalene and acenaphthene), 3-ring PAHs (Phenanthrene) and 4-ring PAHs (Benzo[k]fluoranthene) were  $12.8 \pm 2.22$ ,  $5.1 \pm 0.9$  and  $1.3 \pm 0.26 \mu\text{g/kg}$ , respectively. Unlike PAHs' contents of raw urban sewage sludge, where three and more carbon rings were dominant, as reported by Quan-Ying et al. [7], 2-ring ng PAHs were the dominant variety in this study. This could be due to the degradation of high-ring PAHs in FBBR and MBBR process and their conversion to low-ring types. The only carcinogenic compound detected in our samples was benzo[k]fluoranthene at extremely low concentration of  $1.3 \pm 0.26 \mu\text{g/kg}$ .

### **Microbial Contamination of Sludge**

The abundant presence of pathogenic bacteria (i.e., fecal coliforms and *E. coli*) was due to the treatment of domestic and wastewater in the treatment plant. The total and fecal coliform concentrations were approximately 10 to  $10^4$  times lower than the values reported by Sidhu et al. [31] for raw sewage sludge. Total coliforms and *E. coli* concentration in the present study were  $10^4$  and  $10^2$  times, respectively, lower than those reported for raw sludge by Lloret et al. [32]. However, the *E. coli* concentration was higher than the value reported by Sidhu et al. [31]. In the case of fecal coliforms, the obtained value was higher than both class A ( $<1000 \text{ MPN/g DS}$ ) and class B ( $<2 \times 10^6 \text{ MPN/gDS}$ ) requirement proposed by USEPA for land application [33]. Also, the concentration of *E. coli* in the present work was not consistent with the requirements set by the European directive on the application of sludge as fertilizer ( $<1000 \text{ MPN/g DS}$ ) [32]. However, for application of sludge to lands, treatment of sludge is necessary primarily for reducing its pathogens. As mentioned above, thermal conditioning before mechanical dewatering can sterilize the sludge.

### **CONCLUSIONS**

This study investigated the characteristics of raw industrial sewage sludge and its capability for use as soil fertilizer. Based on our findings and the facts presented in the Discussion section, the following conclusions and recommendations can be made:

- Organic matters, nitrogen, phosphorous and potassium contents of studied sludge were higher than those in the digested sludge. Therefore, the value of the investigated sludge as fertilizer was higher. Other physio-chemical characteristics of the studied sludge were consistent with the range of values for raw and stabilized sewage sludge samples as reported in the literature. Also, there was no significant problem against

the application of sludge in soil compared to the international guidelines.

- The concentrations of heavy metals in the sludge were significantly low without exceeding the limitations for land application. However, the dissipation of heavy metals in raw sludge is lower than in digested sludge because of degradation of metals in organic compounds.

- Regarding such contaminants as PCBs, BTEX and PAHs, the concentration values (except for BTEX) were lower than those reported in the literature and the international requirements for land application. Thermal conditioning should be employed before the filter press for toluene removal.

- The only significant problem for the sludge samples used in our study for land application was unmet microbial requirements. To resolve this issue, there is a need for a pretreatment. Thermal conditioning is a viable option that is capable of destroying the pathogens and the organic contaminants.

Finally, it can be concluded that for land application of sludge, wastewater source and treatment processes should be considered before considering the high cost of sludge treatment. Also, careful analyses should be conducted on raw sludge to identify the simplest and least expensive pretreatment processes before using sewage sludge from any source.

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## REFERENCES

1. Ignatowicz K. The impact of sewage sludge treatment on the content of selected heavy metals and their fractions. *Environmental Research*. 2017;156:19-22.
2. Oleszczuk P. Phytotoxicity of municipal sewage sludge composts related to physico-chemical properties, PAHs and heavy metals. *Ecotoxicology and Environmental Safety*. 2008;69(3):496-505.
3. Warman P, Termeer W. Evaluation of sewage sludge, septic waste and sludge compost applications to corn and forage: yields and N, P and K content of crops and soils. *Bioresource Technology*. 2005;96(8):955-61.
4. Singh R, Agrawal M. Potential benefits and risks of land application of sewage sludge. *Waste management*. 2008;28(2):347-58.
5. Mailler R, Gasperi J, Patureau D, Vulliet E, Delgenes N, Danel A, et al. Fate of emerging and priority micropollutants during the sewage sludge treatment: Case study of Paris conurbation. Part 1: Contamination of the different types of sewage sludge. *Waste management*. 2017;59:379-93.
6. Suciú NA, Lamastra L, Trevisan M. PAHs content of sewage sludge in Europe and its use as soil fertilizer. *Waste Management*. 2015;41:119-27.
7. Cai Q-Y, Mo C-H, Wu Q-T, Zeng Q-Y, Katsoyiannis A. Occurrence of organic contaminants in sewage sludges from eleven wastewater treatment plants, China. *Chemosphere*. 2007;68(9):1751-62.

