

TECHNOLOGICAL AND TOXICOLOGICAL ASPECTS OF THE COAGULATION OF LEACHATES FROM MUNICIPAL SOLID WASTE LANDFILL

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TECHNOLOGICZNE I TOKSYKOLOGICZNE ASPEKTY KOAGULACJI ODCIEKÓW Z WYSYPISKA ODPADÓW KOMUNALNYCH

Odcieki ze składowisk odpadów komunalnych należy zaliczać do grupy silnie zanieczyszczonych ścieków przemysłowych. Wynika to z obecności w ich składzie różnych związków organicznych i nieorganicznych o wysokim stężeniu oraz toksycznych właściwościach. Istotne więc jest prawidłowe oczyszczanie odcieków przed odprowadzeniem do środowiska. Jedną z metod chemicznych wykorzystywanych do oczyszczania odcieków jest koagulacja. Podstawowym celem badań zaprezentowanych w niniejszej pracy było określenie wpływu koagulacji w połączeniu z sedymentacją na charakterystykę fizyczno-chemiczną i toksykologiczną odcieków pochodzących z jednego z wysypisk odpadów w Polsce. Badania koagulacji prowadzono w warunkach laboratoryjnych metodą „jar-test” używając w procesie chlorku poliglinu oraz chlorku żelazowego. Odcieki „surowe”, jak również odcieki po koagulacji poddawano testom toksyczności z uwzględnieniem testu inhibicji wzrostu z glonami, trzech mikrobiotestów typu Toxkit z larwami skorupiaków, testu typu IQ Toxicity Test ze skorupiakami oraz testu LUMISTox z bakteriami luminescencyjnymi. W przeprowadzonych badaniach ustalono, iż większą sprawnością technologiczną w usuwaniu związków organicznych z odcieków odznaczał się chlorek żelazowy (0,92 g Fe³⁺/ChZT usunięte) niż chlorek poliglinu (1,22 g Al³⁺/ChZT usunięte). Dla optymalnych dawek koagulantów najkorzystniejsze efekty koagulacji osiągnięto przy pH = 6,5–6,8 dopasowywanym za pomocą NaOH. Koagulacja prowadzona w optymalnych warunkach pozwalała uzyskać zmniejszenie zawartości związków organicznych wyrażonych wartościami ChZT w granicach 40–84%. Ten efekt usunięcia związków organicznych z badanych odcieków nie wpłynął w znaczący sposób na zmniejszenie ich toksyczności. Z powyższych powodów proces koagulacji może być użyteczny jedynie jako jeden z elementów układu technologicznego oczyszczania odcieków z wysypisk odpadów komunalnych. Zastosowana w badaniach bateria testów wykazała swoją przydatność do oceny toksyczności odcieków o różnym stopniu ich zanieczyszczenia i na różnym etapie ich oczyszczania.

Summary

Leachates from municipal solid waste landfills should be included in the group of strongly contaminated industrial wastewaters. This results from the presence of highly concentrated various organic and inorganic compounds, which frequently have toxic properties. Therefore, the proper purification of the leachates prior to their discharging to the environment is of great importance. One of the chemical methods that can be used for the purification of leachates is coagulation. The main objective of the experiments presented in the current study was to determine the effect of coagulation, combined with sedimentation, on the physico-

chemical and toxicological characteristics of leachates from one of a municipal solid waste landfill in Poland. Standard „jar-test” experiments were employed for coagulation. Polyaluminum chloride and ferric chloride were used as coagulants. Raw leachates as well as those after coagulation were tested for toxicity using a battery of tests embracing algal growth inhibition test, microbiotests and IQ Toxicity Tests with crustaceans and bacterial luminescence inhibition test (LUMIStox). The studies carried out demonstrated that ferric chloride ($0.92 \text{ g Fe}^{3+}/\text{COD}_{\text{Cr}}$ removed) is more effective technologically in the removal of organic compounds from leachates than polyaluminum chloride ($1.22 \text{ g Al}^{3+}/\text{COD}_{\text{Cr}}$ removed). For optimal doses of coagulants the most advantageous coagulation effects were achieved at pH 6.5–6.6, adjusted with the use of NaOH. Coagulation conducted under optimal conditions allows for reducing the content of organic compounds, as expressed by COD_{Cr} values, from 40 to 84%. This effect of organic compound removal from leachates in the process of coagulation did not result in significant decrease of their toxicity. For the above reasons the coagulation process can be useful only as one of the elements of a technological setup for the purification of leachates from municipal solid waste landfills. The battery of tests used in the studies proved usefulness for the evaluation of the toxicity of leachates with varied degree of contamination as well as at various stages of their purification.

