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CHEMICAL COMPOSITION AND BIOLOGICAL PROPERTIES OF WEATHERED DRILLING WASTES

Chemical and biological properties of 8 samples of drilling wastes from the long-term storage sites in the areas of oil various chemical composition (content of petroleum contaminants 0.6–27.6 wt. %, content of toxic heavy metals 117–730 mg/kg d.m.), and a low susceptibility to biodegradation (within the range of 11–58% during the 60-days experiment) were determined. I was found that samples having higher aliphatic/aromatic hydrocarbons ratio were more susceptible to biodegradation. Considering the high contents of the petroleum contaminants, in which the polar component *i.e.* resins and asphaltenes, are present, all the tested wastes a treat hazard to the environment. The components of potential mutagenic and carcinogenic properties have been found only in the single samples from a wastes series before and after biodegradation.

1. INTRODUCTION

During the drilling work in oil and gas mining, significant quantities of wastes are produced, which, in the case of land drilling, are collected at the vicinity of oils well installations or transferred to the collective storage yards in pits or bulk landfill. Drilling wastes are mainly composed of the used up drilling fluid and the cuttings. The wastes are complex, heterogeneous, multi-component mixture of chemicals, both inorganic and organic. They contain: heavy metal ions, mineral salts, oils and greases used in the drilling process, hydrocarbons from reservoirs, biocides, strong alkalis, and surfactants [1]. These substances, characterised by varied physical and chemical properties, impact on fauna and flora, as well as on the human health. Some of the compounds are toxic in nature.

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Among the chemicals present in drilling wastes, polycyclic aromatic hydrocarbons and heavy metals are considered the most toxic, especially for the marine fauna when drilling is performed off shore [1–3]. Deposited land drilling wastes could be dangerous to the local water and soil environment. The hazard is caused mainly by the presence of water soluble substances such as chloride ions and reducing agents [1]. The wastes containing oil-based drilling fluids are hazardous to both, land and marine life [1, 3].

In Poland, the problem of environmental hazard derived from drilling wastes mainly concerns the Podkarpacie Region, where wastes are collected in the waste pits, often for several tens of years and requires fast utilization. At present, the most economic, effective and friendly to the environment methods of utilization of wastes containing pollutants such as petroleum and coal tars are biological methods, consisting in accelerating and optimising natural processes of microbiological decomposition taking place in the environment [4–8]. Taking into consideration the fact that the progress in biodegradation depends on the chemical composition of hydrocarbons and their concentration, when the utilisation is performed with the use of biological methods, precise characteristic and the evaluation of biodegradability of petroleum pollutants are necessary [5]. Chemical characteristic of petroleum pollutants includes determination of: total contents of organic pollutants, total contents of hydrocarbons (after removal of polar compounds from extracts), individual compounds, first of all benzene, toluene, ethylbenzene, xylenes (BTEX), as well as selected polynuclear aromatic hydrocarbons (PAH), content of groups (fractions) of oil components, e.g. aliphatic hydrocarbons, aromatic hydrocarbons, resins and asphaltenes [9, 10]. Resins and asphaltenes appear in petroleum contamination, the origin of which is crude oil, high-boiling petroleum fractions, as well as in the aged oil wastes [10, 11]. Determination of potential mutagenic and carcinogenic properties of compounds present in the wastes is also necessary.

Various ways of impacting living organisms may complicate determination of carcinogenic properties. The research on carcinogenicity of compounds has to be conducted with the application of long-term animal tests, and with evaluation of their mutagenicity (the ability of a compound, to induction of mutation), bacteria are applied. Chemical compounds with mutagenic properties could be carcinogenic as well. For assessment of the potential mutagenic properties, among others, the Ames test is applied, where the sample extracts are obtained using DMSO [12, 13]. The mutagenic properties generally show petroleum-derived products which contain significant amounts of PAHs such as high boiling petroleum fractions [14], used mineral oils [15] and coal tars [16].

The information available in the literature generally indicates that petroleum pollutants studied by the Ames method, do not show mutagenic properties or low mutagenicity [17–19].

The aim of this study was to assess the feasibility of biological methods for the remediation of storage sites of drilling wastes from the exploration and production of oil and gas, based on investigations of chemical composition and biological properties.

