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Biological Treatment of Gas-Works Sewage

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Abstract

Gas-wo rks sewage, for the sake of its complex composition, contains organic xenobiotics, mainly phenols and polycyclic aromatic hydrocarbons (PAH's). It is well known that these substances are very dangerous to live organisms. Therefore, the commercial scale purification process of the sewage was elaborated and carried out by way of biological treatment. For this purpose the bacteria strains of *Pseudomonas* and *Bacillus* type already existing in a surface layer of the sewage were applied as biopreparat and whey as a bacteria medium. Purification was carried out for two similar kinds of sewage: typical gas water (in Inowroclaw) and sewage generated by dilution of a gas pitch (in Torun). This avoided the serious possibility of soil and water pollution.

Keywords: gas pitch; gas-works water; xenobiotics: biopreparat; bacteria strains; biodegradation

Introduction

The problem of soil and water contamination by the crude oil and petroleum industry is one of the most important, and, unfortunately, very actual and still unsolved global problems. The potential sources of the same health hazard are also places and reservoirs where residues from town gas production, coking plants and asphalt-bituminous wastes are deposited. These substances, for the sake of their complex composition (besides inorganic pollutants, e.g. heavy metals and ammonium compounds) also contain organic xenobiotics, mainly phenols and polyaromatic hydrocarbons (PAH's).

The introduction of phenolic sewage to surface water causes unfavourable changes in the flora and fauna, and unpleasant odour and flavour of the water. Phenols are also able to accumulate in the bodies of fish. In the case of chlorination of drinking water containing phenols, chlorophenols are formed and they cause the hideous taste and odour of water which is already perceived by consumers at a concentration of 0.5 μg/dm^3 [1, 2],

It is well-known that compounds from the PAH group belong to the most dangerous organic xenobiotics. They are also able to accumulate in living organisms and some of them have muta- and carcinogenic properties [3-6]. This is a reason for investigation and development of **the** most effective method for the below-mentioned toxicant degradation and natural environment protection.

Our local problem began about 30 years ago, when inferior (less caloric) and toxic illuminating gas was replaced by **natural** gas. The gas works stopped its production but there remained many residuals, for example a gas pitch. The gas pitch from unworking plants of Northern Poland was transported to Torun and then deposited in our reservoir. The atmospheric falls diluted pitch over thirty years and formed sewage, so **at the** end of 1994 there was about 7000 m^3 of sewage. Because the steel reservoir was almost 90 years old and very close to the Vistula River (see Fig. 1), an ecological disaster was probable [7].

A similar problem arose in Inowroctaw, a health resort located about 40 km south-west of Torun (see Fig. 1), where a gas-works had also been closed. The hazardous residues of town-gas production (mainly gas water and pitch) remained in an underground 500 m^3 brick reservoir, a potential source of soil and water pollution.

There exist many methods of phenolic sewage purification based on physical and chemical methods, but the most effective is biological treatment [8-15]. For example, Bossert and Bartha [16] have isolated 22 bacteria and 31 fungi strains which cause hydrocarbons degradation. It is well known that it is possible to isolate specific cultures whose ability to degrade phenolic compounds is much higher than the

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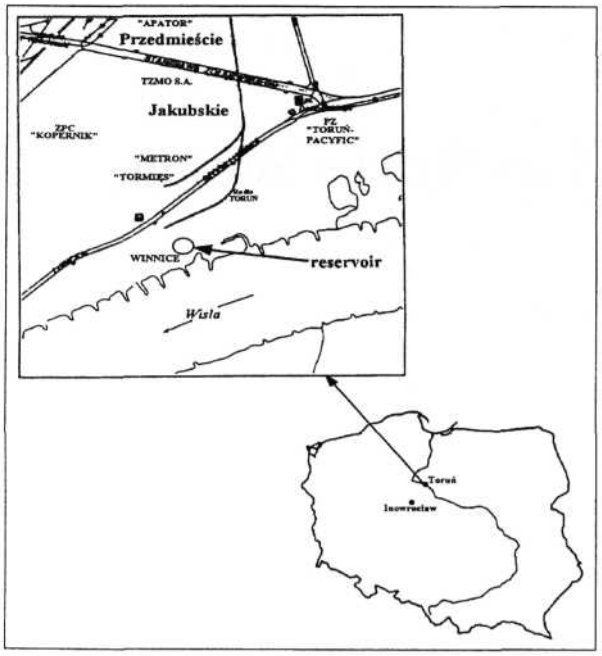