INTRODUCTION

Leachates result from the degradation of municipal waste combined with the percolation of rainwater. A major problem connected with the discharge of leachates to the environment is their contamination by various organic compounds, where humic substances constitute an important group, as well as inorganic substances like ammonia, heavy metals and salts mainly represented by chlorides and carbonates [6, 11, 21, 28]. There are several factors affecting the composition of leachates and their production. The most important are: waste composition, age of landfill, hydrogeology of the site, climate, season, moisture routing through the fill [6, 21]. The migration of the leachates into surrounding soils, ground and surface waters can cause considerable pollution problems [15, 18]. For this reason their treatment is necessary in order to prevent serious damage of environment.

Various treatments are possible, such as: biological degradation, coagulation, adsorption, membrane filtration or oxidation [3–5, 8, 12–14, 17, 23, 27]. The nature and composition of leachates changes from one site to another so biological treatment or a combination of physico-chemical and biological treatments is required in order to meet the standards.

The information in the literature on the subject indicates that one of effective methods for the initial or final purification of leachates from landfills is coagulation using Al^{3+} salts or Fe^{3+} salts. Coagulation, depending on the conditions in which the process is conducted (type and dose of coagulant, pH of reaction, addition of polyelectrolyte), enables a reduction of the organic compounds in the leachates, expressed by COD_{Cr} , by even 56%, and this includes even those compounds that are refractory to biodegradation. Although several studies on the topic have been conducted [1, 20, 24, 26, 28], there is still insufficient information regarding the optimal conditions for efficient coagulation (assessment of pH effect) and limited information on the aspect of the effect of coagulation on changes in the toxicity of leachates. Toxicological assays, besides studies on the physico-chemical parameters of the leachates, create the possibility of estimating the harmfulness of leachates for organisms of the food chains in various ecosystems as well as for human health.

AIM AND SCOPE OF STUDIES

The main aim of the studies was to determine the chemical effect of pretreatment of

leachates from landfill of solid municipal wastes, carried out using the volumetric coagulation method, combined with sedimentation, on their physico-chemical and toxicological characteristics.

The technological studies embraced determination of the effectiveness of partial purification of the leachates using Al^{3+} and Fe^{3+} salts and to determine the optimal dose of coagulant as well as optimal pH of the reaction.

Toxicological studies of the leachates embraced a battery of tests including: algal growth inhibition test with *Scenedesmus quadricauda* (producers), three microbioassays of the Toxkits type using larvae of the crustaceans *Artemia franciscana*, *Thamnocephalus platyurus*, *Daphnia magna* and IQ Toxicity Test with *Daphnia magna* (consumers), as well as LUMIStox test with luminescent bacteria *Vibrio fischeri* (decomposers).

MATERIALS AND METHODS

The source of the leachates used in the studies was a landfill of solid municipal wastes in Lubna near Warsaw. Since 1978 approximately 2 million cubic meters of wastes from the Warsaw agglomeration have been dumped. Samples of the leachates were taken three times in the period March – May, 2001 from a well of the drainage system collecting leachates from the oldest part of the landfill.

The coagulation of the leachates was carried out according to the standard „jar test” procedure, that is after adding different amounts of the reagents to consecutive samples of the leachates with volume 1 dm³, the samples were rapidly mixed (about 200 rpm) for 1 min and then mixed slowly (about 20 rpm) for 15 min. After this time the samples were subjected to 2-hour sedimentation.

A 10% FeCl_3 solution or alternatively PAC (a solution of polyaluminum chloride with 8.2% Al^{3+} content) was used as coagulants. The pH of the reaction mixture was adjusted from 3.3 to 9.0 using a 20% HCl solution or 10% NaOH solution.

The effect of the coagulation of the leachates was estimated on the basis of changes of their quality, depending on type and dose of reagents used and pH value.

Changes in the toxicity of the leachates were determined for raw leachates and after coagulation and sedimentation carried out in optimal conditions for the coagulant with the most effective action.

Algal growth inhibition tests with *Scenedesmus quadricauda* were performed according to ISO 8692 Standard [9]. Crustacean microbioassays and IQ Toxicity Test were carried out according to the Standard Operational Procedures provided in the respective Toxkits (Artotoxkit M [2], Thamnotoxkit F [25] and Daphtoxkit F magna [7]) and procedure described by Janssen et al. [10]. Tests with the luminescent bacteria *Vibrio fischeri* (strain NRRL-11171) were performed according to the instructions given by the Dr Lange Corporation [16] using LUMIStox type 1.07 equipment. In order to prevent total suspended solid (TSS) interferences on bacteria luminescence, samples of leachates were filtered using a 0.45 μm pore size membrane. Correction due to the interfering color of samples was also made.

The results of the bioassay were expressed as L(E)C50's (in% dilution) and converted into Toxic Units (TU) with the formula $\text{TU} = [1/\text{L(E)C50} * 100]$ given by Sprague and Ramsay [22].

