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Original Research

Assessing the Sorption Capacity of Sewage Sludge with Respect to Organic Halogen Derivative Compounds

Elżbieta Bezak-Mazur*, Lidia Dąbek, Ewa Ozimina*****

Faculty of Civil and Environmental Engineering, Kielce University of Technology
Al. Tysiąclecia Państwa Polskiego 7, 25-314 Kielce, Poland

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Abstract

This paper determines the sorption capacity of sewage sludge of various organic substances in relation to halogen organic compounds, which are among the main environmental contaminants. The assessment is based on iodine adsorption values and the *p*-chlorophenol adsorption isotherms. Additionally, the leaching efficiency of *p*-chlorophenol from sludge into the water solution under the influence of selected physical and chemical factors such as UV radiation, electric discharges and freeze-thaw conditioning has been examined. The results suggest that sewage sludge shows good sorption capacity and that under favourable conditions only a portion of adsorbed *p*-chlorophenol was leached to the aqueous phase.

Keywords: sewage sludge, sorption, leaching, *p*-chlorophenol, adsorbable organic halogens (AOX)

Introduction

One of the most important problems faced by environmental engineers today is the management of sewage sludge generated by municipal wastewater treatment plants. Because of its specific physical and chemical properties, i.e. high contents of nitrogen, phosphorous, potassium, calcium, and magnesium, and consistency similar to that of humified peat, sewage sludge is considered a valuable product to be used for soil improvement or recultivation [1]. However, if sewage sludge is contaminated with heavy metals or other toxic substances, it may threaten the environment. Since the presence of organic compounds is an important factor limiting the agricultural applications of sewage sludge, it has become essential to determine their contents. The most hazardous compounds found in sewage sludge are organic halogens, polycyclic aromatic hydrocarbons, polychlorobiphenyls, and dioxins/furans [2]. Standards concerning the content limits of organic toxicants in sewage sludge have been introduced in very few countries, including Germany, Austria, and Switzerland (Table 1) [2].

Because of the danger that the compounds pose, sewage sludge should be analyzed for content, bonding, and susceptibility to soil-water penetration. It is important that the sorption capacity and bond durability be determined, especially in the case of polar organic compounds susceptible to leaching in an aqueous environment. In this analysis, we focus on organic halogen derivative compounds representing a group of the most dangerous contaminants. They are characterized by high durability, high toxicity toward living organisms, and poor biodegradability [3]. The compounds originate from the wastewater itself, as well as chemical reactions occurring during wastewater treatment and sludge processing. These reactions are due to the presence of strong chlorine-based oxidants such as Cl_2, Cl^*, Cl^+, ClO_2^-, and ClO^-. An example is the haloform reaction observed during wastewater treatment or sludge processing. It greatly contributes to the generation of organic halogens [4].

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*e-mail: bezak@tu.kielce.pl
**e-mail: ldabek@tu.kielce.pl
***e-mail: ewa.ozimina@tu.kielce.pl

Table 1. Concentration limits for organic compounds and dioxins in land-applied sewage sludge accepted by several EU member states [2].

Organic compounds	Maximum concentration (mg/kg dry weight basis)
AOX[1]	500
LAS[2]	2,600
DEHP[3]	100
NPE[4]	50
PAH[5]	6
PCB[6]	0.8
PCDD/F[7]	100 ngTE/kg d.w.

[1] Adsorbable Organic Halogens,
[2] Linear Alkylbenzene Sulphonates,
[3] di-(2-ethylhelxyl) phtalates,
[4] Nonyl Phenol Ethoxylates,
[5] Polycyclic Aromatic Hydrocarbons,
[6] Poly-Chlorinated Biphenyls,
[7] Polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

Sorption is one of the mechanisms involved in the bonding of organic substances in sewage sludge. The sorption capacity of this material is dependent on the presence of organic matter, which consists of substances susceptible to humus formation. The material possesses an expanded porous structure. The presence of organic matter in sewage sludge is also a significant soil-forming factor [5-7]. This study aims at assessing the sorption capacity of selected sewage sludge material with regard to organic halogen derivative compounds. The assessment was based on iodine adsorption values and *p*-chlorophenol adsorption isotherms.