Fig. 1. Location of puryfying sites.

biodegradability of microorganisms present in the natural environment [17]. However, it seems that the ideal microorganisms for this purpose have to be isolated from such an environment where aromatic compounds are present as substrates. Moreover, the products formed during biopreparat activity should not cause secondary environmental pollution. Dluhy et al. give in their work [10] a scheme of phenol degradation using bacteria strains of *Alcaligenes* (ortho cleavage) and *Pseudomonas* (meta cleavage) - Fig. 2. The individual steps of biological degradation indicate that products of phenol decay are not onerous to the environment. A continuous control of the purification process by means of fast and precise analytical methods was also needed.

It was therefore decided to adopt a method elaborated upon earlier in our laboratory [2] to the commercial scale and biological treatment of the above-mentioned sewage to avoid ecological disaster. This work describes the purification process of gas-works sewage using controlled biological preparat.

Experimental

Methodology of Purification Process

The purification process was conducted through several steps, namely:

- removing the gas pitch suspension from the sewage in a coke absorber,
- transport of solution to the biological treatment plant,
- addition of bacteria medium (whey) to the solution and aeration,
- addition of biopreparat,
- biological treatment, and
- the purified sewage dump to the municipal sewage system.

In the biological treatment bacteria strains already existing in phenolic sewage (i.e. those which are characteristic of a given environment) were used. Phenols and PAHs degrading bacteria strains were isolated from the surface layer of sewage by the Ralston and Vala method [18]. Of these, the most active were chosen; after identification it was confirmed that they belong to the aerobic bacteria of *Pseudomonas* and *Bacillus* types. From those strains inoculum was prepared [2].

The sewage coming from Inowroclaw was transported to Toruri and purified in our biotreatment plant. It was typical gas water; therefore, the phenols and PAH content was higher than in former sewage.

It is necessary to notice that the plant construction held to be very tight because of volatile phenol content. A maximum manufactured unit amounts to 400 m^3

