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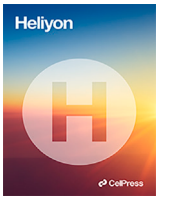

Research article

Physico-chemical characterization and possible uses of sludge processed from an urban sewage treatment plant

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ABSTRACT

Nowadays, the challenge is to transform dehydrated sewage sludge resulting from wastewater treatment plants from waste into resource. Following this objective, the sludge was further dried and submitted to X-ray diffraction (XRD) and FTIR analysis. The sludge was first dried in ventilated and unventilated spaces at 50 °C and 100 °C, for 60 and 100 minutes (min) in each case. The final mass and evaporation degree of the sludge depends on the initial mass, ventilation type, drying time, and temperature. The ventilated drying space is preferred for temperature control, homogeneity, and higher evaporation degree. The influence of the drying process on the structure and behavior of the sewage sludge was emphasized through X-ray diffraction (XRD) and FTIR analysis. The XRD shows good structural properties of the sludge samples given by the reduction of the particle size through evaporation. According to FTIR, evaporation influences the depolymerization of the silicate network. The hydroxyl units and metallic ion modifiers can improve the sludge structure, but its intensity decreases through evaporation. With high content of solid substance, and good relation between the composition of the sludge and its structure and behavior, the dried sewage sludge can be used in: (i) agriculture, (ii) construction, (iii) the energy sector.

1. Introduction

Significant amounts of sludge result from wastewater treatment plants (WWTPs) [1]. The sewage sludge that accumulates is practically wet matter [2] that currently has very little use: (i) stored on special platforms equipped with drainage systems or directly on the ground [3], until a removal solution is found to make room for more sludge, and (ii) in some branches of agriculture, to improve the quality of soils through the phosphorus and nitrogen that they contain [4]. Unfortunately, large amounts of dehydrated sewage sludge are deposited in improvised conditions, thus the sludge becomes a source of pollution [5]. When using sludge in agriculture, it is necessary to comply with the legislation governing this activity, both world-wide and at the national level. All normative acts in force establish the limits for the elements that are contained, to both the land on which the sludge is to be deposited and the sludge itself [6–12]. To achieve all the required limits, the wet sludge needs to be further dried. Drying the dehydrated sewage sludge simply offers a solution for the reintroduction of the dehydrated sludge into the natural circuit, with

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Fig. 1. The oven used for sludge drying.

minimal pollution and price, making sewage sludge a resource. Regrettably, the quantities of the resulting raw sewage sludge from the WWTPs are extremely high in Romania [13] because of the lack of a further drying operations. For this reason, a simple separate drying operation of the sewage sludge is needed to reduce the volumes of the sewage sludge, and to obtain properly dried sewage sludge that can be used in other sectors. Our literature survey concluded that are not clear evidences in the literature about how to proceed further. Therefore, for sustainability, a very simple drying operation is proposed by the present article. The main objective is to further reduce the volume and mass of the dehydrated sewage sludge, kill possible pathogens, and reduce transportation costs. Experiments were performed to: (i) the physical and chemical characterization of sewage sludge, (ii) the evolution of the final mass of the analyzed sewage sludge samples, evaporation degree (ED), and humidity when submitting the samples to ventilated and unventilated drying, (iii) the influence of the drying process on the structure and behavior of the dried sewage sludge (by using the X-ray diffraction XRD and Fourier-transform infrared spectroscopy FTIR), (iv) possible uses of dried sewage sludge in other sectors according to its properties and the limits established by the normative acts in force. The mass of the sludge is found to be a linear function of the venting conditions, temperature, and time. All parameters of the model function were found to be statistically significant. The model may serve to optimize the sludge treatment.

2. Materials and methods

2.1. Materials

Eight samples were taken from the raw dehydrated sludge resulting from the treatment process of an urban WWTP with an amount of 506 sludge t/d (tonnes/day). All samples were numbered from 1 to 8 for a better analysis. Dry sludge samples were investigated physically and chemically for determination of the sludge composition. Then, four samples were used for drying the dehydrated sludge in the unventilated space, and four samples for drying in the ventilated drying area.

2.2. The physical and chemical analysis of the dehydrated sludge samples

The investigated dehydrated sludge samples were subjected to physico-chemical analysis, regarding the elements' composition of the sludge, toxicology (for polychlorinated biphenyls, PCBs), and heavy metals which can pollute the environment [14]. All analyses were realized before the drying process since only the humidity and the solid substances change during this stage. This analysis emphasized the composition of the sludge and established its possible further uses in other domains according to normative act in force [15].

2.3. Drying methodology

The drying of dehydrated sludge can continue the dehydration process with simple technology, and it can radically change the state of the sludge. To demonstrate this, several experiments were performed in the laboratory, by heating samples of dehydrated sludge in conditions as close as possible to those in the treatment plant. The samples were simultaneously heated in ventilated and unventilated spaces of ovens, as the one presented in Fig. 1.

Every set of 4 samples was divided into 2 samples heated and dried at 50 °C, and 2 samples dried at 100 °C. Moreover, the first sample was extracted after 60 min, and the last sludge sample after 100 min of drying. This rule was applied in all four experimental cases: (1) drying without ventilation at 50 °C, (2) drying without ventilation at 100 °C, (3) drying with ventilation at 50 °C, and (4)

Table 1
The experimental design and factor levels for the drying of the samples.