2. MATERIALS AND METHODS

Samples. Drilling wastes originated from winning pits or collective storage yards of crude oil mines from the Podkarpacie territory. Analytical samples were averaged from 3–5 samples taken at various depths (10–50 cm) and locations of drilling pits.

Chemical analyses. Water content was determined by the gravimetric method [20]. Total extractable materials (TEM) were determined as follows: 30 g samples of wastes were mixed with anhydrous sodium sulfate and left for 24 h for binding water. Then they were placed in a cellulose thimble and extracted for 8 h with dichloromethane (DCM) in the Soxhlet apparatus. The extract contents (TEM) were determined gravimetrically after vacuum evaporating of the solvent. To determine asphaltenes content, 20 cm^3 of *n*-hexane was added to the weighed extract sample (ca. 0.5 g). The solution was left for 18 h, and then filtered. The asphaltenes deposition was dried of and weighed.

Aliphatic (aliph), aromatic (arom) hydrocarbons and resins were determined by the liquid chromatography method based on modification of a standard procedure [21]. Silica gel was the stationary phase in a column, and as eluents *n*-hexane, toluene, and tetrahydrofurane were subsequently used. The following fractions were obtained: aliphatic hydrocarbons, aromatic hydrocarbons and resins. After evaporating solvents, separated fractions were determined gravimetrically. Concentrations of total petroleum hydrocarbons (TPH) were calculated by summing concentrations of aliphatic and aromatic hydrocarbons.

Heavy metal contents was determined by the emission spectrometry with inductively coupled plasma ICP-AES according to the standard procedure PB–08/2:2000 (based on BS EN ISO 11885:2001) [22].

Evaluation of mutagenictiy by the Ames test. The Ames test was performed using the test bacterial strain of *Salmonella typhimirium* TA 98 and TA 100, with different sensitivity to various types of contamination. The test was conducted with and without the S9 fraction in order to detect presence of pro-mutagens in the test samples. The test strains are nutritional mutants unable to synthesize histidine. Under the influence of substances having mutagenic properties, a reversion takes place which manifest itself with growth in colony of revertants at the histidine-free substrate. The number of colonies appearing is the measure of mutagenic activity of the tested preparations. Before initiating the tests, the genetic markers of the test strains were checked according to the method described elsewhere [23]. The samples for the Ames test were prepared by their dissolving in DMSO, and next the extract coming from 1 mg and its half-dilution were directly placed at a test plate. The results were presented in the form of mutagenicity index (ratio) MR, being a quotient of the average number of revertants induced by the tested sample at a plate and the average number of spontaneously created revertants. According to the procedure, such tests could be considered mutagenic, for which the ratio MR ≥ 2, and which show linear dependence of dose–response [23].

Evaluation of waste susceptibility to biodegradation. Susceptibility of wastes to biodegradation was analysed in the vase experiment. The mass of wastes placed in the individual vases amounted to 500 g. As inoculation of drilling wastes, the autochthonic bacteria were applied, and their number after inoculation was 10^5 cells in 1 g of wastes. The ratio of C:N:P in the wastes subject to biodegradation was fixed at the level of 100:10:1. During 60 days of biodegradation, the humidity of the wastes was kept ca. 50% of WHC, and temperature at the 22–25 °C level.

3. RESULTS AND DISCUSSION

3.1. CHEMICAL CHARACTERISTICS OF DRILLING WASTES

Drilling wastes consist of varied diversified, multi-component and very complex mixtures, the composition of which is subject to changes during storage and purification processes [1]. The essential parameter determining transformations in the stored wastes is the content of petroleum hydrocarbons, ageing in the environmental conditions as a result of multiple processes such as evaporating, dissolving in water or natural biodegradation, etc.

Table 1

Contents of water, extracts in drilling wastes, and composition of group extracts

Sample	Composition of wastes [wt. %]		Group composition of extract [wt. %]*				TPH (% TEM)	TPH in wastes [mg/kg d.m.]
	Water	TEM	Aliphatics	Aromatics	Resins	Asph.		
Wanda 86	28.46	3.36	47.24	29.93	5.80	4.65	77.17	36 269.9
Wanda 103	40.94	5.55	56.83	26.81	5.13	2.54	83.64	78 621.6
Wanda 106	39.71	0.57	–	–	–	–	–	–
Wanda 113	26.68	3.26	47.01	29.07	8.28	8.15	76.08	33 855.6
Wanda 118	24.09	1.46	46.21	22.41	9.10	11.17	68.62	13 175.0
Graby 20	46.79	4.30	40.36	29.62	3.80	7.83	69.98	56 543.8
Graby 61	28.73	15.82	44.36	18.62	10.04	19.52	62.98	139 815.6
Gaten 47	41.48	27.59	41.11	23.43	2.37	19.22	64.53	304 452.5

*Losses caused by the presence of non-eluted compounds from silica gel and volatile compounds easily evaporating during dissolvent removal were not included.