ANALYTICAL TECHNIQUES

The range of analytical monitoring of the quality of the studied leachates is presented in Table 1. Analyses of the basic physico-chemical parameters were made according to standard methods for the examination of water and wastewater recommended by the Polish Committee for Standardization and recognized by the International Organization for Standardization (PN-EN ISO). Determinations of the BOD_5 values of the leachates were made using OXITOP apparatus from PHU Eko. TOC content was measured using Shimadzu TOC-5000 apparatus. The concentration of heavy metals was determined in unfiltered samples of the leachates by atomic absorption spectrometry using Philips ASA PU 9100X spectrometer.

RESULTS AND DISCUSSION

Quality of leachates

The results of the physico-chemical analyses of the studied leachates are given in Table 1. They point above all to the variable and at the same time heavy contamination of the leachates with both organic compounds (COD_{Cr} in the range 1960–3960 $mg\ O_2/dm^3$, BOD_5 from 960 to 2390 $mg\ O_2/dm^3$), and mineral compounds (conductivity 12000–34000 $\mu S/cm$, concentration chlorides 1170–3660 $mg\ Cl/dm^3$). The specific brown or darkened brown color of the leachates, high turbidity (202–495 NTU) and large amount of suspended solids (160–290 mg/dm^3) indicate that the contaminants in the leachates were in various forms of dispersion. High values of BOD_5 , organic carbon, nitrogen compounds (especially ammonium nitrogen, from 338 to 1363 $mg\ N/dm^3$) and the presence of phosphorus compounds pointed to the presence in the analyzed leachates of organic compounds that are likely to be degraded in biochemical processes. A characteristic feature of the leachates was high alkalinity and considerable content of iron (190–320 mg/dm^3) and heavy metals, in particular chromium (2.5 mg/dm^3), lead (0.84 mg/dm^3) and copper (0.61 mg/dm^3).

It should be emphasized that the values of the physico-chemical parameters of the studied leachates considerably departed from the values that are admissible for industrial wastewaters discharged to the environment [19]. This indicates the hazard they can pose for waters or soil.

Effects of coagulation

The course and effectiveness of the coagulation of the leachates was determined on the basis of changes of basic parameters characterizing their quality, i.e. turbidity and COD_{Cr} , which are a measure of pollutants whose phase structure is subject to change as the result of coagulation of a suspension that is then subjected to sedimentation. The results of studies on coagulation carried out with the use of PAC and $FeCl_3$ are presented in Figs. 1 and 2. Table 2, on the other hand, compiles the effects of the pretreatment of leachates obtained under optimal conditions of the process for the coagulant distinguished by greater effectiveness that is $FeCl_3$.

In the case of both coagulants, the doses used in the study were from 360 to 2880 $mg\ Me^{3+}/dm^3$. With these amounts of coagulant the pH of the reaction environment changed from 5.0 to 7.0. The doses of 1260, 1890 and 2520 $mg\ Al^{3+}/dm^3$ for PAC and 1080, 1440 as well as 2520 $mg\ Fe^{3+}/dm^3$ for $FeCl_3$ were found optimal in consecutive experimental series, which

Table 1. Quality of raw leachates from municipal landfill

Parameter	Raw leachates			Permissible values of parameters for treated industrial wastewater [19]
	Series 1	Series 2	Series 3	
Color	darkened brown	brown	darkened brown	–
Turbidity (NTU)	202	496	258	–
pH	7.2	7.0	7.3	6.5–8.5
Suspended solids (mg/dm ³)	290	160	200	35
Alkalinity (mg/dm ³ as CaCO ₃)	8000	4100	5000	–
COD _{Cr} (mg O ₂ /dm ³)	3960	1960	2680	125
BOD ₅ (mg O ₂ /dm ³)	2390	960	1000	25
TOC (mg C/dm ³)	1480	610	1440	30
Ammonium (mg N/dm ³)	702	338	1363	10
Nitrates (mg N/dm ³)	7.55	6.50	7.70	30
Nitrites (mg N/dm ³)	0.31	0.35	0.40	1
Total phosphorus (mg P/dm ³)	5.35	3.20	3.95	3
Sulfates (mg SO ₄ /dm ³)	840	500	700	500
Chlorides (mg Cl/dm ³)	2240	1170	3660	1000
Conductivity (μS/cm)	24000	12000	34000	–
Fe (total) (mg/dm ³)	320	190	240	10
Cd (mg/dm ³)	ND	ND	ND	ND
Cr (total) (mg/dm ³)	0.25	0.65	2.50	0.5
Zn (mg/dm ³)	1.18	0.02	0.72	2
Pb (mg/dm ³)	0.08	0.12	0.84	0.5
Ni (mg/dm ³)	0.33	0.37	0.12	0.5
Cu (mg/dm ³)	0.20	0.61	0.28	0.5

ND – not detected

is indicated by the dependences presented in Fig. 1. For these doses the effect of pH on the outcome of coagulation was determined. The run of the curves in Fig. 2 indicates that the greatest effects of purification of the leachates were obtained at pH 6.5–6.8 for PAC (turbidity reduced by 58.0–99.6%, drop in COD_{Cr} of from 39.4 to 81.1%) and at pH 6.5–6.6 for FeCl₃ (turbidity reduced by 58.0 to 98.4%, drop in COD_{Cr} of from 41.0 to 83.7%).