No.	Ventilation	Temperature	Time
1	v0	t0	m0
2	v0	t0	m1
3	v0	t1	m0
4	v0	t1	m1
5	v1	t0	m0
6	v1	t0	m1
7	v1	t1	m0
8	v1	t1	m1

No.	Factor	Level	Value
1	v	0	"No"
2	v	1	"Yes"
3	t	0	50°
4	t	1	100°
5	m	0	60 min
6	m	1	100 min

drying with ventilation at 100 °C. In the beginning of the experiments, when all samples were placed in the corresponding drying rooms, they all had an amount of solid substance (SS) of 23% and humidity of 77%.

The two different temperatures of 50 °C and 100 °C were chosen in both ventilation cases, to highlight the direct relationship between temperature, the evaporation degree, and humidity of the analyzed samples. These two temperatures of 50 °C and 100 °C were chosen for different reasons: (i) after 150 °C, a significant loss of the volatile solids is encountered (due to the thermal degradation of the sludge) [16]; (ii) low-temperature drying technologies are more and more studied and used nowadays, to save energy, money, and contribute to a more friendly, less polluted or nonpolluted environment [17].

2.4. Determination of the sample mass and evaporation degree

Sludge samples were heated, dried, and then extracted as follows: the first sample was extracted from the oven after 60 min, and the second sample was extracted after 100 min. This methodology was applied for a better and more appropriate comparison between the sludge samples analyzed in the two drying cases – with and without ventilation. An important aspect must be mentioned regarding the sludge samples: during the drying process, the risk of cake surface formation can occur. The formation of this cake surface can impede the normal drying of the sludge sample, thus it must be avoided. If under any circumstances, it still occurs, the sludge must be stirred, preferably with a glass rod, to bring the liquid part back to the surface of the sample; then, the sludge sample must be again weighed and put back into the drying area. Before and after the drying process, samples were weighed with a complex KERN PES/PEJ robust laboratory and an industrial precision scale for heavy items (KERN PEJ 2200-2M model), with European Commission (86/278/EEC) type approval (for a precision of ± 0.02 g). After determining the initial mass of the sludge samples m_1, their final mass m_2 (after the drying process) was taken, and concluding with the calculation of the evaporation degree (ED), with Eq. (1):

$$ED = \frac{m_1 - m_2}{m_1} \times 100\% \tag{1}$$

All data collected on the mass of the analyzed samples further led to the values of the ED and are all presented in Section 3.

2.5. The analysis of the sludge

To see how the drying and evaporation processes influence the structure and behavior of the sludge samples, and their possible uses, five sludge samples were chosen and analyzed through X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) [18]. Elemental, PCBs and heavy metal analysis followed standard protocols listed along with the measured data in §3.1. For the X-ray and IR analyses 5 of the 8 studied samples were chosen (samples 1, 2, 4, 6, and 8). One would ask why only 5? The answer is following: (i) the authors considered the most unfavorable and favorable drying conditions - the extremes of the experiment; (ii) the ED is the same for the unventilated sludge sample at 100 °C for 100 min, and the case of the ventilated drying process for 50 °C during 100 min; (iii) trying to keep a lower drying temperature for energy savings and expenditure purposes. The analyses were performed with two performant diffraction and infrared equipment: the Jasco 6200 FTIR spectrometer (USA, 2009, @ Technical University of Cluj-Napoca) and the Shimadzu XRD-6000 (Japan, 2011, @ Technical University of Cluj-Napoca) diffractometer. The experimental design for the conditions in which the samples were taken is given in Table 1.

Table 2
Elemental mass analysis of the sludge.

Sample	pH	Pc [%]	N [%]	C (organic) [%]	P [%]	K [%]
1	6.55	54.63	2.62	21.31	1.63	0.43
2	5.94	64.60	3.88	29.49	2.00	0.43
3	5.77	57.17	3.30	28.54	1.94	0.32
4	5.66	56.07	2.89	30.45	1.86	0.33
5	5.93	52.40	2.11	23.00	1.85	0.27
6	6.43	57.34	2.26	20.58	1.76	0.27
7	6.81	59.96	4.33	33.09	2.01	0.47
8	6.35	57.31	2.97	27.29	1.88	0.30
Avg.	6.18	57.44	3.05	26.72	1.87	0.35
Std.	0.41	3.64	0.77	4.58	0.13	0.08

Table 3
Toxicological analysis: Polychlorinated biphenyls (mg/kg dry matter).

Sample	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	Total PCB
1	0.002	und	und	0.001	0.001	0.002	0.001	0.007
2	0.006	0.007	0.004	0.001	und	0.001	0.001	0.020
3	und	und	und	und	und	0.001	und	0.001
4	0.002	und	0.001	und	und	0.001	und	0.004
5	und	und	und	und	und	0.001	und	0.001
6	0.002	0.002	0.002	und	und	Und	0.001	0.007
7	0.002	und	und	und	und	0.004	0.002	0.008
8	und	und	und	und	und	0.002	und	0.002
Avg.	0.0028	0.0045	0.0023	0.0010	0.0010	0.0017	0.0013	0.0063
Std.	0.0018	0.0035	0.0015	0.0000		0.0011	0.0005	0.0062

2.6. Statistical analysis

All samples have been taken from the same point of origin (same WWTP), but each were subjected to different drying conditions. However, in the regard of the elemental, toxicological and heavy metal content analyses all are repeated measurements and average and standard deviations were calculated. The mass after dying is expected to be affected by one or more (perhaps all) designed factors (Ventilation, Temperature, Time, see Table 1) and the effect to be additive. In this instance the statistical analysis of the model follows the prescription of an multiple linear regression model and the significance of the parameters is extracted from Student t tests. The values will be provided for convenience with their 95% confidence intervals [19].

3. Results and discussion

The sludge has been collected from a WWTP just after digesting stage and just before drying stage.