The total AOX parameter, which is used to determine the content of organic halogen derivative compounds adsorbable on activated carbon, was applied to analyze the changes in the concentration of *p*-chlorophenol in the water solution due to sorption and leaching. As shown by Bezak et al. [8], the parameter is particularly suitable for assessing the changes in the concentration of organic halogen derivative compounds soluble in water solution and easily migrating from the sludge to the aqueous phase. As can be seen from Table 1, the AOX parameter was also employed to assess the content of organic halogen derivative compounds in sewage sludge with agricultural application [2]. The content of substances from this group should not exceed 500 mgCl/kg d.w. Bernacka and Pawłowska [2] presents the content limits of organic halogen derivative compounds for sewage sludge obtained from municipal wastewater treatment plants in several countries: Germany 155-244 mgCl/kg d.w., Austria 173-480 mgCl/kg d.w., and Poland 120-470 mgCl/kg d.w. As can be seen, the real amount of organic halogens in sewage sludge is much lower than the admissible value. It is essential to find out how dangerous it is to apply sewage sludge with an increased amount of organic halogen derivative compounds (the AOX group) on soil. The material analyzed in this work was exposed to selected physical and chemical factors: UV radiation, electric discharges and temperature changes (cyclic freezing and thawing). The aim was to establish their influence on the leaching of *p*-chlorophenol from sludge into the water solution.

The analysis was conducted for sewage sludge from three municipal wastewater treatment plants located near Kielce. The material differed in the amount of organic matter.

Experimental Procedures

Testing was performed for the following material:

- sewage sludge obtained through mechanical-biological wastewater treatment, denoted as sewage sludge I,
- sewage sludge obtained by using the activated sludge method with a suspended biological resource, denoted as sewage sludge II,
- sewage sludge obtained by using the one-stage three-phase activated sludge method, denoted as sewage sludge III.

The sludge samples were collected according to the procedure given in the PN-EN ISO 5667-13:2004 standard.

Determining the Physical and Chemical Properties of the Sewage Sludge Material

The physical and chemical properties of the sewage sludge samples were determined in accordance with the Regulation of the Minister of the Environment concerning municipal sewage sludge (Journal of Laws of the Republic of Poland 2002, No. 134, item 1140). Analysis included the determination of:

a) pH (using the method given in the PN-EN 12176:2002 standard),
b) dry mass content, in % (according to the PN-EN 12880 standard),
c) organic substance content as % of d.w. (according to the PN-EN 12880 standard),
d) total nitrogen content (including ammonium nitrogen) as % of d.w. (according to the PN-C-04576-16:1975 standard),
e) total phosphorus content as % of d.w. (according to the PN-C-04537-14 standard),
f) calcium and magnesium contents as % of d.w. (according to the PN-C-04551-04:1981 standard),
g) metal content (using the voltamperometric method after microwave mineralization),
h) AOX parameter according to the PN-EN ISO 9582:2007 standard; this required leaching the AOXs to the aqueous phase by applying 35-kHz frequency ultrasounds. The methodology is described in detail in Ref. [8].

The mean values of the above parameters are presented in Table 2.

The sludge microstructure was analyzed by means of a LEO 435 VP scanning microscope.

Table 2. Physical and chemical characteristics of the sludge.

Parameter	Maximum content of heavy metals allowed in sludge to be used on agricultural land and for land reclamation [1]	Sewage sludge		
		I	II	III
pH		8.46	6.68	8.83
Dry matter, %		18.96	16.64	21.5
Organic substance, % d.w.		61.94	75.10	78.54
Total nitrogen, % d.w.		1.91	0.96	2.84
Ammonium nitrogen, % d.w.		0.31	0.58	0.35
Total phosphorus, % d.w.		1.61	2.18	2.12
Calcium, % d.w.		1.16	2.6	1.18
Magnesium, % d.w.		0.32	0.55	0.54
Lead, mg/kg d.w.	500	27.6	29.9	18.35
Cadmium, mg/kg d.w.	10	2.09	2.34	2.16
Mercury, mg/kg d.w.	5	0.08	0.04	0.17
Nickel, mg/kg d.w.	100	18.99	11.2	13.39
Zink, mg/kg d.w.	2.500	1,061	1,081	1,223
Copper, mg/kg d.w.	800	30.7	31.9	17.9
Chromium, mg/kg d.w.	500	49.76	12.56	12.4
AOX, mgCl/kg d.w.		96.68	65.8	75.4