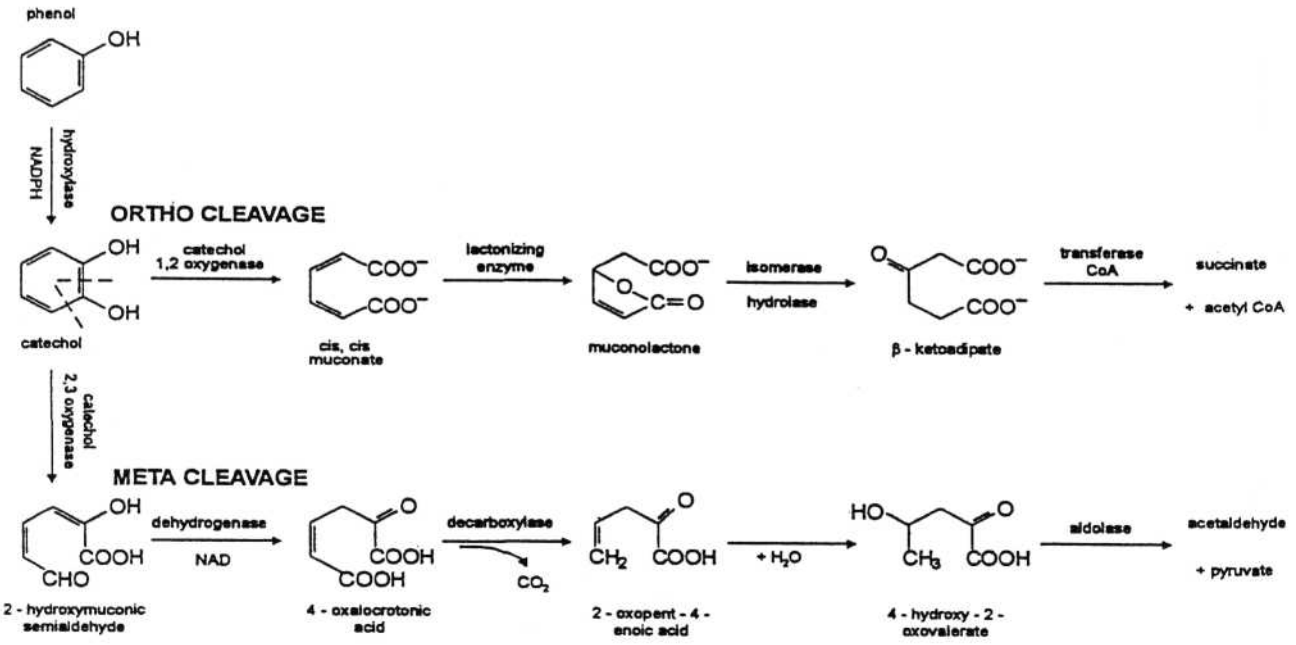

Fig. 2. Catabolic pathway of phenol degradation according to Dluhy, et al. [10, 11],

Analytical Procedures

For current control of purification process the concentration of phenols and oxygen (as well as pH) total suspension and chemical oxygen demand (COD) values were determined. The enlarged analysis of sewage (see Table 1) was also carried out several times. According to Polish environmental standards (Polska Norma), volatile phenols were determined using the photocolorimectric method with 4-aminoantipyrine [19]. Unfortunately, it is a very time consuming method and, therefore, a new analytical pathway utilizing *off-line* coupled solid phase extraction (SPE) and high-performance liquid chromatography in reversed phase mode (RP HPLC) has been elaborated. This method was based on the U.S. Environment Protection Agency (EPA) procedures concerning phenols (EPA metod N° 623) and PAHs (EPA method N° 610) determination. Detailed description of both methods, included SPE and HPLC column choice and separation conditions optimalization, is given in an other paper [20].

Heavy metals were determined with the aid of atomic absorption spectrometry (AAS) and other analysis - using standard physico-chemical methods [1], as follows:

chlorides - argentometric titration,
sulphates - gravimetric method with $BaCl_2$,
N-NH_4 - distillation method with acid-base titration,
oxygen - Winkler method,
total suspension - gravimetric method, etheric extract - etheric extraction and distillation method.

Reagents and Instruments

Most parts of chemicals were purchased from Polskie Odczynniki Chemiczne - POCh (Gliwice, Poland) and of p.a. grade. Standards for HPLC determination of phenols and PAHs were from S. Witko/J.T.Baker (Lodz, Poland). Methanol, acetonitrile and acetic acid *"for HPLC"* purity were also purchased from S. Witko/J.T.Baker. The deionized water was purified in laboratory using a Millipore (El Paso, Texas, USA) Milli-Q reagent water system.

Instrumental analysis was carried out using the following apparatus:

- HPLC system, model 1050 Hewlett Packard (Waldbronn, Germany) with a diode array detector and a Rheodyne (Berkeley, CA, USA) model 7125 sampling valve fitted with a 20 µl loop. A homemade HPLC column (125 x 4.6 mm i.d.) with SG-AP phase - 5 µm (hydrophobic-hydrophylic character) [20] was used. It was a selective packing material in all our measurements. The retention data were recorded and processed using a Hewlett Packard Vectra QS/16S com puter with ChemStation-3.
- atomic absorption spectrometer, type PU 9100x (Phi lips, Cambridge, England) fitted with graphite cuvete and autosampler,
- photocolorimeter Spekol 11 (Carl Zeiss, Jena, Ger many),
- spectrophotometer SQ-118 (Merck, Darmstadt, Ger many),
- pH meter N5170E (Teleko, Warszawa, Poland).