3.1. Composition of the sludge

The sludge was subjected to a physical-chemical analysis to see if the sludge samples met the required parameters concerning its possible use in other domains, as established further in this paper. The following tables (Table 2 – Table 4) contain the results of the analysis regarding the elemental composition of the sludge, toxicology, and heavy metal pollution.

These results are given against the maximum limits (see *max. value* entry in Table 4) given by the normative acts in force to see if the dried sludge samples can be directly used or if other treatments are necessary before or after this processing stage.

In Table 2 pH is the acidity of the sample (in the conventional logarithmic scale), Pc is the loss after cacination (SR EN 15935:2013 SR EN 15169:2007 STAS 12586-87), N is the content in Nitrogen (STAS 12200-85, SR ISO 11261:2000 STAS 7184/2-85), C (organic) is the organic carbon content SR ISO 14235:1998, P is the phosphorus content (STAS 1784/7-79, SR ISO 11263/1998, SR EN 16192:2012, STAS 12205-84, SR EN 14672:2006). In Table 3 is the content in polychlorurated biphenyls (SR ISO 10382:2007, EPA 8270D:1998, SR EN 15308:2017). In Table 4 is the content in heavy metals (SR ISO 11047:1999, ISO 20279:2005, ISO 20280:2007, EPA 7000A:1992, EPA 7062A:1994, EPA 7742:1994, SR EN 16192:2012, SR 13179:1994, SR 13181:1994-Zn, SR 13225:1995, STAS 12678-88, STAS 12833-90, STAS 12834-90, STAS 12876-90, STAS 13094-92, STAS 13117-92, EPA 7000A:1992, EPA 7062A:1994, EPA 7742:1994).

The values found for PCB concentrations are well below the limits for land disposal (86/278/EEC directive) and furthermore, the values for heavy metal concentrations recommend it for use in agriculture (values below the limits enforced by the national legislation, [15]).

Table 4
Heavy metal pollution analysis (mg/kg dry matter).

Sample	As	Cd	Cu	Cr	Ni	Pb	Zn	Co	Hg
1	2.401	0.327	371	106	34.9	42.8	1052	4.21	0.45
2	0.943	0.638	361	39.5	25.0	37.0	1538	1.84	0.47
3	0.497	1.091	494	49.2	41.2	31.2	1567	1.64	0.45
4	0.273	1.372	473	89.9	37.1	38.0	1698	6.86	0.48
5	0.287	0.515	382	103	36.1	45.8	1420	7.53	0.51
6	0.124	0.961	358	52.7	37.1	39.9	1288	8.18	0.41
7	0.162	0.924	336	51.6	20.4	35.1	1120	3.66	0.78
8	0.414	2.305	471	92.0	39.9	49.5	1939	8.66	0.45
Avg.	0.638	1.017	406	73.0	34.0	39.9	1453	5.32	0.50
Std.	0.758	0.618	63	27.2	7.3	5.9	297	2.83	0.12
[10]	41	39	1500		420	300	2800		17
[11,12]		20.000 to 40.000	1000 to 1750		300.0 to 400.0	750.0 to 1200.0	2500 to 4000		16.00 to 25.00
max. value	10	10	500	500	100	300	2000	50	5

Table 5
Evaporation degrees of the investigated samples.

Sample No.	Ventilation Yes/No	Temperature [°C]	Time [min]	ED %
1	No	50	60	10
2	No	50	100	22
3	No	100	60	39
4	No	100	100	55
5	Yes	50	60	44
6	Yes	50	100	56
7	Yes	100	60	68
8	Yes	100	100	84

In the regard of reference values, one can use [20], which provide a wide reference. Table 1 and Table 3 in [20] provide the limits set by legislation in the regard of Cd, Cu, Hg, Ni, Pb and Zn concentration (Table 1) and PCBs (Table 3) for sludge use in agriculture in different countries, including Romania.

When compared with the data from a recent study in Czech Republic [21] our values for Total PCB are significantly lower - 95.7 ± 104 μg/kg PCBs (value ± standard deviation) from 40 samples in [21] compared with 6.3 ± 6.2 μg/kg PCBs from 8 samples in our study.

Taking as reference an older study from Grece [22], we found in our sludge ("Urban sludge" column in Table 2 of [22]) about 14 times less As, 4 times less Cd, 2 times less Pb, and about 1.5 times less Cr and about 1.5 times more Zn and 2 times more Cu. The values for heavy metals for sludge used in agriculture are well below the limits (set by 86/278/EEC directive).

3.2. Drying of the sludge

The simultaneous presentation of the ED for the 8 sludge samples highlights the parameters that influence the drying process (Table 5).

If one is interested in recovering the final mass information from ED values, then the inverted Eq. (1) should use ($m_2 = m_1(1 - ED/100)$).

Evaporation degree (ED) in Table 1 is based on a simple calculation with the final mass of the samples (see Eq. (1)). The difference between ventilated and unventilated drying processes is high (around 30%, except for the 60-minute drying test). In the ventilated environment, all values of the evaporation degree are clearly higher than in the unventilated one, no matter the heating temperature. The values of the ED without ventilation at 100 °C are close to those encountered in the ventilation case at 50 °C. This means there is no need to heat the sludge samples at double temperature, only to ensure the needed ventilation and temperature control.

By heating the samples in different periods (60 and 100 min), the direct influence of the heating time on the amount of evaporated water is emphasized. Heating the dehydrated sludge samples at different temperatures (50 °C and 100 °C) established the relationship between the heating temperature and the ED. The higher the heating temperature is, the higher the evaporation degree is.