Determining the Sorption Capacity of the Sewage Sludge Material

The sorption capacity of the sewage sludge material was assessed based on iodine adsorption values and the *p*-chlorophenol adsorption isotherms. The iodine adsorption values were determined in accordance with ASTM designation method D4607-94. It was necessary, however, to adjust the procedure to the specific character of the material. The adsorption isotherms were defined for *p*-chlorophenol leached from the water solution under static conditions. The sewage sludge material was weighed and divided into five conic flasks: approx. 2.0, 5, 7.5, 10, and 12.5 g. All the samples were treated with 50 cm^3 of water solution of *p*-chlorophenol with a concentration of 3.7 mgCl/L. Then, they were shaken in a GFL-3005 shaker (Gesellschaft für Labortechnik GmbH, Germany) at a rotational speed of 300 rev./min for 4 hours at 20ºC. The *p*-chlorophenol solution was separated from the sludge mechanically for 10 minutes using a laboratory centrifuge operating at a rotational speed of 4,000 rev./min. The equilibrium concentration of *p*-chlorophenol was measured with the AOX parameter.

Determining the Concentration of *p*-chlorophenol with the AOX Parameter

The concentration of *p*-chlorophenol was measured with the AOX parameter in accordance with the PN-EN ISO 9582:2007 standard using a Behr-CL10 system and a Behr SE-II sorption column (Behr Labortechnik GmbH) [9]. The solution above the sludge layer was sampled after sedimentation of the solid phase. The sample was then subjected to centrifuging.

The Effect of UV Radiation on the Leaching of AOXs from the Sewage Sludge

The sewage sludge treated with *p*-chlorophenol was spread on a Petri dish (approx. 0.5 cm) and exposed to ultraviolet radiation (254 nm) for 0.5, 1, 2, 3, and 4 hours using a Philips UVC 36W lamp. After exposure, a three-gram sample was treated with 25 cm^3 of $NaNO_3$ solution (c=0.2 M, pH=2) and subjected to 35 kHz ultrasounds for one hour. The aqueous phase was separated from the sludge mechanically. The concentration of AOXs was determined by applying the methodology described in the PN-EN ISO 9582:2007 standard [9].

The Effect of Electric Discharges on the Leaching of AOXs from Sewage Sludge

The sewage sludge was exposed to electric discharges. An electric field was created between the point-to-plate electrode system – 27 mm in distance by applying a voltage of 30 kV for 0.25, 0.5, 1, 1.5, and 2 hours. After exposure, a three-gram sample was treated with 25 cm^3 of $NaNO_3$ solution (c=0.2 M, pH=2) and exposed to 35 kHz ultrasounds for one hour. The aqueous phase was separated from the sludge mechanically. The concentration of AOXs was determined using the methodology described in the PN-EN ISO 9582:2007 standard [9].

The Effect of Temperature Changes during Freeze/Thaw Cycles on the Leaching of AOXs from the Sewage Sludge

The sewage sludge treated with *p*-chlorophenol was exposed to temperature changes in an air-conditioned chamber. The freezing and thawing temperatures ranged from -20ºC to +15ºC. The full freeze-thaw cycle lasted 8 hours. The sludge was placed in the air-conditioned chamber for 3, 9, 18, 27, 42, 48, and 60 cycles. Then, sludge samples were collected, treated with 25 cm^3 of $NaNO_3$ solution (c=0.2 M, pH=2) and exposed to 35 kHz ultrasounds for one hour. The aqueous phase was separated from the sludge mechanically. The AOX concentration was determined using the methodology described in the PN-EN ISO 9582:2007 standard [9]. Additionally, the material was exposed to low temperatures in order to determine the changes in the microscopic structure. The observations were conducted using an Olympus stereomicroscope equipped with a reflected light system.

It should be emphasized that sewage sludge is a non-homogeneous material that is difficult to analyze. The results provided in the paper are means of at least three independently measured values within the method error.

The experimental data were processed mathematically using Statistica 7.0.

Results and Discussion

The physical and chemical characteristics of the sewage sludge material are presented in Table 2.