Table 2. Quality of leachates from municipal landfill after coagulation by FeCl_3 and 2-hour sedimentation

Series 1	2520 mg $\text{Fe}^{3+}/\text{dm}^3$ and 130 mg NaOH/dm^3
Series 2	1080 mg $\text{Fe}^{3+}/\text{dm}^3$ and 150 mg NaOH/dm^3
Series 3	1440 mg $\text{Fe}^{3+}/\text{dm}^3$ and 100 mg NaOH/dm^3

Parameter	Leachates after coagulation and sedimentation		
	Series 1	Series 2	Series 3
Color	brown-green	lightly yellow	lightly brown
Turbidity (NTU)	50	8	110
pH	6.6	6.5	6.6
Suspended solids (mg/dm^3)	21	10	17
Alkalinity (mg/dm^3 as CaCO_3)	6000	1750	3000
COD_{Cr} ($\text{mg O}_2/\text{dm}^3$)	1480	320	1580
BOD_5 ($\text{mg O}_2/\text{dm}^3$)	1100	130	750
TOC ($\text{mg C}/\text{dm}^3$)	324	166	990
Ammonium ($\text{mg N}/\text{dm}^3$)	290	144	1026
Nitrates ($\text{mg N}/\text{dm}^3$)	2.58	3.15	0.80
Nitrites ($\text{mg N}/\text{dm}^3$)	0.17	0.29	0.23
Total phosphorus ($\text{mg P}/\text{dm}^3$)	0.78	2.48	0.36
Chlorides ($\text{mg Cl}/\text{dm}^3$)	2910	2200	4250
Conductivity ($\mu\text{S}/\text{cm}$)	27000	15500	41000
Fe (total) (mg/dm^3)	50	20	35
Cd (mg/dm^3)	ND	ND	ND
Cr (mg/dm^3)	0.04	0.29	0.18
Zn (mg/dm^3)	0.38	ND	0.45
Pb (mg/dm^3)	ND	0.10	0.10
Ni (mg/dm^3)	0.33	0.35	0.10
Cu (mg/dm^3)	0.09	0.39	0.22

ND – not detected

The optimal pH of the reaction environment was obtained through the addition of NaOH to the coagulated samples of leachates. The optimal pH range determined by us differs from that given by Amokrane et al. [1] and Tasi et al. [24]. According to the mentioned authors, the most advantageous course of coagulation requires prior alkalization of the leachates to $\text{pH} > 9$. The studies presented in this work indicate that excessively high pH does not