3.2.1. Without ventilation

At 50 °C, water evaporation increases from 10% for the one dried for 60 min, reaching 22% in the end, after 100 min of drying. The evaporation phenomenon is intensified by increasing the temperature from 50 °C to 100 °C. After 60 min of drying at 100 °C, the

(a) Dehydrated sludge (b) Dried sludge

Fig. 2. Dehydrated (from the treatment process, "a") vs. dried ("b") sludge.

evaporation degree reaches 39%, while after 100 min of drying, the value of the ED increases to 55%. Following these experiments, it was highlighted that the evaporation of water is influenced by the temperature and the time allocated to the drying operation when the drying space is unventilated. Increasing the evaporation rate from 10% to 39% after 60 min, with the temperature rising from 50 °C to 100 °C, represents an almost 4-fold increase. After 100 minutes of drying, the increase is from 22% to 55%, therefore 2.5 times. The evaporation rate is assumed to change continuously during drying. One should note that the lack of temperature homogeneity in the drying space, due to the absence of ventilation, may lead to relatively high evaporation instantaneous growth rates. The values recorded from these experiments highlighted the links between temperature, drying time, and evaporation degree.

3.2.2. With ventilation

Under the same conditions of temperature and time, the experiments were also realized in a ventilated drying space for drying the dehydrated sludge. At a temperature of 50 °C and a drying time of 60 min, the evaporation degree is 44%. By raising the drying temperature to 100 °C, and keeping the same drying period, the evaporation rate increases to 68%, representing an increase of 1.5 times. For the drying period of 100 min, the evaporation degree is 56% at a temperature of 50 °C and increases to 84% at 100 °C - also a 1.5-fold increase. As can be seen, the increase in the evaporation process is relatively constant in the case of the ventilated drying process. The value of the evaporation degree increases in the case of ventilation of the drying area; this increment is more uniform compared to the situation encountered in the case of unventilated drying areas. The uniformity of the degree of growth, namely the constant increase of the ED with the increase of the temperature, demonstrates the advantage of a ventilated drying space. Ventilation of the drying area considerably increases the drying efficiency. It is observed that the differences when drying at 50 °C and 100 °C respectively, and the differences between the evaporation degrees, are smaller in the case of the ventilated space. Proper ventilation can lower the drying temperature while keeping the drying efficiency unchanged.

3.3. Final mass of the sludge samples

A representative dehydrated sludge sample before and after drying is presented in Fig. 2.

Upon interpreting the results, it is shown the mass of the sludge samples decreases in time once the temperature rises from 50 °C to 100 °C in both unventilated and ventilated drying areas. As was to be expected, the smallest masses of the samples were registered during the ventilated drying process at 100 °C (when the mass reached the final value of 9.6 g after 100 min of drying – which represents only 16% of the initial mass of the sludge sample). Based on the initial and final mass achieved by sludge samples, the general linear model from Eq. (2) provided the best agreement with the experimental data:

$$Mass = a_1 - a_2 \cdot Vent - a_3 \cdot Temp - a_4 \cdot Time \tag{2}$$

where $Mass$ is the final mass of the sample (in grams, from the initial hydrated sample of 100 ± 0.02 g), $Vent = 0$ if no ventilation is used and $Vent = 1$ if ventilation is used ($Vent$ is a binary response variable), $Temp$ is the drying temperature (in °C), and $Time$ is the drying time (in minutes).

If $Mass$ is expressed in grams from the initial sample of 100 g, $Temp$ is provided in °C, and $Time$ is provided in minutes, then the a_1, a_2, a_3, and a_4 parameters have the following units: a_1 and a_2 in g, a_3 in g/°C and a_4 in g/min.

Using our experimental data, following values were obtained:

- $a_1 = 81.56_{\pm 6.62}$ [g];
- $a_2 = 17.4_{\pm 3.32}$ [g];
- $a_3 = 0.304_{\pm 0.066}$ [g/°C];
- $a_4 = 0.228_{\pm 0.058}$ [g/min].

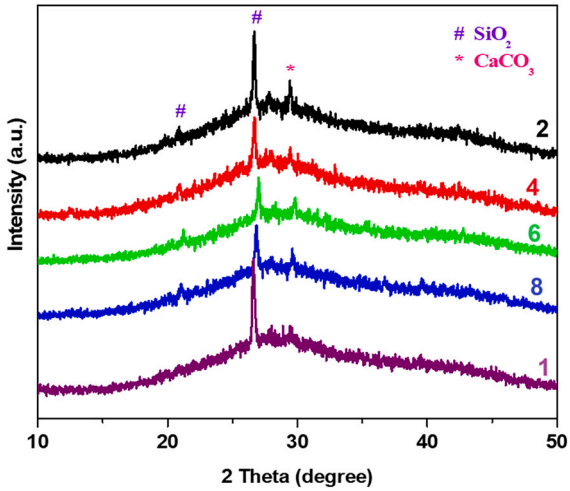


Fig. 3. The X-ray diffractograms.

Table 6
The medium dimensions of the crystalline particles, alongside the maximum intensity peaks.

Sample (no.)	Bragg angle θ (in °)		Width β (in mrad)		Particles size D (in nm)	
	SiO_2	$CaCO_3$	SiO_2	$CaCO_3$	SiO_2	$CaCO_3$
2	26.68	29.42	3.316	4.014	48.85	41.4
4	26.70	29.44	3.665	2.792	44.21	59.54
6	27.00	29.80	3.316	4.188	48.99	39.83
8	26.84	29.59	4.363	3.490	37.18	47.7
1	26.60	29.42	4.014	2.617	40.33	63.5

The values above are given along with their 95% confidence intervals (containing a 5% risk of being in error). One can observe that all values are statistically significant (zero value is not contained in the intervals), so all associated variables ($Vent$, $Temp$ and $Time$) have explanatory power in the model expressing the final mass of the sludge. The whole model given by Eq. (2) is also statistically significant (with $F = 113$, and $p_F = 7 \cdot 10^{-7}$) explaining over 96% of the variability observed in the experimental data ($r^2_{adj} = 0.968$).