As can be seen from Table 2, the analyzed material satisfied the basic criteria of agricultural application determined in the Regulations of the Minister of the Environment concerning municipal sewage sludge (Journal of Laws of the Republic of Poland 2002 No. 134, item 114) [1]. The amount of organic halogen derivative compounds measured with the AOX parameter did not exceed 100 mg Cl/kg d.w. The AOX content was determined using the method described in the DIN 38414 standard [12] for bottom sludge. However, the standard had to be adjusted to the specific character of sewage sludge. In the DIN 38414 standard, it is recommended that bottom deposits should be dried prior to testing. In the case of sewage sludge, this requirement should be treated with reservation, because dried sewage sludge loses water-wettability. Sewage sludge obtained in wastewater treatment systems is in a hydrated state and as such is applied on arable land. It was established that the results obtained for sludge not subjected to drying was closer to those reported under real conditions.

In this analysis, the AOX content was established for non-dried sludge. In addition, the AOXs were leached from the sewage sludge using 35 kHz ultrasounds instead of shaking.

As sewage sludge contains solid particles and water, it can be classified as a two-phase (liquid-solid) system with a complex structure. This complexity results from the variety of particles and macroparticles and their interactions [10].

Fig. 1 shows images of the surface structure of sewage sludge I recorded at two selected points by means of a scanning electron microscope (magnification x500).

The images show that the analyzed sewage sludge had an expanded, non-homogeneous and non-uniform surface structure. Areas of both higher and lower density can be seen.

The basic parameters used for assessing the sorption capacity of sorbents are: the specific surface area, pore size distribution and chemical activity. However, the methods of their determination cannot be used to study non-dried sludge. As the properties of dried sludge change, the values obtained do not correspond to ones obtained under real conditions. Therefore, the above parameters are not sufficiently reliable to be used for assessing the sorption capacity of sewage sludge. In this analysis, therefore, the sorption capacity of sewage sludge was determined based on the iodine values, the isotherms of *p*-chlorophenol adsorption from the water solution on the sludge and the organic substance contents.

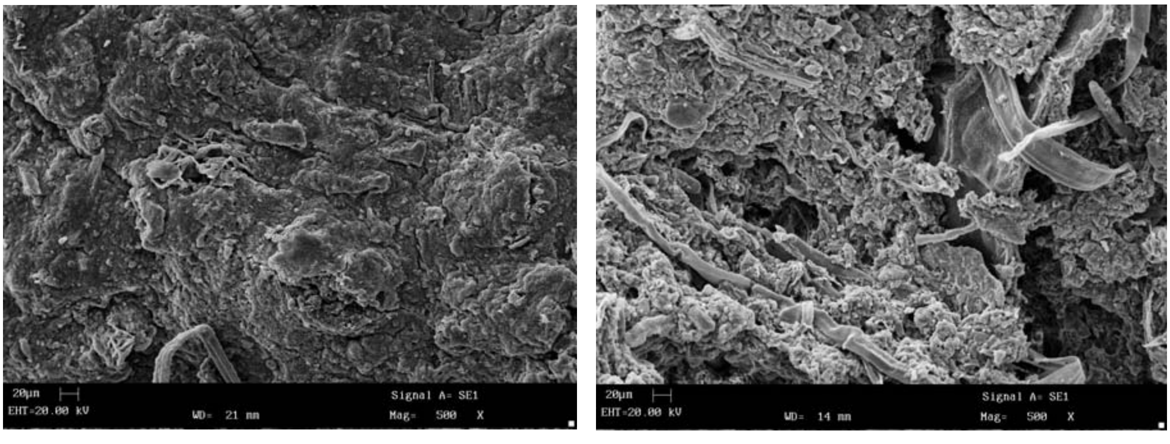

Fig. 1. Microscopic surface structure of sewage sludge I (magnification x500).

Table 3. Assessment of the sorption capacity of the sewage sludge material.

Item	Sample	Organic substance content, %	Iodine adsorption value, mgI/g d.w.	Sorption of *p*-chlorophenol, μgCl/g d.w.
1.	Sewage sludge I	65.30	483	105.20
2.	Sewage sludge II	75.10	571	135.63
3.	Sewage sludge III	78.54	661	150.55

Table 4. Estimators of the parameters of the function $A=kc_{eq}^{1/n}$ describing the Freundlich isotherms for the analyzed sewage sludge material.

