AST Advances in Science and Technology Research Journal

Advances in Science and Technology Research Journal, 2025, 19(8), 260–272 https://doi.org/10.12913/22998624/205207 ISSN 2299-8624, License CC-BY 4.0 Received: 2025.05.01 Accepted: 2025.06.15 Published: 2025.07.01

Environmental pollution with polycyclic aromatic hydrocarbons contained in sewage sludge – the mathematical model

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ABSTRACT

Sewage sludge constitutes a type of waste generated during wastewater treatment in any treatment plant. The sludge that meets the quality conditions specified in the legal regulations, due to fertilising properties, can be used for natural purposes (in the recovery process on the surface of the earth or for the reclamation cover of landfills). However, sewage sludge contains various organic microcontaminants, such as, for example, Polycyclic aromatic hydrocarbons (PAHs) that are toxic to aquatic and soil organisms, and the legal regulations do not specify the acceptable concentrations of these compounds. However, the restrictions concerning PAHs in European legislation are proposed. The aim of the study was to use fractional order derivatives to develop a mathematical model describing changes in the concentration of PAHs in sewage sludge stored under natural conditions. The concentrations of selected PAHs were monitored for 3 months at fixed time intervals under the conditions reflecting the use of sludge for natural purposes. A qualitative and quantitative analysis of PAHs was carried out using the GC-MS system. For the mathematical description of changes in the concentration values of individual compounds, fractional order derivatives were used and approximation was carried out using the classical equation of the first order. The developed mathematical model allows for predicting changes in PAH concentrations regarding sludge as well as determining the time necessary to obtain the required concentration of these compounds.

Keywords: mathematical, model, PAHs, GC and MS, sludge.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are included in the group of persistent organic pollutants (POPs) in legal regulations such as: European Union Regulation EC No 850/2004 and national regulations based on the Stockholm Convention [1, 2]. They are also listed as a priority pollutant in the regulations relating to the quality of the aquatic environment in both the Water Directive as well as national regulations [3, 4]. In the proposed changes regarding the European legislation on the conditions for

using sewage sludge in agriculture, the allowed total concentrations of PAHs are set at 6 mg/kg d.m. [5]. The polycyclic aromatic hydrocarbons in sewage sludge come from wastewater, where during treatment they are adsorbed on particulates and separated from wastewater in the form of sewage sludge [6–9].

The presence of PAHs has been confirmed in mineral, organic sludge, both raw and biochemically stabilised [10–12]. During the final treatment of sludge (centrifugation, pressing), a significant part of the PAHs is collected in the solid phase, while the rest penetrates into the sedimentary liquids. The dehydrated sludge discharged from wastewater treatment plants can be used in a natural or agricultural manner due to the content of nutrients (nitrogen, phosphorus, and potassium). That is why, they can act as a reclamation factor for degraded areas applied in the recovery process on the surface of the earth or for the reclamation cover of landfills [13].

According to legal regulations, using sludge in agriculture is limited mainly due to the presence of selected heavy metals and pathogenic organisms [14]. However, the presence of relatively high concentrations of various organic persistent and toxic organic pollutants, including PAHs, has been confirmed in sludge. The content of PAHs in sludge can reach up to 80 mg/kg d.m. and depends on the type of technological processes of sewage treatment as well as the share and type of industrial sewage [15, 16]. Therefore, the proposed changes concerning the European regulations on using sludge concern determining acceptable concentrations of PAHs and other xenobiotics (polychlorinated biphenyls PCBs, polychlorinated dibenzodioxins PCDD, polychlorinated dibenzofurans PCDF, di-(2-ethylhexyl) phthalates DEHP, adsorbed organic halogens AOX, and linear alkylbenzene sulfonates LAS [5].

It should be noted that during sludge usage in a natural manner or its storage, a significant amount of PAHs is introduced into the environment [17-19]. The presence of PAHs in the environment is important from the point of view of toxic effects on organisms, including potentially toxic to humans [20]. The carcinogenic, mutagenic, and teratogenic effects of these compounds on test organisms have been confirmed multiple times in toxicological studies [21–24]. The persistence of these compounds has been confirmed by determining the decomposition time in various environments, e.g. aquatic, soil, and sewage sludge. Despite the fact that they are classified as persistent under the conditions of the aquatic or soil environment, their slow degradation and/or biodegradation is possible under changing environmental conditions. The efficiency of the decomposition of these compounds varies depending on the different PAHs and environmental parameters.