The model from Eq. (2) was derived under the supposition that all variables have additive effects, and no multiplicative effects are present. Since the model is statistically significant (all coefficients are statistically significant - their confidence intervals do not cross 0, and the whole model is statistically significant - $p_F < 5\%$), it can be concluded that each variable has an important additive effect on drying the sludge. It should be noted that the multiplicative effects of the variables are not excluded, and a separate analysis, with more samples and more levels, should be conducted to derive a statistically significant model in that regard.

Since all samples had the same initial mass, it should be noted that the model from Eq. (2) does not account for the possible influence of the initial mass (size of the sludge sample) on the value of the final mass. One may say that Eq. (2) give the effects in terms of the relative mass, but, however, this statement is not entirely true since in the drying process, especially when it occurs for short time and without venting, clusters containing large amounts of water may be still trapped inside when the sample is large.

3.4. Diffraction studies

The X-ray diffractograms given in Fig. 3 indicate the presence of two crystalline phases: SiO_2 with a hexagonal structure and $CaCO_3$ with a rhombohedral structure. The maximum peak of the SiO_2 crystalline phase is centered at about 26.68° hkl (101) for sample no. 2 and is about the same for sample no. 1, is slightly lower for samples 4, 6, and 8 and slightly higher for the sample no. 5. If, for sample no. 6, the peak is the lowest, it is a little higher for sample 1, but with a shift to smaller of the 2 theta angle (26.60°). As for the $CaCO_3$ crystalline phase, the most visible and intense peak is reached in sample 2, while for sample 1, it presents the minimum value (as confirmed by the XRD analysis).

All the distribution of the crystalline particles is influenced by their dimensions and position in the samples. Therefore, the medium dimensions of the particles were calculated (according to the Debye-Scherrer equation [23], Eq. (3)), and are presented in Table 6, and further analyzed:

$$D = \frac{0.94 \cdot \lambda}{\beta \cdot \cos(\theta)} \tag{3}$$

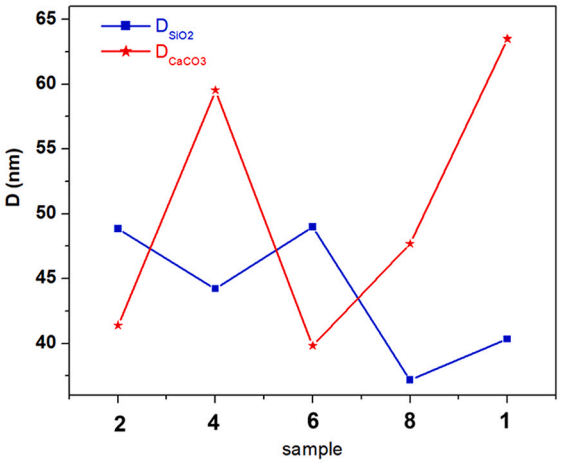


Fig. 4. The evolution of the medium dimensions of the crystalline particles depending on the nature of the analyzed sample.

where D is the particle medium size, λ represents the wavelength of the X-rays, $\lambda = 0.154$ nm, β is the width (full width of half-maximum) of the X-ray diffraction peak, in radian (rad), and θ is the diffraction angle for the maximum peak (or Bragg angle), in rad too.

Some interesting observations can be emphasized by comparing the XRD data and the medium dimensions of the crystalline particles (Fig. 4).

The XRD analysis showed samples 6 and 1 were the most fragile when discussing the SiO_2 crystalline phase. For sample 6, the maximum peak registered the lowest value of all, with an offset of 2 bigger theta angles of the diffraction peak. For sample 1, the diffraction maximum peak significantly increased, but with an offset of 2 smaller theta angles. On the contrary, the dimensions of the crystalline particles are higher for sample 6 than for sample 1. This antagonism and structural modification can be caused by the presence of heavy metals in the sludge samples; some of the metallic ions can substitute some of the silicon-oxygen bonds, oxygen being weaker than silicon. Overall, for the SiO_2 crystalline phase, the medium dimensions of the particles are high for samples 2 and 6, and small for the rest of them. The smallest values were registered for sample 8, not far from sample 1, around 40 nm (see Fig. 4). This decrease is a normal consequence of the evaporation process of the sludge samples. Comparing, the $CaCO_3$ crystalline phase, samples 4 and then 1 encountered the highest values of the medium dimensions (around 60 and 64 nm, respectively). For the rest of the samples, the dimensions of the particles are considerably small: 40 nm for sample 6, closely followed by samples 1 and further by 8.

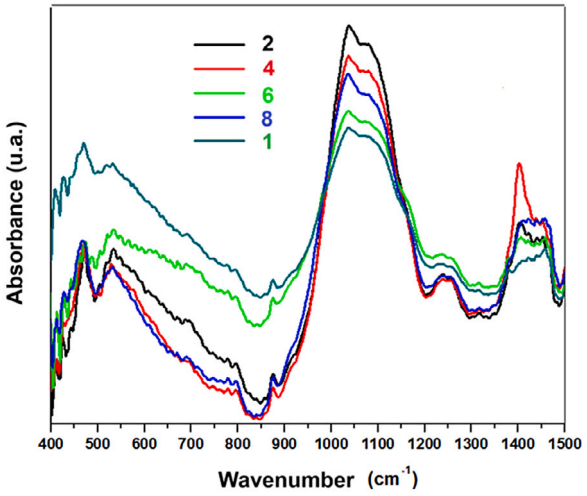
When compared with a similar study [24], the XRD analysis has shown that our sludge is with a far less complicated structure (the only ones proeminent peaks are from SiO_2 and $CaCO_3$) but again, as also the elemental (Table 3) and heavy metal (Table 5) - analyses has shown, our sludge is far less contaminated with heavy metals, while in [24] study, the purpose of the investigations was the exploration of the ways of removal of dyes, which usually contains heavy metals.