Sludge	k	n	R^2
Sewage sludge I	29.386	0.7845	0.9825
Sewage sludge II	48.386	0.8844	0.9498
Sewage sludge III	45.331	0.7665	0.9021

The iodine number is used to characterize sorbents with regard to sorption of large particles, for instance organic compounds. The results are presented in Table 3.

The iodine adsorption values ranged from 483 to 661 mg I/g d.w. The results confirmed good sorption capacity of the material tested. The iodine adsorption values were compatible with the content of organic substances. Sewage sludge III was characterized by the highest amount of organic substances (78.54%) and the highest iodine adsorption value (661 mg I/g d.w.). Sewage sludge I, on the other hand, contained the smallest amount of organic matter (65.31%) and the lowest iodine adsorption value (440 mg I/g d.w.).

The isotherms of *p*-chlorophenol adsorption from the aqueous phase on the sludge were determined under static conditions. The sorption equilibrium was reached after four hours. As can be seen from the table, the highest sorption capacity was reported for sewage sludge III. In this case, the sorption of *p*-chlorophenol measured with the AOX parameter was 150 μg Cl/g d.w. The sorption capacity of sewage sludge II was 136 μg Cl/g d.w.

The results obtained in the analysis were consistent with the findings and requirements described in Refs. [6]. The sludge samples were characterized by the highest amount of organic substances and high iodine adsorption value. In the case of sewage sludge I, the amount of organic matter was smaller and the iodine adsorption value was lower. There was also a decrease in the sorption capacity of *p*-chlorophenol, which amounted to approximately 105 μgCl/g d.w. The adsorption equilibrium was established based on the Freundlich isotherm,

$$A = kc_{eq}^{1/n},$$

...which is suitable for describing adsorption from diluted, two-component water solutions [11]. Parameters *k* and *n,* as well as the coefficient of determination, R^2, were computed using the quasi-Newton method (Statistica 7.0.) [13]. Table 4 summarizes the function parameters determined by mathematical calculation of the Freundlich isotherms.

The coefficient of determination, R^2, was more than 0.9, which confirms high accuracy of the Freundlich isotherms selected for the description of the real results obtained under laboratory conditions. Moreover, the value of parameter *k* determining the sorption volume is higher for sludge, with a higher content of organic matter responsible for sorption capacity. The value of parameter *n* shows a close adsorbate/adsorbent relationship.

The next stage of the study involved leaching the AOXs from the sewage sludge under model conditions. It was essential to establish what factors affect the release of the adsorbed substances back to the water solution. The tests were conducted for sewage sludge I, which was characterized by the lowest sorption capacity. The physical and chemical factors selected to be tested were UV radiation, electric discharges and freeze-thaw conditioning.

The tests required treating the sewage sludge samples with *p*-chlorophenol (100-500 mg Cl/kg d.w.). The amount added was more than the sorption capacity for *p*-chlorophenol from the aqueous phase. The leaching was performed under favourable conditions (solution of $NaNO_3$ in water; pH=2; exposure to ultrasounds). Then, the content of AOXs in the aqueous phase was assessed. The amount of *p*-chlorophenol leached from the sludge was determined using the AOX parameter, as illustrated in Table 5.

From the table it is clear that the content of AOXs leached from the sludge to the aqueous phase was directly proportional to the concentration of *p*-chlorophenol in the sludge. If the initial content of *p*-chlorophenol in the sludge was 100 mg Cl/kg d.w., the AOX parameter in the aqueous phase was approximately 2 mg Cl/L. A fivefold increase in the concentration of *p*-chlorophenol to 500 mg Cl/kg d.w. caused an increase in the content of AOXs in the leached solution to approximately 5.8 mg Cl/L. The experimental data coincided with results presented in the literature. It was reported that a considerable amount of *p*-chlorophenol introduced to the sludge was permanently bonded and it was not leached to the solution even under favourable conditions [6, 8].

One of the factors affecting AOXs in the sludge is UV radiation present in the environment. The radiation causes air ionization and, accordingly, the formation of ozone, which is a strong oxidant. The sludge with 500 mg CL/kg d.w. of *p*-chlorophenol was exposed to UV radiation, followed by AOX leaching into the aqueous phase. Fig. 2 shows the relationship between the concentration of AOXs and the exposure time.