The tested drilling wastes constituted from multiphase matrixes with water contents from 24 wt. % to 47 wt. %. (Table 1). Besides of water, the main components in the analysed samples were the organic contaminants extracted with the use of DCM. The content of TEM was in the range of 0.6–27 wt. % (6000–270 000 mg/kg, Table 1), while the samples with several percent contents of those substances predominated. Diverse but lower content of organic extracts (144–13 537 mg/kg) occurring in the wastes drilling in Poland was reported by Raczkowski and Steczko [1]. The studied extracts, besides hydrocarbons, contain polar substances such as resins and asphaltenes. These are compounds of high molecular weight, containing heteroatoms (nitrogen, sulphur, oxygen) characterised by the lowest susceptibility to biodegradation [10]. Some functional groups present in those compounds, e.g. pyrrole group, are distinguished by high toxicity to microorganisms. A source for resins and asphaltenes could be crude oil coming from a bore-hole. It has been shown that resins could be produced as metabolites during the biodegradation of crude oil. Thus, concentration of those compounds in wastes stored for long time has a tendency to increase.

The analysis of the group composition (Table 1) has shown that the main components of the extracts were aliphatic (40–57 wt. %) and aromatic (18–30 wt. %) hydrocarbons. Content of resins and asphaltenes were various and amounted correspondingly 2–10 wt. % and 2–19 wt. %. The TPH of extracts ranged from 63 wt. % to 84 wt. %. In all samples of wastes, the concentrations of TPH were over 13 175 mg/kg d.m., reaching the value of 304 452 mg/kg d.m. The highest permissible content of petroleum pollutants in soil (determined as the so called mineral oil – hydrocarbons C_{12}–C_{35}) in the industrial terrains is 3000 mg/kg d.m. [24]. Thus, concentration of petroleum pollutants in the tested samples significantly exceeds the standard allowable contents of those substances in soil. The drilling wastes in Podkarpacie Region studied by Steliga [25] also contain large amounts of TPH. Also, a high concentration of TPH (140 000–99 000 mg/kg) in soil contaminated with drilling wastes has been reported by Arce-Ortega [26] and Rojas-Avelizapa [27].

3.2. METAL CONTENT

The substances that could significantly impact the toxicity of drilling waste are heavy metals, which besides the crude oil itself qualify the wastes as the hazardous category.

Table 2

Metal content in drilling wastes

Sample	Metal content [mg/kg d.m.]						
	Cr	Ni	Cu	Zn	Pb	Sum (without Fe)	Fe
Wanda 86	24.5	27.6	33.3	42.0	13.0	140.4	26 720
Wanda 103	31.3	39.3	75.2	76.6	30.0	252.4	26 097
Wanda 106	27.2	26.7	31.8	39.1	12.0	136.8	26 020
Wanda 113	24.3	26.6	37.4	45.8	12.5	146.6	22 045
Wanda 118	17.2	22.9	28.3	37.6	11.5	117.5	14 969
Graby 20	33.0	35.1	43.5	53.7	16.0	181.3	24 845
Graby 61	19.6	31.0	38.8	31.6	11.5	132.5	26 470
Gaten 47	35.6	46.8	160.1	276.0	211.5	730	29 500

The total content of toxic heavy metals (Cr, Ni, Zn, Pb, Cu) ranged from 117 to 730 mg/kg d.m. (Table 2), however, for the majority of samples tit did not exceed 150 mg/kg d.m., being the dangerous level for soil environment.

3.3. EVALUATION OF POTENTIAL MUTAGENIC AND CARCINOGENIC PROPERTIES

The management of drilling wastes and most of all their fast utilisation should minimise its negative impact on the environment. Proper evaluation of composition and toxicity of the wastes as well as selection of the utilisation method is essential. Toxicological data, characterising doses of a substance inducing the specific health threat, e.g. a cancer disease, are currently used in the so called risk analysis, which enables evaluation of impact of contaminations on humans.