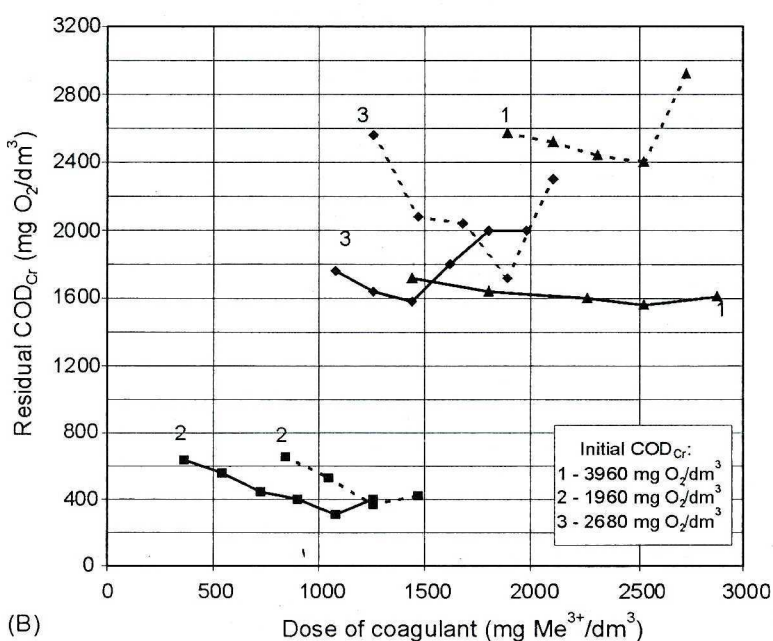
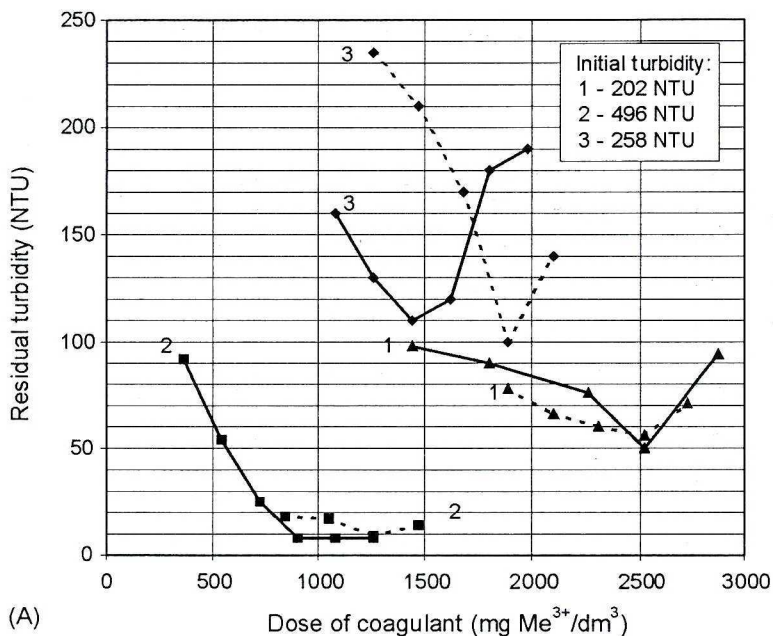
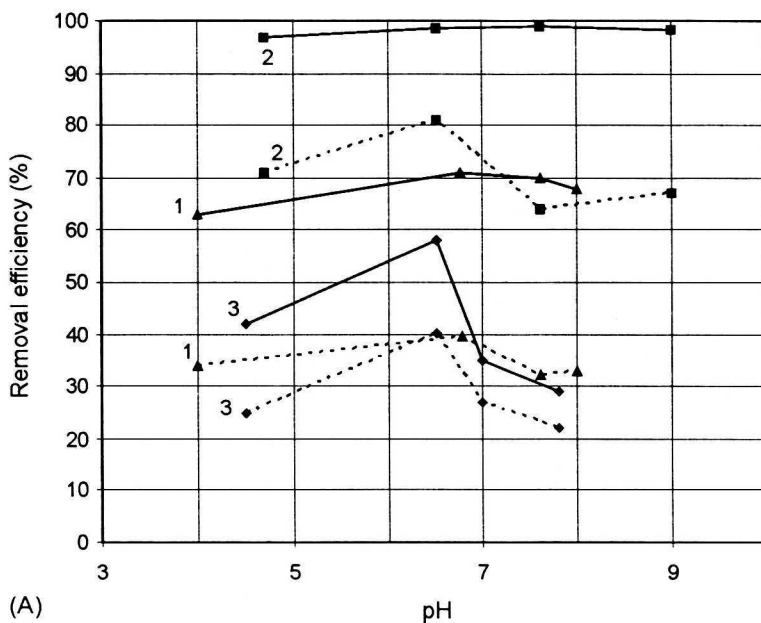
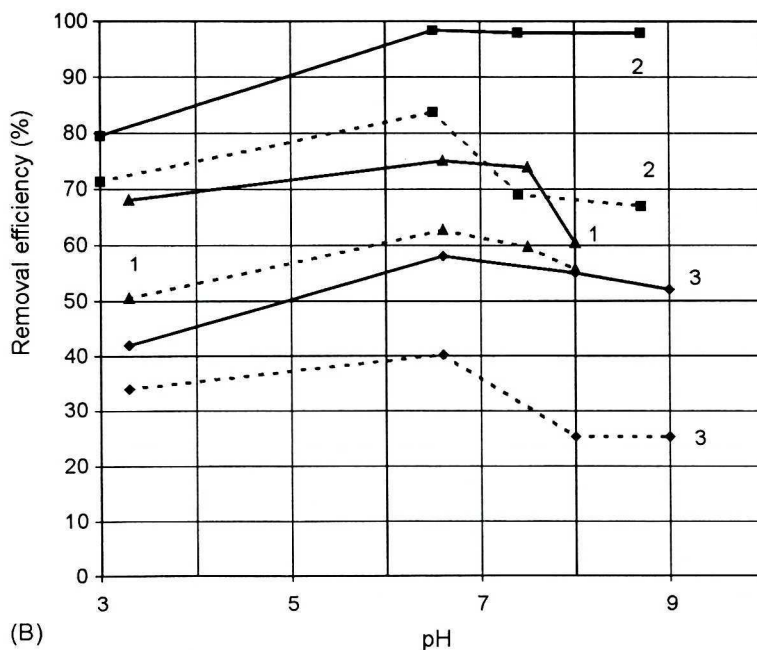


Fig. 1. Relations between the treated landfill leachates turbidity (A) or COD_{Cr} (B) and the dose of coagulants
 pH in the point of min for FeCl₃: 1 - 6.4; 2 - 6.2; 3 - 6.5; for PAC: 1 - 6.8; 2 - 6.0; 3 - 6.2;
 (-) FeCl₃; (- - -) PAC



(A)



(B)

Fig. 2. The turbidity and COD_{Cr} removal efficiency as a function of pH in coagulation landfill leachates at optimum dose of PAC (A) or $FeCl_3$ (B)