Table 5. Concentration of the AOXs leached from the sewage sludge and the amount of combined residue.

Amount of *p*-chlorophenol added to the sludge, mg Cl/kg d.w.	100	200	300	400	500
Concentration of AOXs in the aqueous phase, mg Cl/L	2.027	2.659	3.750	4.617	5.819
Combined residue, mg Cl/kg d.w.	97.98	128.53	181.26	223.17	281.27

The amount of AOXs in the solution measured after a half-hour exposure to UV radiation and then to ultrasounds was 5.6 mg Cl/L. For a zero sample, the amount was 6.0 mg Cl/L. The UV radiation resulted in sludge changes that were responsible for a decrease in the amount of AOXs leached to the solution. Increasing the exposure time led to gradual degradation of *p*-chlorophenol and a decrease in the amount of AOXs in the solution. After four-hour exposure, the amount was 3.7 mg Cl/L. It should be emphasized that the UV radiation affected mainly the sludge surface and that it was accompanied by heat transfer. Increasing the radiation intensity or exposure time is inadvisable, as it leads to the drying and sintering of the outer layer of the sludge.

The relationship between the amount of AOXs leached from the sludge exposed to UV radiation and the exposure time (t) can be represented as:

$$AOX\ (t) = AOX\ (t_0)e^{-bt}$$

...which corresponds to the first order reaction kinetics, where *b* is equal to the constant of the reaction rate. The equation parameters were determined using the quasi-Newton method (Statistica 7.0). The equation:

$$AOX\ (t) = 5.96e^{-0.114t}$$

...is suitable for describing the real relationships between the data obtained under laboratory conditions, which is confirmed by the coefficient of determination, R^2, whose value was more than 0.95.

The next factor affecting the content of *p*-chlorophenol is high-energy electric discharges. The sewage sludge material treated with 500 mg Cl/kg d.w. of *p*-chlorophenol was exposed to electric discharges at an input voltage of 30 kV. Fig. 3 shows the relationship between the amount of AOXs leached from the sludge and the time of exposure to electric discharges.

The application of high-energy electric discharges resulted in the formation of highly-concentrated space charges penetrating the sludge structure. The applied voltage was responsible for intensive air ionization in the electrode-to-electrode space, and in consequence, the formation of ozone, which had a direct impact on the sludge components. The influence of electric discharges was stronger than that of UV radiation. The amount of AOXs leached to the solution after 15-minute exposure to discharges was 6.6 mg Cl/L. Increasing exposure time to one hour led to a decrease in AOX concentration in the solution to 4.84 mg Cl/L. A further increase in exposure time caused a further decrease in AOX concentration. After two-hour exposure, the concentration of the AOXs leached from the sludge reached 3.3 mg Cl/L, which was 50% less than the maximum value. It can thus be concluded that high energy electric discharges cause the degradation of AOXs in the sewage sludge.

Similarly, the relationship between the amount of AOXs leached from the sludge exposed to electric discharges and exposure time (t) is described by the function:

$$AOX\ (t) = AOX\ (t_0)e^{-bt}$$

...in accordance with the first order reaction kinetics, where *b* is equal to the constant of the reaction rate. The function parameters were determined using a quasi-Newton program, Statistica 7.0. The equation:

$$AOX\ (t) = 7.0e^{-0.378t}$$

...describes the real relationships between the laboratory results, which is confirmed by the coefficient of determination R^2 (more than 0.95).

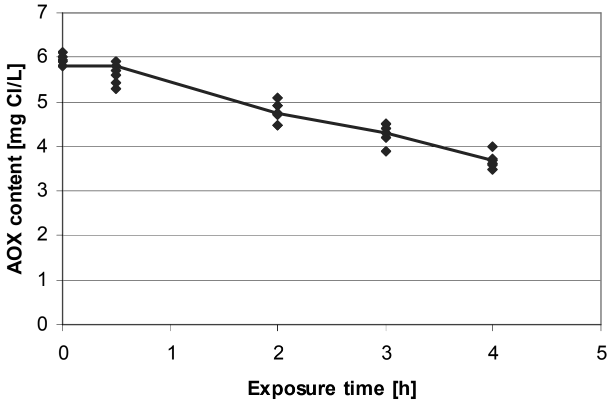

Fig. 2. Content of AOXs in the aqueous phase vs. the time of exposure to UV radiation.