The intensity of biodegradation and chemical transformations depends on the properties of individual bonds, which is related to the chemical structure, the presence and ability of microorganisms in the environment to perform metabolic or cometabolic transformations of these compounds. Temperature, water content, the value of the oxidation and reduction potential, or the presence of oxygen are mentioned as the physical-chemical parameters of the environment [25–27]. Under the natural conditions in soils or a mixture of soil with sludge, the halflife was between 3 and 3.111 days and 15 to 408 days, respectively, for the tested mixtures (soil with sludge) and soil [28]. This confirms the persistence of PAHs under natural conditions, because the time of complete decomposition may be several years, and thus they can remain in the environment for several growing seasons. This is important from the point of view of crop contamination. That is because it has been shown that these compounds penetrate into the roots of plants and migrate to other parts [29]. Therefore, it is possible for PAHs to penetrate into animal feed and food products.

The results of the studies described in the literature are usually difficult to compare due to the heterogeneity of the materials consisting in sewage sludge, their diverse properties as well as the different conditions under which they were obtained. Often, the studies described in the literature relate to model soils, into which single hydrocarbons are introduced in a known amount. Such conditions do not occur in the environment. The hydrocarbons retained in sludge during wastewater treatment processes are present in the mixture, and only a few up to dozenor-so connections are analysed. The biochemical sludge processing carried out in the process of aerobic or anaerobic stabilisation is implemented by a mixed population of microorganisms [30-32]. In the process of sewage sludge hygienisation, the decomposition of organic compounds takes place and at the same time the amount of PAHs can be reduced up to 95%.

However, the literature also describes such studies, which show that liming, the purpose of which is to, among others, deactivate microorganisms and may increase the persistence of some hydrocarbons [33]. The objective of the study was to use fractional order derivatives to determine a mathematical model of changes in the concentration of PAHs in the stored sludge. The mathematical model allows predicting changes in the concentrations of PAHs during sludge storage and determining the time necessary to obtain the assumed concentration.

EXPERIMENTAL AND CALCULATION METHODOLOGY

Materials

The research was carried out using the sewage sludge obtained from a municipal wastewater treatment plant (from the region of Silesia), to which municipal sewage is supplied. The population equivalent (PE) value for the treatment plant exceeds 200,000. Stabilised sludge was obtained from the wastewater treatment plant as a solid phase (cake) from the sludge dewatered on presses. The sludge was previously subjected to 2-stage biochemical stabilisation in closed mesophilic fermentation chambers and open chambers. The sewage sludge were initially characterised by analysing selected physicalchemical properties.

The degree of mineralising organic substances was determined by the content of organic compounds and hydration of sludge, as well as the alkalinity and pH in supra-sedimentary liquids. The determinations were made in accordance with the generally accepted methodology [34]. The content of organic compounds and water in the sludge was determined by weight, while the pH and alkalinity – potentiometrically. The hydration of the sewage sludge obtained from the treatment plant was 81%. The average content of organic substances was at the level of 53%. The mean pH value of supra-sedimentary liquids was at the level of 7.6, and the alkalinity - 4.18 mgCaCO₂/L. Taking into account the above, it can be concluded that the sewage sludge was biochemically stabilised to a sufficient degree.

Research methodology

In order to monitor the changes relating to concentrations of PAHs in sewage sludge, 14 samples weighing 10 g were prepared under the accepted conditions in 100 ml glass flasks. Sewage sludge was stored under laboratory conditions without access to light, at a temperature of 20 °C for 90 days. PAHs were determined 7 times during the sludge incubation: at the beginning of the experiment and after 15, 30, 45, 60, 75, and 90 days. The extraction of PAHs was carried out each time from the entire volume of the sludge sample in two repetitions (the "sacrificing the entire sample" method).

Qualitative and quantitative determination of PAHs

The determination of PAHs was carried out using the gas chromatography technique with a detector being a GC-MS mass spectrometer. The organic matrix was separated from the sludge during extraction with a mixture of solvents: cyclohexane and dichloromethane (in a ratio of 5:1 (v/v)) [9, 12, 16]. A mixture of sludge and solvents was placed in an ultrasonic scrubber for 15 minutes. Then, the solvent phase was separated from the sludge and concentrated to a volume of 10 mL in a nitrogen stream. Afterwards, the extracts were purified on silica gel under vacuum conditions as solid phase extraction (SPE). The purified extracts were re-concentrated to a volume of 1 ml and sent for chromatographic analysis. The qualitative and quantitative analysis was carried out using the Fisons gas chromatograph (model CGC8000/MS800). The DB-5 column (30-m length, 0.25 mm diameter, 1 µm film) was used for the separation. The carrier gas consisted in helium (flow rate -0.5 ml min⁻¹). The temperature programme of the furnace was as follows: up to 40 °C for 1 min, heating 5 °C/min to 120 °C, and the final temperature of 280 °C was maintained for 60 minutes. Eight compounds belonging to group 16 of PAH-EPA were determined. These were 2,- 3,- and 4-ring PAHs such as: Naphtalene Naph, acenaphtylene Acyl, acenaphtene Ac, fluorene Flu, phenanthrene Phen, anthracene Antr, fluoranthene Fl, pyrene Pyr. In order to verify the procedure of preparing samples, recovering the standard PAH mixture was determined in parallel. A mixture of 16 PAHs with a concentration of 3,000 µg/kg.d.m. was introduced into the sludge sample. Then, after mixing, it was extracted and analysed according to the procedure described above. The average recovery value was between 84 and 104%. These values fall within the range of data published in the literature (0-128%) determined for matrices contaminated with organic substances [11, 25, 35].