(A) Optimum dose of PAC: 1 – 2520 $mg\ Al^{3+}/dm^3$; 2 – 1260 $mg\ Al^{3+}/dm^3$; 3 – 1890 $mg\ Al^{3+}/dm^3$ and dose of NaOH for optimum pH: 1 – 0 mg/dm^3 , pH = 6.8; 2 – 170 mg/dm^3 , pH = 6.5; 3 – 120 mg/dm^3 , pH = 6.5.
 (B) Optimum dose of $FeCl_3$: 1 – 2520 $mg\ Fe^{3+}/dm^3$; 2 – 1080 $mg\ Fe^{3+}/dm^3$; 3 – 1440 $mg\ Fe^{3+}/dm^3$ and dose of NaOH for optimum pH: 1 – 130 mg/dm^3 , pH = 6.6; 2 – 150 mg/dm^3 , pH = 6.5; 3 – 100 mg/dm^3 , pH = 6.5; (–) turbidity; (– – –) COD_{Cr} .

enhance the effect of the purification of leachates in the process of coagulation. It does, however, demand the dosage of large amounts of alkalizing reagent, which favors the formation of greater amounts of sludge and entails the need for to adjust the final pH to values close to 7.0.

It should be emphasized that differences in the degree of contamination of the leachates caused that the course of the process of coagulation was not identical. In other words the coagulation of the individual samples of leachates required different doses of coagulants and for each sample coagulation resulted in a different degree of reduction of the values of the analyzed pollution indices. However, the obtained results do indicate certain dependence between optimal dose of coagulant and the properties of raw leachates. The higher was the dose, the greater the concentration of the leachate contaminants, as expressed by COD_{Cr} . It was found out that in order to remove 1 g COD_{Cr} under optimal coagulation parameters, it was necessary to use on average 0.92 g Fe^{3+} or 1.22 g Al^{3+} .

The pH of the reaction environment had a significant effect on the course of the coagulation and obtained quality of the leachates. Coagulation at slightly acidic pH was most probably caused by the presence of humic acids in the studied leachates.

The process of the pretreatment of leachates by the coagulation method resulted in the formation of sludge. The amount of this sludge was considerable, since it ranged, depending on the coagulant used, from 37 to 63% of the volume of the purified leachates for PAC and from 19 to 36% for $FeCl_3$.

In general it can be said that the process of the coagulation of leachates resulted in an improvement in their quality (Table 2). This improvement was clearly visible in the physical properties of the leachates, that is reduced turbidity and color intensity, as well as in amount of suspensions. Coagulation conducted under optimal conditions, combined with sedimentation, ensured above all a high degree of removal of colloids and suspended solids that sediments with difficulty, and to a lower degree those substances that occur in soluble form. This phenomenon was confirmed in the considerable loss of organic substances, expressed above all by COD_{Cr} values (average decreasing by 62.4%), BOD_5 (by 55.2%) and TOC (by 52.0%), whereas the content of the remaining ones being only in a soluble form in the leachates after coagulation, was still high (COD_{Cr} from 320 to 1580 mg O_2/dm^3 , BOD_5 from 130 to 1100 mg O_2/dm^3 , TOC from 166 to 990 mg C/dm^3). In addition, as a result of coagulation the content of phosphorus and nitrogen in the pretreated leachates decreased, though it should be stressed that the concentration of remaining ammonium nitrogen was very high (144–1026 mg N/dm^3). The content of iron and heavy metals also decreased. When optimal pH for $FeCl_3$ was used such metals as chromium, lead and zinc were removed to about 50–90%, whereas removal of copper and nickel was lower and averaged about 20%. In turn, in the case of the presence of mineral compounds an increase in the salinity of the leachates was observed, in which a crucial role was played by the chloride ion introduced into the leachates together with the coagulant (concentration of chlorides up to 4250 mg Cl/dm^3).

Taking into account the analysis of the obtained results presented above, it should be stressed that the process of coagulation can be treated only as a procedure for the partial purification of leachates from municipal solid waste landfill. Leachates after coagulation continued to contain excessively high levels of both organic and mineral contaminants, thus posing a serious hazard for the environment.

Changes in toxicity of leachates

The results of toxicological studies of raw leachates and leachates after coagulation are presented in Fig. 3.