3.5. FTIR analysis

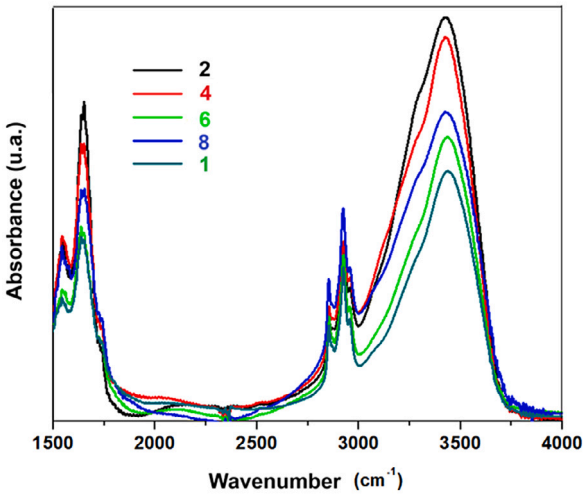
All the FTIR analysis is strongly related to the XRD analysis. The FTIR analysis indicates some specific regions of the different structural units, especially regarding the SiO_2 crystalline phase for the first analysis with small wavenumbers (from 400 to 500 cm^{-1}), and $CaCO_3$ for wavenumbers up to 1350-1500 cm^{-1}. All the infrared specters for all five samples involved in the analysis are presented in Fig. 5. Because of the large wavenumber from 400 to 4000 cm^{-1}, the completely different variations of the transmittance, and their significance for the structure, composition, behavior, and possible uses of the sludge samples, Fig. 5 was divided into two: Fig. 5a for wavenumbers from 400 to 1500 cm^{-1}, and Fig. 5b for wavenumbers from 1500 to 4000 cm^{-1}.

The split is supported by the fact that in the domain above 1500 cm^{-1} appears vibrations of H–O and H–O–H groups while in the domain below 1500 cm^{-1} predominant are Si–O and Si–O–Si stretching (see for instance Table 4 in [25]).

The first IF band situated between 400 and 500 cm^{-1} is assigned to the deformation vibrations of the Si-O-Si angles. The IR bands with wavenumbers situated between 470 and 875 cm^{-1} originate from the Pb–O stretching vibrations from the [PbO_4] tetragonal structural units, and [PbO_6] octahedrons, respectively. The intensity of these IR bands suddenly increases near 500 cm^{-1}, especially for samples 6 and 1, with the maximum value for the fifth sample (see Fig. 5a). This evolution can be explained and determined by the high presence of lead ions in the sludge samples, especially in sample 8 (49.5 mg/kg dry matter) compared to sample 2, which registered the lowest Pb value, of only 37 mg/kg dry matter. On the second IR band region (from 500 to 850 cm^{-1}) of the stretching vibrations, other metals besides lead play an important role: arsenic, cadmium, nickel, copper, chromium, and mercury. They all determine the appearance and existence of multiple metal-oxygen bonds (Me–O) from the [MeO_n] structural units. The intensity of the IR bands is still the highest for sample 1, closely followed by sample 6. As for samples 4 and 8, their IR intensity reaches the smallest values. This means that in samples 6 and 1, the number of metal-oxygen bonds is considerably higher compared to the rest of the sludge samples. The IR bands domain between 800 and 1300 cm^{-1} is allocated to Si–O stretching vibration from different



(a) Wavenumbers between 400 and 1500 cm^{-1}



(b) Wavenumbers between 1500 and 4000 cm^{-1}

Fig. 5. The FTIR specters of sludge samples.

silicate structural units. The IR bands at 1040 and 1080 cm^{-1} correspond to the Si-O stretching vibration from the metasilicate (Q2, $[SiO_3^{2-}]$) and disilicate (Q3, $[Si_2O_5^{2-}]$) units. Their intensity gradually decreases as follows: 2 > 4 > 8 > 6 > 1, reaching the minimum values for samples 6 and 1. On the contrary, at 800, 920, and 1240 cm^{-1} (corresponding to ortho- $[SiO_4^{4-}]$, pyro- $[Si_2O_7^{6-}]$, and tectosilicate (three-dimensional structure) ($[SiO_2)_n$] units), samples 6 and 1 reach the maximum values of the IR intensity. These results may be explained by the conversion of the disilicate and metasilicate units into ortho-, pyro-, and tectosilicate units through drying/heating and evaporation processes. The depolymerization of the silicate network of the SiO_2 crystalline phase takes place here.

These IR bands were assigned to symmetric Si–O stretching vibrations of $[SiO_4]$ silicate units containing tetrahedral units with zero to four non-bridging oxygens, namely, tectosilicate, disilicate, metasilicate, pyrosilicate, and orthosilicate units denoted as Q4, Q3, Q2, Q1, and Q0 respectively [26]. The IR features allow distinguishing bands located at about 1100 – 1250 cm^{-1}, 1000 – 1100 cm^{-1}, 900 – 1000 cm^{-1}, near 900 cm^{-1}, near 850 cm^{-1} of each dominant at the tectosilicate, disilicate, metasilicate, pyrosilicate, and orthosilicate units [27].