MATHEMATICAL MODELS

Classical model

The mathematical model of changes regarding the concentrations of PAHs under the accepted test conditions was described using fractional order derivatives. For comparison, a model of changes concerning the concentrations of PAHs was also made based on the most commonly used classic differential equation of the first order [36]. The classic mathematical model of changes relating to the concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge is a first-order differential Equation 1:

$$\frac{dC}{dt} + kC = 0 \tag{1}$$

where: C – concentration of PAHs, k – reaction coefficient of rate of the first order

The solution to this equation is Equation 2:

$$C = C_0 e^{-kt} \tag{2}$$

where: C_0 – PAHs concentration at the beginning of observation for t = 0.

The value of the k coefficient depends on the test substance and on many other factors related to the conditions of concentration measurement. Therefore, it cannot be predetermined.

Model based on fractional-calculus

Fractional order derivatives, also known as differential-integrals, are a generalisation of the well-known dynamic systems which were hitherto described by means of "classical" differential equations containing derivatives of integer order. According to many authors, the origin of the concept of differential-integral fractional order calculus dates back to 1695, when two mathematicians, de L'Hospital and Leibniz, considered the possibility of the existence of a derivative of order 1/2. This was taken up and extended in later centuries by such mathematicians as: Euler, Liouville, Abel, Grünwald, Letnikov, Riemann, and in more modern times by Caputo, Podlubny, Nishimoto, Riesz, Fabrizio [37]. The application aspect of this calculus emerged only in the 1970s, and since then it has become the subject of many specialised conferences and hundreds of publications-in his work [38], prof. J.A. Tenreiro Machado lists more than 30 fields in which fractional order calculus has been successfully applied. There are three equal definitions of the fractional order derivative: two for continuous functions: Riemann-Liouville's and Caputo's, and one for discrete functions: Grünwald-Letnikov's. In this paper, Caputo's definition will be used because

its important feature is that the initial conditions involve integer order derivatives. These derivatives have a more complete physical meaning than the fractional order derivatives found in the Riemann-Liouville definition.

The derivative of order α ($\alpha \in \mathbf{R}_{+}$), in Caputo's sense, is called an operator (3) [37, 39, 40]:

$${}_{a}^{C}D_{t}^{\alpha}f(t) = \frac{1}{\Gamma(k-\alpha)} \int_{a}^{t} \frac{f^{(k)}(\tau)}{(t-\tau)^{\alpha+1-k}} d\tau, \quad (3)$$

where: $k - 1 \le \alpha \le k$.

The Laplace transform method is a very commonly used tool for solving differential equations including fractional order differential equations. The relations on the basis of which the Laplace transform of fractional-order derivatives is determined can be calculated using the relation for the transform of the n^{th} -order classical derivative - for the fractional derivative in the Caputo sense, Equation 4 can be obtained [37, 41, 42]:

$$L\{{}_{0}^{C}D_{x}^{\alpha}f(t);s\} = s^{\alpha}F(s) - \sum_{k=0}^{n-1} s^{\alpha-k-1}f^{k}(0),$$

$$n-1 \le \alpha < n$$
(4)

where: F(s) is the transform of the sought function f(t).

To determine the inverse Laplace transform of fractional order systems, the most common methods are those that allow approximating the factor s^{α} by the quotient of polynomials containing integer powers of s. Such a method, among others, is continued fraction expansion (CFE), which is derived from the expansion into an infinite fraction of the expression [43, 44].

1.

$$(1+x)^{\alpha} = \frac{1}{1 - \frac{\alpha x}{1 + \frac{(1+\alpha)x}{2 + \frac{(1-\alpha)x}{3 + \frac{(2-\alpha)x}{2 + \frac{(2-\alpha)x}{5 + \dots}}}}}$$
(5)

. .