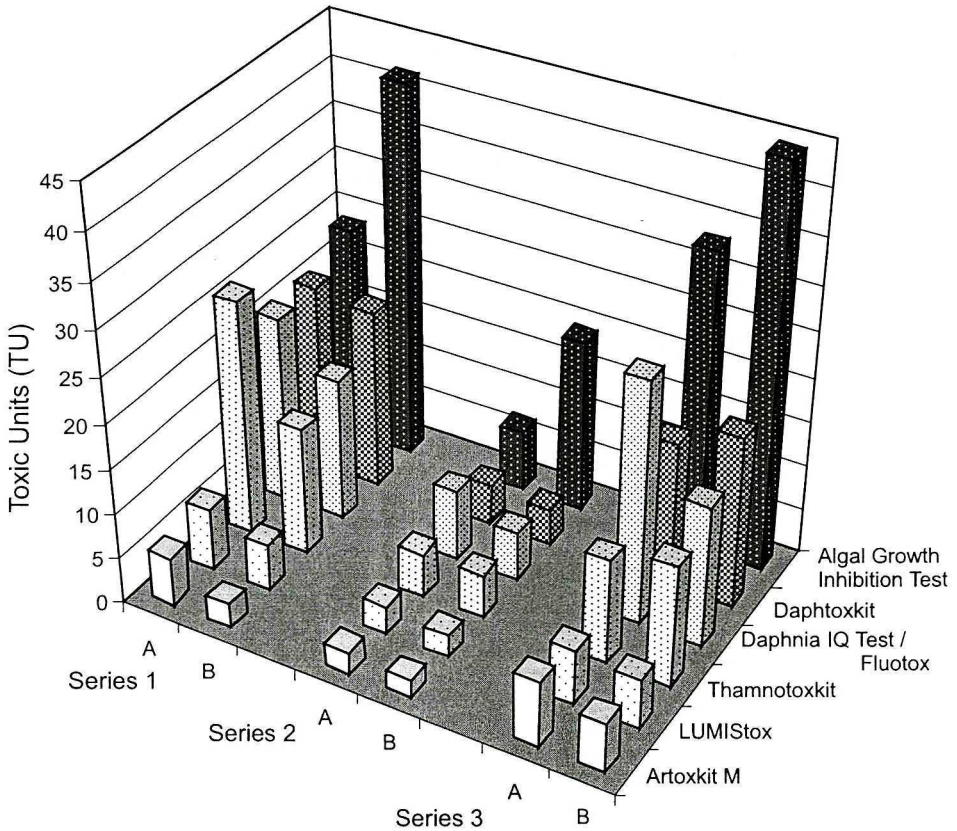


Fig. 3. Toxicity results (in Toxic Units) for three series of raw leachates and after coagulation
A – raw leachates B – leachates after coagulation

Algal growth inhibition tests with the alga Scenedesmus quadricauda

The green algae used in the tests generally demonstrated high sensitivity to the action of the raw leachates in each of the studied series. Leachates of series 1 and 3 proved the most toxic for these organisms, as indicated by the high values of chronic toxicity units (TU_c) of 23.8 and 33.3, respectively. The least toxic for them were the leachates of series 2, which were distinguished by best quality and for which the TU_c value after 72 hours was 6.8.

The process of coagulation resulted in the increased toxicity of the leachates in all study series, regardless of their quality. The leachates of series 2 were found to be particularly toxic and showed a three-fold increase in toxicity following the process, compared to raw leachates.

Tests with larvae of the crustacean *Daphnia magna* (Daphtoxkit F Magna)

The values of acute toxicity units (TU_a) for the three series of raw leachates obtained in tests using *Daphnia magna* were differentiated, depending on the quality of the leachates. After 24 hour contact the TU_a values of the leachates from the individual series were 21.0; 4.5 and 16.3, respectively. After 48 h the values for leachates of series 2, which are characterized by best quality, persisted at the same level whereas for the leachates of the remaining two series a further increase to 24.4 and 31.0 was observed. This is reflected by the results on the quality of the leachates, including high COD_{Cr} and BOD_5 values and considerable TOC and ammonium nitrogen content.

After coagulation a varied toxic effect of leachates, depending on their composition, was observed. For leachates of series 1 and 2 a reduction in toxic effect after 24 h, as expressed by the TU_a values of 20.0 and 3.9, respectively was seen. In the case of series 3 an increase of the toxic effect was observed (TU_a value of 19.6).

Tests with larvae of the crustacean *Thamnocephalus platyurus* (Thamnotoxkit F)

The results of Thamnotoxkit test with raw leachates were similar as for Daphtoxkit, after 24 h contact being 26.3, 4.7 and 11.6 TU_a , respectively. After coagulation a considerable reduction in the toxic effect of leachates of series 1, and a significant increase in series 3, as indicated by the TU_a values of 14.3 and 13.5, respectively, was observed. In the case of the leachates of series 2 the toxic effect remained at the same level.

Tests with larvae of the crustacean *Artemia franciscana* (Artoxkit M)

In general the larvae of the crustacean *Artemia franciscana* appeared less sensitive to the action of the raw leachates and the following coagulation, compared to other crustaceans. This is indicated by the lowest values of the toxicity of raw leachates for all three studies series, these being 5.4; 2.4 and 7.3 TU_a , respectively and showing a further decrease to 2.7; 2.0 and 5.5 TU_a , after coagulation. As indicated by the TU_a values presented above, the coagulation process resulted in reduced harmfulness of the leachates for *Artemia* larvae in all series.