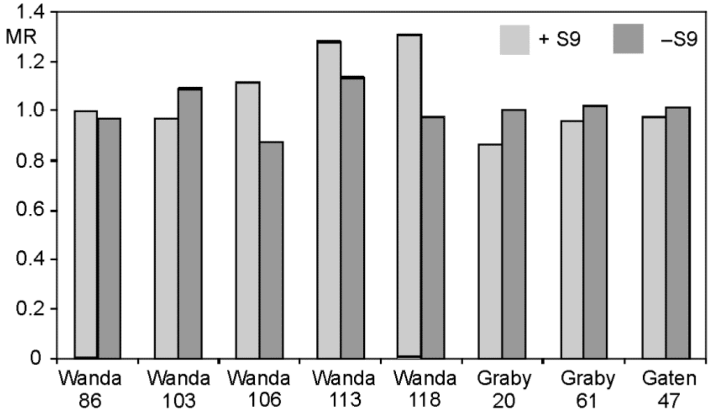

Fig. 1. Mutagenicity ratio (MR) obtained for samples of drilling wastes using the test bacterial strain *Salmonella typhimurium* TA 100

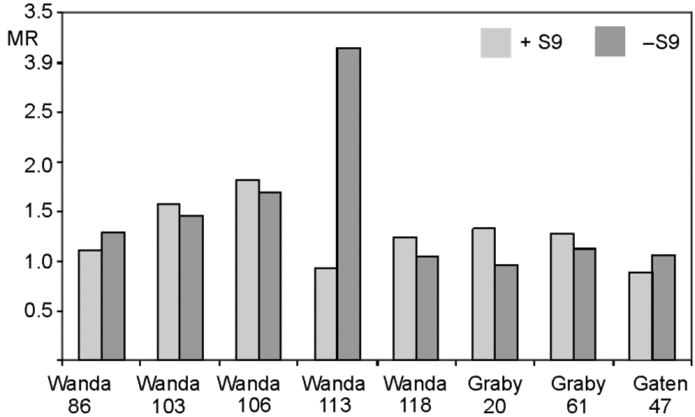

Fig. 2. Mutagenicity ratio (MR) obtained for samples of drilling wastes using the test bacterial strain *Salmonella typhimurium* TA 98

The research on mutagenic and carcinogenic activity of drilling wastes using the Ames test (Figs. 1, 2) have shown that among the analysed 8 samples, one sample (Wanda 113) displayed the mutagenicity ratio higher than 2, testifying for a possibility of its contamination with compounds having potentially mutagenic and carcinogenic properties.

As results from the data (Table 1), very high concentration of petroleum hydrocarbons, within the range of 13 175–304 452 mg/kg d.m. of wastes, as well as the polar compounds: resins (2–10 wt. %) and asphaltenes (2–20 wt. % of extract), do not correlate with the mutagenicity ratio. However, the concentration level for petroleum substances in wastes is a significant parameter when selecting the proper conditions for its utilisation, especially when using the biological methods.

In terms of toxicity of wastes more important is the contents of aromatic hydrocarbons, and particularly the polycyclic ones. As a criterion for evaluating a potential carcinogenicity of oil samples, the content of 3 wt. % of DMSO extract (containing 3–7 cyclic PAH) is assumed, however, conditions concerning sample content have to be fulfilled – they should not contain more than 5% of components boiling below 300 °C and asphaltenes [28]. The obtaining of samples with defined boiling temperature ranges requires big quantities of extracts, which, in the case of environmental samples, is rather difficult.

3.4. EVALUATION OF SUSCEPTIBILITY OF WASTES TO BIODEGRADATION

It has been found that drilling wastes have shown variable susceptibility to biodegradation (11.0–58.4%) (Table 3).