By substituting x = s - l and taking successive expressions for consideration, one obtains approximations of s^{α} of the corresponding orders of A, related to the accuracy of the representation.

According to this method, the factor s^{α} can be presented as the quotient of polynomials of the variable s and α order derivative – both variables occur here in integer powers – Equation 6.

$$s^{\alpha} \cong \frac{N(s,\alpha)}{D(s,\alpha)} = \frac{\sum_{k=0}^{A} P_{Ak}(\alpha) s^{A-k}}{\sum_{k=0}^{A} Q_{Ak}(\alpha) s^{A-k}}$$
(6)

where: A – order of approximation, $P_{Ak}(\alpha)$, $Q_{Ak}(\alpha)$, α – polynomials of degree A.

Of course, a more accurate representation of the factor s^{α} can be obtained by enlarging the order of approximation which, however, leads to more elaborate formulas and makes calculations more difficult. Taking this into account, analyses were made in the paper [45] and it was found that an approximation of order A = 5 (for fifth-degree polynomials) gives the accuracy that is relatively best. Increasing the order of approximation, in addition to an increased number of components in the polynomials, and thus a larger number of poles and a more complex numerical implementation, gives a relatively negligible change in the solution, which is interpreted as a slight improvement in accuracy. In the end, it was found that a reasonably good approximation at a moderate computational cost could be achieved for the order of 3–5.

$$P_{30} = Q_{33} = \alpha^{3} + 6\alpha^{2} + 11\alpha + 6$$

$$P_{31} = Q_{32} = -3\alpha^{3} - 6\alpha^{2} + 27\alpha + 54$$

$$P_{32} = Q_{31} = 3\alpha^{3} - 6\alpha^{2} - 27\alpha + 54$$

$$P_{33} = Q_{30} = -\alpha^{3} + 6\alpha^{2} - 11\alpha + 6$$
(7)

Whereas, assuming the order of approximation to be A = 5, these polynomials take the following form (see Equation 8).

Thus, the fractional-order model will be in the form of Equation 9:

$$\frac{d^{\alpha}C}{dt^{\alpha}} + kC = 0 \tag{9}$$

where: $\frac{d^{\alpha}}{dt^{\alpha}}$ stands for fractional-order derivative operator. Performing the Laplace transformation according to the formula (4), the form (10) was obtained

$$L\left\{\frac{d^{\alpha}C}{dt^{\alpha}} + kC\right\} = s^{\alpha}C(s) - -s^{\alpha-1}C(0) + kC(s) =$$
(10)
0 for $0 < \alpha < 1$

where: C(s) – transform of the concentration function C(t), C(0) – concentration value at time t = 0 (at the beginning of the observation).

Determining C(s) from Equation 10 yielded the following:

$$C(s) = \frac{s^{\alpha-1}C(0)}{\left(s^{\alpha}+k\right)} = \frac{s^{\alpha}C(0)}{s\left(s^{\alpha}+k\right)}$$
(11)

Then using the CFE method

$$C(s) = \frac{N(s,\alpha)C(0)}{s(N(s,\alpha) + kD(s,\alpha))}$$

for $s^{\alpha} = \frac{N(s,\alpha)}{D(s,\alpha)}$ (12)

and further on:

$$C(s) = \frac{Num(s,\alpha)}{Den(s,\alpha)}$$
(13)

Using the order of approximation A = 3, the formulas -(6) and (7), the relationship (13) assumes the form (14) and (15)

$$Num(s, \alpha) = s^{3}C(0) (\alpha^{3} + 6\alpha^{2} + 11\alpha + 6) + +s^{2}C(0)(-3\alpha^{3} - 6\alpha^{2} + 27\alpha + 54) + +sC(0)(3\alpha^{3} - 6\alpha^{2} - 27\alpha + 54) + + C(0)(-\alpha^{3} + 6\alpha^{2} - 11\alpha + 6)$$
(14)

For specific values of k and the order of the fractional derivative α , expressions (14, 15) will be polynomials of the variable s only, so the

$$P_{50}(\alpha) = Q_{55}(\alpha) = -\alpha^{5} - 15\alpha^{4} - 85\alpha^{3} - 225\alpha^{2} - 274\alpha - 120$$

$$P_{51}(\alpha) = Q_{54}(\alpha) = 5\alpha^{5} + 45\alpha^{4} + 55\alpha^{3} - 1005\alpha^{2} - 3250\alpha - 3000$$

$$P_{52}(\alpha) = Q_{53}(\alpha) = 10\alpha^{5} - 30\alpha^{4} - 410\alpha^{3} + 1230\alpha^{2} + 4000\alpha - 12000$$