For 1350 to 1500 cm^{-1}, the IR bands correspond to carbonate units [28] and indicate the formation of the $CaCO_3$ (according to XRD). The minimum intensity was reached in the case of samples 6 and 1, while the maximum was registered for sample 4 (actually, the IR intensity of sample 4 is significantly higher than all the rest). Starting with the wavenumber of 1350 cm^{-1}, samples 6 and 1 present the lowest values of the IR intensity compared to everything that happened until this point (see Fig. 5b). The 3422 cm^{-1} IR band is associated with O–H stretching vibrations from the absorbed water. Also, the IR bands situated at 1640 and 2925 cm^{-1}

appear due to the deformation vibrations of the H–O–H angles and hydroxyl units [29,30]. The intensity of these IR bands decreases through drying and evaporation and reaches the lowest values for samples 6 and 1, as stated before.

In conclusion, the presence of metallic ions in the studied sludge samples led to a depolymerization of the silicate structure/network in the SiO_2 crystalline phase through heating-drying-evaporation. The host matrix depolymerization degree is higher in sludge samples 6 and 1 and lower in samples 4 and 8. The metallic ions produce Si–O–Si angles deformation vibrations and/or Si–O stretching vibrations from disilicate and metasilicate units; pyro-, ortho-, and tectosilicate shorter chains are formed as a result.

The oxygen ion excess derived from the depolymerization of the silicate structure leads to metal–oxygen bonds that form the $[MeO_n]$ structural units. The XRD data shows the position of the main diffraction peaks for the SiO_2 crystalline phase: the 26.62° position for the hexagonal structure moves to 2 bigger theta diffraction angles for samples from 2 to 8, while for sludge sample 1, it modifies with smaller angles. As for the $CaCO_3$ crystalline phase with rhombohedral structure, the position of the 100% intensity diffraction peak is situated at 29.40° and moves to 2 bigger theta diffraction angles for all samples, with smaller variation in the case of samples 2, 4, and 1. These structural evolutions are the result/consequence of the presence of the metallic ions that modify the silicate and carbonate structures/networks.

However, the amount of metallic ions in our samples is significantly smaller than in the ones analyzed in [21] and in [24].

3.6. Possible uses of the dried sludge

The drying operation of the sewage sludge can be done immediately after the dehydration process and reduces the amount of dehydrated sludge to facilitate the work of those who manage this product. In other words, less sludge to be transported to the storage site results from the drying process. This is due to the greater rate of ED translated into a higher quantity of released water during the drying operation (comparing the cellulose [31] where the water amount is significantly lower). Dried sludge becomes much easier to handle and use. Besides storage, dried sludge can be further used in other life sectors (with amendments in some cases): agriculture, building materials, and the energy sector. This aspect is confirmed by the comparison made between the obtained values for the investigated sludge samples and the limits imposed by the Romanian, European, and American normative acts in force, along with other research studies in this field.

Further, the only constrain enforced by the legislation in Romania about the use of the sludge in agriculture is about the content in heavy metals. As the results shown, all samples (and their averaged values) are well inside the limits for this use.

- Agriculture. Various factors and parameters must be considered regarding the physical-chemical composition of the sludge and its structure. The PCBs are banned in the USA [10], while in the European Union and Romania respectively, they are permitted in a concentration under 0.8 mg/kg dried matter [11,12]. Regarding the heavy metals present in the sewage sludge that can be used in agriculture, all values registered for the analyzed samples (including their average value) are within the limits (towards the minimum limits) or even under the limits imposed by the worldwide normative acts in force [10–12,20]. Since all the requirements are achieved by the analyzed dried sludge, it can be further used with success in some branches of the agriculture domain, as follows:
  - Spreading on agricultural (excepting pastures, fruit tree plantations, and vegetable crops [12]) or forestry land [32]:
    - dehydrated sludge is very difficult to spread due to excessive moisture;
    - by drying, the sludge becomes much easier to handle and can be spread with equipment used to spread manure;
    - the composition of the analyzed sludge emphasizes there is no danger of contamination of the soil, plants, and humans; therefore, the dried sludge represents a safer type of fertilizer (compared to chemical ones);
    - the condition is to quickly mix the dried sewage sludge with soil after application [33];
  - Completion of degraded areas with ruptures and damage [34];
  - Application on agricultural soil affected by runoffs, floodplains, or erosion: not recommended [35];
  - Making compost and flower soil [36]:
    - dehydrated sludge in the preparation of flower soil is difficult to handle and requires a long period of drying under natural conditions, in order to be packed in bags. The smell of dehydrated sludge is often unpleasant;
    - through the drying process, dehydrated sludge can acquire a pleasant odor by introducing flavored natural essences into the warm air;
    - dried dehydrated sludge does not require drying periods after the preparation of the flower soil. It can be packed in bags and sent for sale immediately after preparation.
- Building materials [1]:
  - In construction, as a filling material, dehydrated sludge is used in the case of foundations and brick construction [1]; the bricks are dried in drying ovens, but the material used in the foundations must be allowed to dry naturally over a relatively long period of time; dried dehydrated sludge is much easier to use in the case of fillings and foundations. Also, dried sludge can be used for lightweight concrete [37], ceramic materials, lightweight aggregates, and supplementary cementitious materials [38,39].
- In power generation systems:
  - sludge may have a use in the energetic system, which is strongly affected by the new wave of price hikes and continuously changing legislative procedures, by developing a complex drying-incineration-energy production system [40];
  - dried sewage sludge can be used for combustible pellets [41].