IQ toxicity test (Fluotox) with the crustaceans *Daphnia magna*

The results of Fluotox tests that are the TU_a values for *Daphnia* after 1 h contact of the crustaceans with raw leachates were higher than obtained with the use of Daphtoxkit tests for 24 h contact, and were 20.8; 7.8 and 27.0, respectively. As shown by these data, the toxic effect measured in test organisms as inhibition of enzyme activity may be manifested far earlier than the lethal effect. Moreover, the toxicity of the leachates in series 2, which are characterized by best quality, appeared in this test far lower with regard to the studied enzyme in *Daphnia magna*, similarly as in the case of the Daphtoxkit test. After coagulation, a lowered toxicity was observed for the leachates from all the studied series, as indicated by the TU_a values of 16.0; 5.4 and 15.7, respectively.

Test with luminescent bacteria *Vibrio fischeri* (Lumistox)

The TU_a values of the raw leachates obtained in tests employing luminescent bacteria after 30 min contact were generally low and depending on series were 6.8; 3.1 and 6.1, respectively. After the process of coagulation these values showed a further decrease, which reflects a further reduction in the harmfulness of the leachates with regard to the microorganisms used.

CONCLUSIONS

The studies conducted allowed for formulation of the following conclusions:

1. Leachates from the studied municipal solid waste landfill were characterized by a specific brown color, high turbidity and high and at the same time variable level of contamination with both organic (COD_{Cr} from 1960 to 3960 mgO_2/dm^3 , BOD_5 from 960 to 390 $\text{mg O}_2/\text{dm}^3$) and mineral compounds (conductivity from 12 to 34 mS/cm). The group of organic compounds was most probably dominated by substances with high molecular weight, such as humic acids. The high salinity was caused mainly by chloride ions. A specific property of the leachates was high concentration of ammonium nitrogen (338–1363 $\text{mg N}/\text{dm}^3$). The studied leachates also contained iron and heavy metals. In view of the above properties the raw leachates should be regarded as industrial wastewaters being hazardous for the environment.
2. In view of the composition and properties of the leachates, including high content of contaminants occurring in colloidal form, as indicated by turbidity and color, the pretreatment of these leachates in the process of coagulation, combined with sedimentation was justified. In view of the fact that the effects of coagulation obtained in these studies were limited, since in the optimal conditions of the process on the average only a 50% reduction in the content of organic compounds was obtained, the process of coagulation should be treated as one of the elements of the technological system of leachate purification. A drawback of the process is the formation of considerable amounts of so-called post-coagulation sludge.
3. It was found that the ferric coagulant was characterized by a greater technological effectiveness (0.92 g $\text{Fe}^{3+}/\text{g COD}_{\text{Cr}}$ removed) than the aluminum coagulant (1.22 g $\text{Al}^{3+}/\text{g COD}_{\text{Cr}}$ removed). For optimal doses of coagulant, whose size depended above all on the COD_{Cr} value of the raw leachates, the most favorable effects of coagulation were achieved at pH 6.5–6.6.
4. Partial purification of the leachates with the use of coagulation brought about an improvement in their quality being the result of the removal of contaminants which occur mainly in the form of compounds that do not solubilize. This was indicated by decreasing color intensity and turbidity values, parameters of organic pollution and metal content. Some contaminants including ammonium nitrogen, remained still to a large extent in the leachates after the pretreatment, continuing to pose a hazard for the environment.
5. The results of the tests using different bioindicators clearly pointed to the harmful effect of raw leachates on the organisms used in the study. The values of toxicity units (TU) obtained in chronic tests with the algae *Scenedesmus quadricauda*, survival tests of the Toxkit type with the crustaceans *Thamnocephalus platyurus* and *Daphnia magna* and IQ Toxicity tests with *Daphnia magna* revealed the considerable toxicity of the leachates running off the landfill.
6. The reduction in the content of organic compounds as a result of coagulation, reflected by COD_{Cr} , BOD_5 and TOC values, did not have any significant effect on reducing the toxicity of the leachates. In some cases, as shown by tests with *Scenedesmus quadricauda* algae and the crustaceans *Daphnia magna* and *Thamnocephalus platyurus*, the toxic effect was even seen to increase as a result of coagulation. This indicates that in some cases pre-treatment involving coagulation may contribute to

increased toxicity of the leachates, by activating certain of their components, whose deleterious effect may be manifested only after the removal of chemical compounds occurring in the leachates in the form of suspensions and colloids.

7. The differentiated toxic effect of leachates on physiological processes (growth, inhibition of the activity of the enzyme β -galactosidase) and the survival of the test organisms used in the studies confirmed the need to use tests employing organisms representing different trophic levels for the overall evaluation of the harmfulness of leachates.
8. The experiments carried out in this study demonstrated the usefulness of the battery of tests used, involving producers (the algae *Scenedesmus quadricauda*), consumers (the crustaceans *Artemia franciscana*, *Thamnocephalus platyurus*, *Daphnia magna*) and decomposers (the luminescent bacteria *Vibrio fischeri*), in the evaluation of the toxicity of leachates with varied degree of contamination.

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