$$P_{53}(\alpha) = Q_{52}(\alpha) = -10\alpha^{5} - 30\alpha^{4} + 410\alpha^{3} + 1230\alpha^{2} - 4000\alpha - 12000$$

$$P_{54}(\alpha) = Q_{51}(\alpha) = -5\alpha^{5} + 45\alpha^{4} - 5\alpha^{3} - 1005\alpha^{2} + 3250\alpha - 3000$$

$$P_{55}(\alpha) = Q_{50}(\alpha) = \alpha^{5} - 15\alpha^{4} + 85\alpha^{3} - 225\alpha^{2} + 274\alpha - 120$$
(8)

$$Den(s,\alpha) = s \left\{ s^{3} \left[(1-k)\alpha^{3} + 6(1+k)\alpha^{2} + 11(1-k)\alpha + 6(1+k) \right] + s^{2} \left[(k-1)3\alpha^{3} - 6(1+k)\alpha^{2} + 27(1-k)\alpha + 54(1+k) \right] + s \left(3\alpha^{3}(1-k) - 6\alpha^{2}(1+k) + 27\alpha(k-1) + 54(1+k) \right) + \left[\alpha^{3}(k-1) + 6\alpha^{2}(1+k) + 11\alpha(k-1) + 6(1+k) \right] \right\}$$

$$(15)$$

function C(s) = L(s)/N(s) is measurable and the degree of the numerator is smaller than the degree of the denominator. In this case, the inverse transform can be determined from Equation (16) [46].

$$L^{-1}{C(s)} = L^{-1}\left\{\frac{L(s)}{N(s)}\right\} =$$
$$= \sum_{k=1}^{K} \operatorname{res}_{s=s_{k}}\left[\frac{L(s)}{N(s)}e^{st}\right]$$
(16)

where: s_k , k = 1, 2, ..., K are the poles of the C(s)transform – the zeros of N(s).

The poles and residues for the C(s) function thus obtained were calculated using the Symbolic Math Toolbox in the MATLAB environment.

RESULTS

Changes in concentrations of PAHs during the tests

The initial total concentration of the eight analysed PAHs in sewage sludge averaged 526 µg/ kg d.m. and was ten times lower than the limit value for 11 compounds listed in the Sludge Directive on the possibility of using sludge in agriculture. The determined concentrations of PAHs fit within the scope of data published in the literature relating to the sewage sludge generated in European treatment plants, however, but they were several times lower than the concentrations of these compounds in the sludge taken from the treatment plants operated in Asia [15, 16]. The concentrations of individual compounds, as well as the total concentration of 16 compounds determined in different sludge types, are characterised by a significant discrepancy. The concentration of PAHs in sludge is influenced by the characteristics of sewage as well as the methods and technological systems for treating and processing sewage sludge. For example, the total concentration of 10 compounds in the sludge studied by Oleszczuk ranged from 2,830 to 9,950 µg/kg d.m. [47]. Higher concentrations were determined in the sludge from the treatment plants in France, as the total concentration of 13 PAHs reached 16,200 μ g/kg d.m. [30]. Oleszczuk's research was dominated by 4-ring hydrocarbons, constituting from 50 to 67% of the total concentration of 10 PAHs [47]. In the studies described in this paper, the total concentration relating to 4-ring hydrocarbons was the highest and accounted for 52% of the total content of the analysed PAHs (274 μ g/kg d.m.)

The concentrations of all tested sewage sludge hydrocarbons decreased in the sludge during incubation. A much lower concentration, in relation to the initial one, was noted after the first week of sludge incubation. During the following period, the decreases in concentrations were less significant. PAHs losses in sludge may have resulted from reactions with other components of the sludge, sorption, photodegradation, oxidation, biodegradation, and evaporation [9, 28, 30]. The experimental conditions ensured limiting photodegradation, as the incubation of sludge samples took place without access to light. Due to the fact that sludge is a heterogeneous material with a complex organic and inorganic matrix, sorption may have played a large role in inhibiting the functioning and biochemical transformations leading to the degradation of PAHs. Other compounds are then formed by, for example, substitution, which were not identified during the analysis. Therefore, in some cases, insignificant fluctuations in terms of concentration were noted during the research.

Mathematical models

On the basis of the values of the determined hydrocarbon concentrations, the parameters of the first order kinetics equations were determined and the obtained results of calculations were presented in Table 1. The results of using the model based on fractional order derivatives are presented in Table 2.

Taking into account the values of the determined concentration measurements (μ g/kg d.m.) of Naphtalene and the criterion of approximation accuracy as root mean square error (RMSE) [48], an approximation of the above-mentioned measurements in the form of a formula was obtained.