8. de Souza Pereira M, Kuch B. Heavy metals, PCDD/F and PCB in sewage sludge samples from two wastewater treatment facilities in Rio de Janeiro State, Brazil. *Chemosphere*. 2005;60(7):844-53.
9. Bright D, Healey N. Contaminant risks from biosolids land application: contemporary organic contaminant levels in digested sewage sludge from five treatment plants in Greater Vancouver, British Columbia. *Environmental Pollution*. 2003;126(1):39-49.
10. El-Hadj TB, Dosta J, Torres R, Mata-Alvarez J. PCB and AOX removal in mesophilic and thermophilic sewage sludge digestion. *Biochemical Engineering Journal*. 2007;36(3):281-7.
11. Sánchez-Brunete C, Miguel E, Tadeo JL. Analysis of 27 polycyclic aromatic hydrocarbons by matrix solid-phase dispersion and isotope dilution gas chromatography-mass spectrometry in sewage sludge from the Spanish area of Madrid. *Journal of Chromatography A*. 2007;1148(2):219-27.
12. Turovskiy IS, Mathai P. *Wastewater sludge processing*: John Wiley & Sons; 2006.
13. Federation WE, Association A. *Standard methods for the examination of water and wastewater*. American Public Health Association (APHA): Washington, DC, USA. 2005.
14. Baruah T, Barthakur H. *A Textbook of Soil Chemical Analysis*. Vikash, New Delhi. 1997.
15. Boltz DF. *Colorimetric determination of nonmetals*. Colorimetric determination of nonmetals. 1958.
16. Swift R, Sparks D. *Methods of soil analysis: Part 3. Chemical methods*. Soil Science Society of America Book Series. 1996;5:1018-20.
17. Parkpain P, Sirisukhodom S, Carbonell-Barrachina A. Heavy metals and nutrients chemistry in sewage sludge amended Thai soils. *Journal of Environmental Science & Health Part A*. 1998;33(4):573-97.
18. Goldstein N. EPA sludge disposal regulation proposed. *BioCycle*. 1989;30(3):44-7.
19. Shrivastava SK, Banerjee DK. Speciation of metals in sewage sludge and sludge-amended soils. *Water, Air, & Soil Pollution*. 2004;152(1):219-32.
20. Weng H-X, Ji Z-Q, Chu Y, Cheng CQ, Zhang J-J. Benzene series in sewage sludge from China and its release characteristics during drying process. *Environmental Earth Sciences*. 2012;65(3):561-9.
21. Stevens JL, Northcott GL, Stern GA, Tomy GT, Jones KC. PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musks, and polychlorinated n-alkanes in UK sewage sludge: survey results and implications. *Environmental Science & Technology*. 2003;37(3):462-7.
22. CCME. *Canadian soil quality guidelines for the protection of environmental and human health: summary tables*. Canada Council of Ministers of the Environment Winnipeg; 2007.
23. Appels L, Baeyens J, Degreè J, Dewil R. Principles and potential of the anaerobic digestion of waste-activated sludge. *Progress in energy and combustion science*. 2008;34(6):755-81.
24. Zaied M, Bellakhal N. Electrocoagulation treatment of black liquor from paper industry. *Journal of hazardous materials*. 2009;163(2):995-1000.

25. Lefebvre O, Moletta R. Treatment of organic pollution in industrial saline wastewater: a literature review. *Water research*. 2006;40(20):3671-82.
26. Gorlach E, Gambus F. Evaluation of sewage sludges as fertilizer in pot experiment. *Acta Agraria et Silvestria Series Agraria*. 1998;36.
27. Eljarrat E, Caixach J, Rivera J. A comparison of TEQ contributions from PCDDs, PCDFs and dioxin-like PCBs in sewage sludges from Catalonia, Spain. *Chemosphere*. 2003;51(7):595-601.
28. Borja J, Taleon DM, Auresenia J, Gallardo S. Polychlorinated biphenyls and their biodegradation. *Process biochemistry*. 2005;40(6):1999-2013.
29. Mrowiec B. Toluene in sewage and sludge in wastewater treatment plants. *Water Science and Technology*. 2014;69(1):128-34.
30. Mrowiec B, Suschka J, Keener TC. Formation and biodegradation of toluene in the anaerobic sludge digestion process. *Water environment research*. 2005;77(3):274-8.
31. Sidhu JP, Toze SG. Human pathogens and their indicators in biosolids: a literature review. *Environment International*. 2009;35(1):187-201.
32. Lloret E, Pastor L, Martínez-Medina A, Blaya J, Pascual JA. Evaluation of the removal of pathogens included in the Proposal for a European Directive on spreading of sludge on land during autothermal thermophilic aerobic digestion (ATAD). *Chemical engineering journal*. 2012;198:171-9.
33. Akgul D, Abbott T, Eskicioglu C. Assessing iron and aluminum-based coagulants for odour and pathogen reductions in sludge digesters and enhanced digestate dewaterability. *Science of The Total Environment*. 2017;598:881-8.