Table 3

Chemical compositions of drilling wastes in the process of biodegradation

Sample	TEM in wastes [wt. % d.m.]	TEM in wastes after biodegradation [wt. % d.m.]	Loss [%]	Ratio Aliph/Arom
Graby 20	8.08	7.18	11.0	1.36
Wanda 118	1.92	1.70	11.5	2.06
Wanda 86	4.70	3.91	16.8	1.58
Wanda 113	4.45	3.58	19.6	1.62
Gaten 47	47.18	31.72	32.8	1.75
Wanda 103	9.40	5.26	44.0	2.12
Wanda 106	0.94	0.51	45.7	–
Graby 61	22.20	9.23	58.4	2.38

The drilling wastes dented Graby 61 was less resistant to biodegradation than other samples used in this study. Probably its availability for a microorganism was caused by lower ratio of aromatic compounds (Table 1). Low content of aliphatic compounds was found in wastes Graby 20 which was more resistant for microbiological conversions. These data indicate the impact of the hydrocarbons content of a certain chemical structure on the biodegradation process. Based on the comparison of aliphatic/aromatic ratio and wastes susceptibility to biodegradation (Table 3, Fig. 3), it was found that samples with higher aliphatic/aromatic hydrocarbons ratio were more susceptible to biodegradation.

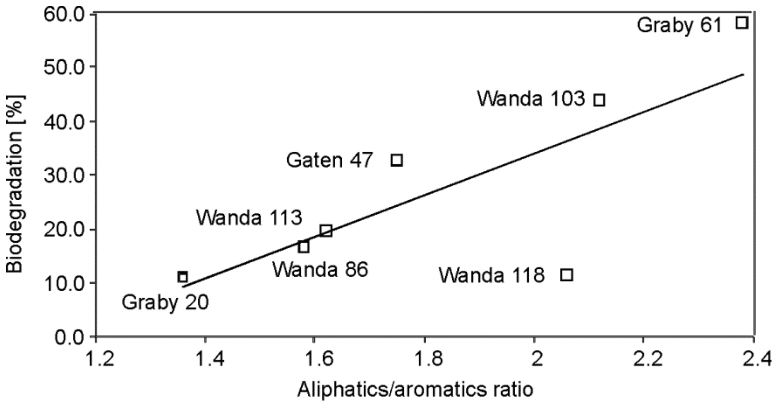

Fig. 3. Effect of aliphatic/aromatic ratio on susceptibility to biodegradation

The biodegradation process led to lowering toxicity of wastes. For 7 samples, the mutagenicity ratio was at the level which did not indicate the presence of mutagenic factors in the wastes. Only in the Graby 20 sample after biodegradation a small increase in the mutagenicity ratio (MR = 2.2) was observed, but in the non-diluted extract. This could indicate a possibility of biodegradation with creation of metabolites of potential mutagenic and carcinogenic properties. Instead, in the wastes sample Wanda 113, during the biodegradation process the elimination of components potentially hazardous to human health occurred, as the mutagenicity index assumed values lover than 2.

4. CONCLUSIONS

The tested drilling wastes constituted from multiphase matrixes containing diversified quantities of water (from 24 to 47 wt. %) and organic contaminants extracted using dichloromethane. Contents of extracts ranged from 6000 to 270 000 mg/kg, while the samples with several percent content of those substances predominated. The group analysis has shown that the main components in the extracts were aliphatic (40–57 wt. %) and aromatic (18–30 wt. %) hydrocarbons. The content of resins and asphaltenes varied amounting correspondingly 2–10 wt. % and 2–19 wt. %. In all samples of wastes the TPH concentration exceeded 13 175 mg/kg d.m., reaching the values of up to 304 452 mg/kg d.m. The total content of toxic heavy metals (Cr, Ni, Zn, Pb, Cu) ranged from 117 to 730 mg/kg d.m., however, for the most of samples it did not exceed 150 mg/kg d.m. The analysis of the waste chemical composition indicates that it constitutes a threat to the environment, mainly because of very high contents of petroleum hydrocarbons, as well as the presence of polar compounds.

The studies of biological properties of the wastes involved the evaluation of its susceptibility to biodegradation, as well as tests enabling application of the tests detection of components with the potential mutagenic and carcinogenic properties. By the Ames method, it has been shown that the presence of mutagenic and carcinogenic components was observed in the wastes from Wanda 113 storage yard. The susceptibility to the biodegradation of individual samples differed significantly, and in the 60 day experiment ranged within 11.0–58.4%. It was found that samples having higher aliphatic/aromatic hydrocarbons ratio were more susceptible to biodegradation. The biodegradation process did not lead to the increase of mutagenicity of the majority of the tested wastes. The obtained results indicate the possibility of using biological methods in the environmental remediation of drilling wastes storage yards.

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