No.	PAHs	C ₀	k	Function	² RMSE	¹ RMSE%
1.	Naphtalene	122.3	2.5400e ⁻⁰²	2.5400e ⁻⁰² $C(t) = 122.3e^{-0.0254t}$		15.84
2.	Acenaphtalene	28.5	1.0080e ⁻⁰¹	$C(t) = 28.5 e^{-0.1008t}$	5.9532e ⁻⁰¹	2.09
3.	Acenaphtene	29	2.2650e ⁻⁰²	$C(t) = 29.0e^{-0.02265t}$	1.6414e ⁺⁰⁰	5.68
4.	Fluorene	23.5	1.3260e ⁻⁰²	$C(t) = 23.5e^{-0.01326t}$	1.2345e ⁺⁰⁰	5.25
5.	Phenanthrene	47.5	3.9400e ⁻⁰³	$C(t) = 47.5e^{-0.00394t}$	5.4347e ⁺⁰⁰	11.44
6.	Anthracene	27.75	2.2680e ⁻⁰²	$C(t) = 27.75^{\text{e-0.02268}}$ t	2.0705e ⁺⁰⁰	7.46
7.	Fluoranthene	129.5	2.3810e ⁻⁰²	$C(t) = 129.5e^{-0.02381t}$	4.1802e ⁺⁰⁰	3.23
8.	Pyrene	117.5	2.7050e ⁻⁰²	$C(t) = 117.5e^{-0.02705t}$	5.7488e ⁺⁰⁰	4.89

 Table 1. Data for the model of changes in concentrations of PAHs according to the kinetics equation of the first order

Note: ¹ related to the highest value, i.e. C0, ² RMSE – root mean square error [48].

Table 2. Data for the model of changes in concentrations of PAHs according to the fractional order kinetics equation

No.	PAHs	Coefficient a	k	RMSE	RMSE%	Change of value RMSE%	
1.	Naph	0.6	20.0e ⁻⁰²	7.4237e ⁺⁰⁰	6.07	-9.77	
		$C(t) = 7.2898e^{-4.1214t} + 17.408e^{-0.67265t} + 57.566e^{-0.10267t} + 37.881$					
2.	Acyl	0.968	1.1590e ⁻⁰¹	1.3585e ⁻⁰¹	0.48	-1.69	
		$C(t) = 0.0017897e^{-2.6264t} + 0.013509e^{-0.38357t} + 28.641e^{-0.023186t} + 0.34436$					
3.	Ace	0.9967	2.3080e ⁻⁰²	1.6396e ⁺⁰⁰	5.65	-0.03	
		$C(t) = 0.0017897e^{-2.6264t} + 0.013509e^{-0.38357t} + 28.641e^{-0.023186t} + 0.34436$					
4.	Flu	0.949	1.7690e ⁻⁰²	1.0950e ⁺⁰⁰	4.65	-0.6	
		$C(t) = 0.017171e^{-2.502t} + 0.10981e^{-0.40623t} + 18.32e^{-0.020168t} + 5.0513$					
5.	Phen	0.9999	3.9410e ⁻⁰³	5.4347e ⁺⁰⁰	11.44	0	
		$C(t) = 47.5e^{-0.00394t}$					
6.	Ant	0.94	3.2200e ⁻⁰²	1.5205e⁺00	5.48	-1.98	
		$C(t) = 0.043866e^{-2.7763t} + 0.28715e^{-0.041241t} + 23.16e^{-0.033208t} + 4.2542$					
7.	FI	0.984	2.6100e ⁻⁰²	3.8611e⁺00	2.98	-0.25	
		$C(t) = 0.043968e^{-2.659t} + 0.32321e^{-0.38984t} + 122.58e^{-0.026518t} + 6.5456$					
8.	Pyr	0.986	2.9360e ⁻⁰²	5.5981e ⁺⁰⁰	4.76	-0.13	
		$C(t) = 0.039357e^{-2.6539t} + 0.29546e^{-0.38897t} + 112.51e^{-0.029612t} + 4.6491$					

$$C(t) = 122.3 e^{-0.0254t}$$
 (17)

Taking into account the derivatives of the fractional order, a model equation was obtained in the form: (18)

$$C(t) = 7.2898e^{-4.1214t} + + 17.408e^{-0.67265t} + + 57.566e^{-0.10267t} + 37.881$$
(18)

Figures 1 and 2 graphically present a comparison of the results concerning concentration measurements – marked by "1" – the results of measurements relating to the concentration of naphthalene and acenaphthylene, respectively, and the approximating function for the model of kinetics of the first order – "2" and the fractional derivative – "3" (this marking applies to Figures 1 to 8).