In addition, our XRD and FTIR testing of the sludge identified it as to be fit for production of glass-ceramics by means of controlled nucleation and crystallization as prospected in [42].

Biological characteristics, ions concentrations, organic content, chemical (COD) and biological (BOD) oxygen demand were not explored in this study but their measurements may further open other uses for the sludge, such as a component of organic fertilizers [43].

Recent reports indicate hydrogen storage [44] as new potential applications.

Further processing of the sludge to sludge ash and biochar add also new uses such as hydration of ternary blended cements (see [45] and [46]) and water contaminants removal (see [47] and [48]).

3.6.1. Limitations and further research directions

The limitation of the study consists of the small quantity of the analyzed dried sewage sludge. Because of the large amounts of sewage sludge delivered every day by the WWTPs, the research must be extended to a bigger scale to see if the ventilated drying process is truly effective. Moreover, when calculating the final mass and the evaporation degree of the dried sludge samples, the multiplicative effects of the parameters are not excluded, and a separate analysis, with more samples and more levels, should be conducted to derive a statistically significant model in that regard.

However, recent studies address further concerns about sludge stabilization [49] and its microbiological content [50]. Analyzing sludge from different sources is also of interest [51], as they can reveal the characteristics and specifics of each wastewater treatment plant and area. This kind of analysis highlights whether the conclusions derived from this study can be generally applied or not.

Dried sludge up to a solid SS value of 70-80% [52] (that can be reached through the evaporation process) can be transferred from the waste category to the material resources category– in agriculture, concrete, ceramic pipes, and resources for the energy system, etc. All the existing normative acts in force should be updated and completed according to the newest and latest market demands. For some sectors (i.e., construction and energy) clear standards and regulations must be made.

No control test is included here and the results from XRD and FTIR tests are not compared with the ones for the sludge which is not undergone the drying process. One should notice that sludge is a relatively homogeneous matrix [53]. To achieve comprehensive results that can be generalized, a number of repetitions and sampling at random points should be deployed.

The vapors resulting from the drying process can be conducted in a cooler and transformed into water that can be reintroduced into the treatment process, just as drinking water is taken from natural sources, used, processed after use, and then returned to the natural circuit.

4. Conclusions

In trying to solve the problem of the ineffective dehydrated sewage sludge resulting from the WWTPs, the ventilated and unventilated drying process is applied to the sewage sludge. The developed model expressing a simple linear regression between the mass of the sludge and the key factors of the drying process (ventilation, temperature and time) and serve as raw model for other more complex studies involving drying of sludge. Furthermore, the model may be extended to a more elaborated one which to include multiplicative effects between factors, which the condition to be taken more samples into analysis. The calculation of the final mass and evaporation degree emphasizes the importance of ventilation in time during the different drying stages. The temperature control in the drying space leads to an increase in the evaporation degree and a smaller final solid mass: in ventilated spaces, the sludge can reach over 50% evaporation degree at 50 °C, the same as at 100 °C in unventilated areas. Therefore, it is not worth spending too much money on rising temperatures at higher values since the same results can be obtained by simply ventilating the drying spaces. During the experiments, the best results were obtained in ventilated spaces at 100 °C - 84% evaporation degree (which was to be expected). The drying process and evaporation degree positively influence the structure of the dried sewage sludge. The evaporation process equals the depolymerization of the silicate network of the SiO_2 crystalline phase. The XRD data shows the particle dimensions for SiO_2 (37-49 nm) and $CaCO_3$ crystalline phase (40-65 nm), together with the position of the main diffraction peaks for the SiO_2 crystalline phase: the 26.62° position for the hexagonal structure moves to 2 bigger theta diffraction angles for some of the samples, or with smaller angles for others. As for the $CaCO_3$ crystalline phase with rhombohedral structure, the position of the 100% intensity diffraction peak is situated at 29.40° and moves to 2 bigger theta diffraction angles for all samples. These structural evolutions are the result/consequence of the presence of the metallic ions that modify the silicate and carbonate structures/networks. Sludge is a natural product result that can be further processed, meaning that it can be returned to the natural circuit. Therefore, the composition and physical-chemical characteristics of the sludge are extremely important for its further possible use in different activity sectors. The dried sewage sludge is slightly acidic to neutral (with an average value of 6.18). This makes it suitable for alkaline soils. The absence of most PCBs and the extremely low values of the ones encountered, alongside the lowest values of the present heavy metals (some of them under the standard limits or near to minimum imposed limits), makes the resulting dried sewage sludge suitable for further uses, as follows: (1) agriculture (as fertilizer, completion of degraded areas, for making compost and soil for flowers), (2) construction (building materials), and (3) energy systems (power generation). Overall, it is recommended that the sewage sludge be dried to avail all its benefits. Nevertheless, future research is recommended for improving the drying process of dehydrated sludge and its further use in different sectors.

CRediT authorship contribution statement

Cornel Sava: Validation, Software, Investigation, Data curation. **Dana-Adriana Iluțiu-Varvara:** Writing – original draft, Methodology, Conceptualization. **Roxana Mare:** Writing – review & editing, Writing – original draft, Software, Methodology, Conceptualiza-

tion. **Marius Daniel Roman:** Methodology, Conceptualization. **Simona Rada:** Software, Investigation, Data curation. **Elena Maria Pică:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation. **Lorentz Jäntschi:** Visualization, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data pertaining our samples is provided in the manuscript. No additional data available to be reported. The work does not pose a biosecurity threat and the chemicals, procedures or equipment do not have any unusual hazards inherent in their use.

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