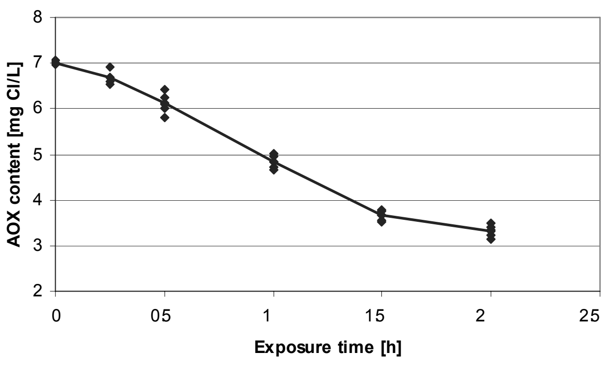

Fig. 3. Content of AOXs in the aqueous phase vs. time of exposure to electric discharges.

Table 6. Variance analysis data sheet.

	Variance analysis The effects are significant for $p < 0.05$							
Variable	SS effect	df effect	MS effect	SS error	df error	MS error	F	p
C_{AOX}, mg Cl/L	7.093372	7	1.013339	1.583455	32	0.049483	20.47854	0.0000

SS effect – sum of squares between groups, df effect – number of degrees of freedom between groups, MS effect – mean squares between groups, SS error – (residual) sum of squares within groups, df error – (residual) number of degrees of freedom within groups, MS error –sum of mean squares within groups, F – test value, p – test probability.

Another factor affecting the content of *p*-chlorofenol is temperature changes. The sludge samples were exposed to repeated freezing/thawing in a special chamber where temperature ranged from -20 to +15. Fig. 4 shows the relationship between the amount of AOXs leached from the sludge treated with *p*-chlorophenol (500 mg Cl/kg d.w.) to the aqueous phase and the number of freeze-thaw cycles.

The concentration of AOXs in the solution, which was determined for the material exposed to cyclic freezing/thawing, treated with $NaNO_3$ and then exposed to ultrasounds, ranged 4.6-5.1 mg Cl/L, irrespective of the number of cycles in the air-conditioned chamber. The leaching efficiency was 41.38-46.45%, respectively.

Under the test conditions, the freeze/thaw processes caused changes in the sludge consistency and structure (Fig. 5), which were due to the changes in the water bonding by the sludge particles.

Figs. 5a and b show the microstructure of the sewage sludge surface. The sludge samples that were not subjected to the selected physical and chemical processes had plastic consistency. The water present in the sludge was bonded by capillary and adhesive forces between the sludge particles – bright points uniformly distributed over the whole area (Fig. 5a). The freeze-thaw cycles caused changes in the sludge structure. It became amorphous and greasy. The structures responsible for bonding the capillary water were damaged. Water formed irregular clusters on the surface (Fig. 5b).

To show the statistical significance of the different concentrations of AOXs leached from the sludge to the solution after repeated freezing and thawing, it was necessary to conduct tests of significance using an analysis of variance (ANOVA) and the Statistica 7.0 program [13].

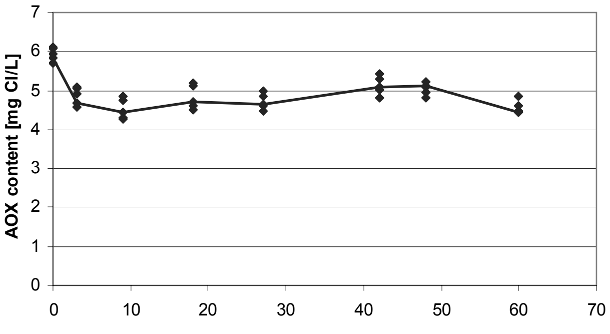

Fig. 4. Content of AOXs in the aqueous phase vs. the number of freeze-thaw cycles.