Figure 1. Comparison of the results of measurements concerning of naphthalene approximation functions respectively (17) and (18)



Figure 2. Comparison of the results of measurements concerning of acenaphtylene and approximation functions respectively (19) and (20)

Changes in acenaphthylene, the determined kinetics equation of the first order takes the form of the Equation 19, and the fractional order (20):

$$C(t) = 28.5 e^{-0.1008t}$$
 (19)

$$C(t) = 0.0017897e^{-2.6264 t} + 0.013509e^{-0.38357 t} + 0.013509e^{-0.38357 t} + 0.34436$$

The results of calculations for acenaphtene are presented in Figure 3, and fluorene – in Figure 4. The kinetics equations take the form of 21, 22, 23 and 24 for acenaphtene and fluorene, respectively:

$$C(t) = 29 e^{-0.02265t}$$
 (21)

$$C(t) = 0.0017897e^{-2.6264t} + 0.013509e^{-0.38357t} + (22) + 28.641e^{-0.023186t} + 0.34436$$

$$C(t) = 23.5 \,\mathrm{e}^{-0.01326t}$$
 (23)

$$C(t) = 0.017171e^{-2.502t} + 0.10981e^{-0.40623t} + 18.32e^{-0.020168t} + 5.0513$$
(24)

Figure 5 presents the changes of phenantrene in sewage sludge in accordance with analytical and calculative data. In this case, regardless of the adopted model, the equation of changes regarding concentrations is identical and takes the form (25) and (26):

$$C(t) = 47.5 e^{-0.00394t}$$
 (25)

$$C(t) = 27.75 \,\mathrm{e}^{-0.02268t} \tag{26}$$

$$C(t) = 0.043866e^{-2.7763t} + 0.28715e^{-0.41241t} + (27) + 23.16e^{-0.033208t} + 4.2542$$

For the measurements relating to the concentrations of anthracene, an approximation of the above-mentioned measurements was obtained in the form of formulas (26) and (27) for the classic model and the fractional order – Figure 6.

Figure 7 presents the results of approximation of fluoranthene concentartion for kinetic models of the first-order and fractional order (28) and (29), respectively:

$$C = 129.5e^{-0.0238t} \tag{28}$$

$$C(t) = 0.043968^{-2.659t} + + 0.32321e^{-0.38984t} + + 122.58e^{-0.026518t} + 6.5456$$
(29)

In turn, for the measurement of pyrene concentrations, an approximation of the above-mentioned measurements was obtained in the form of Equations (30) and (31) for classic first-order and fractional order models, respectively:

$$C = 117.5e^{-0.027t} \tag{30}$$

$$C(t) = 0.039357e^{-2.6539t} + 0.29546e^{-0.38897t} + (31) + 112.51e^{-0.029612t} + 4.6491$$

On the basis of the calculations, it can be concluded that using derivatives of fractional order does not always provide measurable benefits. For hydrocarbons, such as: Acenaphtene,



Figure 3. Comparison of the results of measurements concerning of acenaphtene approximation functions and approximation functions (21) and (22), respectively respectively and (24)



Figure 4. Comparison of the results of measurements concerning of fluorene and and approximation functions

Fluorene, Anthracene, Fluoranthene, Pyrene (items 3, 4, 7, 8 – Table 2) the improvement in approximation accuracy was less than 1% (Table 2 – RMSE% change less than 1). In the case of phenanthren (item 5 – Table 2) no better approximation than the classic model was found using fractional derivatives. The fractional derivative order tended to 1.0, which may indicate the correctness of the used algorithm of kinetics of the first order. For such hydrocarbons as acenaphtylene and anthracene (items: 2, 6 – Table 2), taking advantage of modelling using fractional order derivatives allows increasing the accuracy by approx. 2%. In turn, the largest change in the value of RMSE% (item 1 – Table 2) is almost



Figure 5. Comparison of the results measurements concerning of phenanthrene and approximation functions (25)



Figure 6. Comparison of the results of of measurements concerning of anthracene and approximation functions (26) and (27), respectively

10% and has been recorded for the course of changes in naphthalene concentrations.

It should be added that taking advantage of a model based on fractional order derivatives requires using an advanced mathematical apparatus and performing from several dozen to several hundred calculations for variable parameters: the order of fractional derivatives - α and the k coefficient, which allow finding optimal values of these parameters. The results of calculations indicate that in some cases approximation with the use of fractional order derivatives gives more than three times less error than in the case of a description made using the classical equation of the first order.



Figure 7. Comparison of the results measurements concerning of fluoranthene approximation functions (28) and (29), respectively



Figure 8. Comparison of the results of of measurements concerning of pyrene and and approximation functions (30) and (31), respectively

Furthermore, knowing the analytical form of the course of changes in the concentration of a given substance, it is possible not only to determine the concentration after a given time, but also to set the inverse functions, which in these cases would allow determining the time interval t_1 required for the decomposition of the substance to obtain the required concentration of $C(t_1)$. Thus, for an approximation with the classic equation of the first order (1), the function is $C(t) = C_0 e^{-kt}$ and the inverse function has the form (32)

$$t_1 = \frac{1}{k} \left[\ln C_0 - \ln C(t_1) \right]$$
(32)

where: $C(t_1)$ i the required concentration, t_1 – the time after which the assumed (required)

concentration can be reached under the conditions prevailing at the time of measurements.

In turn, for approximation with a fractional equation of the first order (12) at a known C_0 and a determined coefficient k and an assumed order of the fractional derivative, the function is as presented below (33):

$$C(t) = C_1 e^{k_1 t} + C_2 e^{k_2 t} + C_3 e^{k_3 t} + C_0 \quad (33)$$

where: C_i (*i* = 0, 1, 2, 3), k_j (*j* = 1, 2, 3) – coefficients resulting from calculating the residuum of the Laplace transform of the concentration of a tested substance.

In this case, it is impossible to obtain the inverse function in an analytical form. Therefore, a graphical method is proposed, consisting in making graphs of the function $f_1(t)$ and $f_2(t)$ specified in equations (34) and finding the cut off t_1 place of intersection for these two graphs, which constitutes a solution to the inverse problem – Figure 9.

$$f_1(t) = C_1 e^{k_1 t} + C_2 e^{k_2 t} + C_3 e^{k_3 t} = C(t) - C_{00} = f_2(t)$$
(34)

An example consists in a solved inverse problem concerning the decomposition of fluorene (item 4 – Tables 1 and 2) and where the classic approximation is expressed by the formula (23) and (24).

Using the obtained fractional order equation and maintaining the conditions as at the time of the measurements, determining the time after which the concentration will reach the value (for



Figure 9. Graphical method for determining the time for which the concentration of fluorene reaches the assumed value

example) of 10 μ g/kg.d.m. at an initial concentration of 23.5 μ g/kg.d.m. will be expressed by Equations 35 and 36:

• for classic approximation, using the formula (34), the following form is obtained (35)

$$t_{1} = \frac{1}{k} [ln C_{0} - ln C (t_{1})] =$$

= $\frac{1}{0.01326} ln \frac{23.5}{10} = 64.43$ (35)

• for approximation in the fractional model (36)

$$f_1(t) = 0.017171e^{-2.502t} + 0.10981e^{-0.40623t} + 18.32e^{-0.020168t}$$
(36)
and $f_2(t) = 10 - 5.0513$

In this case, the determined time approximates 64.9 and thus coincides with the value of time obtained on the basis of the classic model. This is confirmed by the possibility of using the developed models to control the value of PAHs concentrations to the permissible levels, allowing for the natural use of sludge. The obtained calculation results are difficult to compare with data found in literature. The available literature lacks a mathematical description of the course of changes concerning concentrations of PAHs in sludge or soils using fractional derivatives.

CONCLUSIONS

During the incubation of sludge, the total concentration of eight PAHs in the sludge was reduced by 81%. This indicates the possibility of abiotic transformations and biodegradation of these compounds during storage. The most intense decrease in terms of concentrations of PAHs was recorded during the first month of sludge incubation. At the same time, it has been shown that the natural use of sewage sludge can be a long-term source of environmental pollution by PAHs. This is particularly important from the point of view of the possibility of accumulating these compounds in plants and contaminating surface and groundwater during rainwater infiltration. The possibility of obtaining PAHs by plants and migration to various parts has been confirmed in studies carried out by many authors, including previous co-authored studies. Modelling the changes in concentrations of PAHs in sludge using fractional order derivatives is in most cases a better tool for predicting the volume of transformations of these compounds compared to the model based on the

classic equation of the first order. Approximation using fractional order derivatives in some cases allows for more than a threefold reduction in error compared to the classic equation of the first order. From analysing this series of measurements, it is possible to draw the conclusions that the use of a model with fractional order derivatives provides measurable benefits in terms of examples in which the use of the classic model gives an approximation accuracy of approx. 5%. Inversing the fractional order equation of the model allows determining the time necessary to obtain the assumed or required concentration of PAHs before directing sludge for use.

Acknowledgements

The research was supported both by statutory subvestion of Czestochowa University of Technology and by Kielce University of Technology.

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