Data from five eight-element tests were used to verify the null hypothesis, H0, assuming that the mean values in the particular groups are the same $\mu_1 = \mu_2 = ... = \mu_5$. The hypothesis was verified against the alternative hypothesis, H_1, where at least two means were different. The analysis of variance was conducted at a significance level of 0.05. The results are presented in Table 6.

The test value, F, was 20.4785 and the test probability was zero. It was concluded that the differences between the means were significant and the null hypothesis had to be rejected.

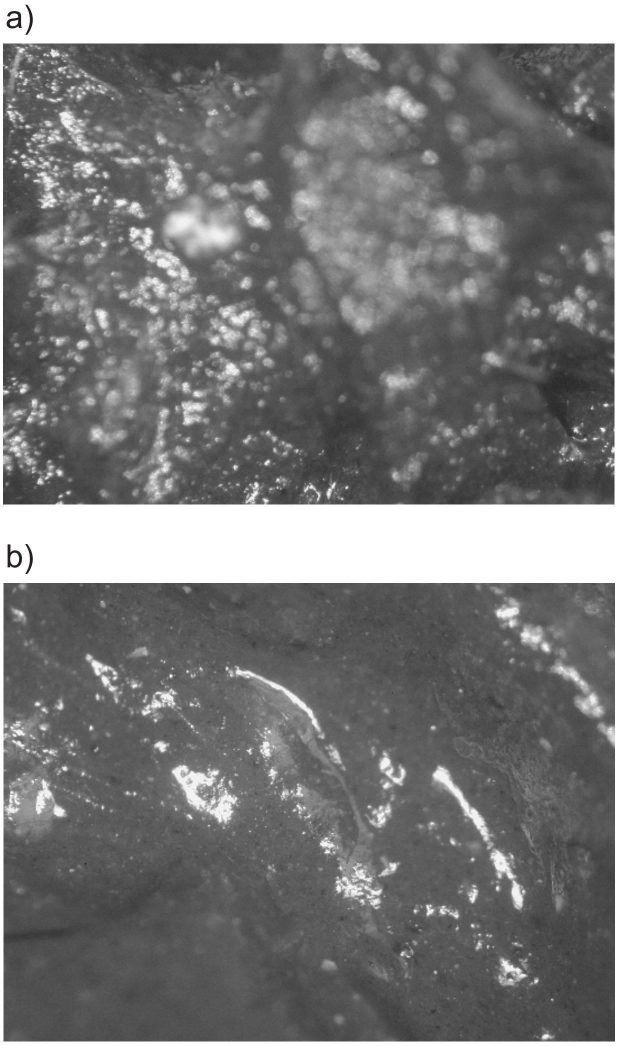

Fig. 5. Microscopic surface structure of sewage sludge, magnification x25: a) sludge before the physical and chemical treatment, b) sludge after cyclic freezing-thawing.

A multiple-comparison post-hoc analysis was performed to find out which differences between the mean values were significant. The RIR, Tukey, Scheffe, Newman-Keulus, and Duncan tests showed the statistical significance of the selected points. The tests confirmed that the comparison of means from different groups was statistically significant. All the tests testify to the significance of the difference in AOX concentration in cycle 0 (before freezing) and the other cycles. This confirms the hypothesis that the freeze-thaw cycles result in changes in the sludge structure and the *p*-chlorophenol sorption mechanism. The other significant differences were due to the non-homogeneity of sewage sludge.

Conclusions

The following conclusions were drawn from the above analysis:

1. Because of its porous structure and high content of organic matter, sludge is likely to be used as a natural sorbent to remove organic contaminants from soil and water.
2. The sorption capacity of sludge is directly proportional to the iodine value and directly proportional to the amount of organic matter.
3. The iodine adsorption value can be a reliable criterion for selecting sewage sludge to be used in the process of sorption of organic halogen derivative compounds adsorbable on activated carbon.
4. The *p*-chlorophenol present in the sludge was permanently bonded; it was not leached into the solution even under favourable conditions.
5. The physical and chemical factors such as UV radiation and electric discharges were responsible for air ionization and, in consequence, ozone formation, which caused the decomposition of *p*-chlorophenol in the sludge. The process is described by first order reaction kinetics.
6. The effects of cyclic freezing and thawing include changes in the sludge structure and the water bonding process. These created favourable conditions for *p*-chlorophenol desorption.

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