Results and Discussion

In Table I the important characteristic data for sewage from Torun before and after purification are presented. Moreover, the demanded value of determined components content, according to polish regulations [21], are also listed. The composition of purified sewage is a mean value of several measurements. As can be seen, the purification effectiveness was very good and for inorganic compounds ranged between 2% for manganese to 95% for N-NH_4. For organic compounds those values ranged between 50% for etheric extract to 90% for volatile phenols. The values of COD and BOD_5

Table 1. The composition of sewage before and after purification (Toruń).

No	Determined value		Composition of raw sewage	Composition of purified sewage	Demanded Value	Purification yield (%)
1	pH		7.16	7.08	6.5 – 9.0	-------
2	Total suspension	(mg/dm^3)	17.7	47.7	330	-------
3	BOD_5	(mgO_2/dm^3)	688.0	205.0	700	70.2
4	COD	(mgO_2/dm^3)	1183.0	307.0	1000	74.0
5	N-NH_4	(mg/dm^3)	120.0	5.3	6	95.6
6	Chlorides	(mg/dm^3)	115.0	21.7	400	81.1
7	Sulphates	(mg/dm^3)	24.5	4.3	300	82.4
8	Iron	(mg/dm^3)	3.223	3.011	10	6.6
9	Cadmium	(mg/dm^3)	0.010	0.002	0.1	80.0
10	Lead	(mg/dm^3)	0.064	0.044	0.1	31.2
11	Manganese	(mg/dm^3)	0.203	0.199	0.2	2.0
12	Copper	(mg/dm^3	0.083	0.013	0.2	84.3
13	Zinc	(mg/dm^3)	0.313	0.238	2	24.0
14	Volatile phenols colorimetric	(mg/dm^3)	201.3	20.1	40	90.0
15	Phenols – HPLC	(mg/dm^3)	525.17	91.30	–	82.6
16	PAH's – HPLC	(µg/dm^3)	11.84	3.01	–	74.6
17	Etheric extract	(mg/dm^3)	72.0	36.8	50	48.9

Table 2. Comparison of purification yield of PAHs and phenols for sewage from Toruń and Inowrodaw.

Determined compounds	The place of sewage storage					
	Toruń			Inowrocław		
	Raw	Purified	Yield (%)	Raw	Purified	Yield (%)
PAHs	11.84 μg/dm³	3.01 μg/dm³	74.6	227.98 μg/dm³	15.46 μg/dm³	93.2
Phenols	525.17 mg/dm³	91.30 mg/dm³	82.6	8195.38 mg/dm³	116.69 mg/dm³	98.6

were reduced 74% and 70%, respectively (Table 1). As can also be seen, the total concentration of phenols determined by means of the HPLC method is significantly higher than in the case of the colorimetric method.

The comparison of purification results for organic xenobiotics only (presented in sewage coming from Inowrodaw and Toruri) is given in Table 2. Analysis of these data shows that for Toruri sewage, reduction of PAHs and phenol content amount to 75% and 83%, but for Inowrodaw sewage - 93% and 99%, respectively (Table 1). It is interesting that in both cases, biotreatment is more effective for phenols (about 7 ± 1%), probably due to the biopreparat.

It is well known that biological processes strongly depend on temperature. Because our purification processes lasted over one year, we can compare its run during cold and warm monthes. And so in Figure 3 the curves of some organic pollutants (volatile phenols and COD) decomposition in winter months, and in Figure 4 (spring), are shown. The graphs show that in winter purification is very complicated and sometimes lasts over a month (see Fig. 3). On the other hand, in spring, pollutant decomposition is quick and simple and lasts only a few days (Fig. 4).

Nevertheless, the quality of our biopreparat was so effective that after the first day of purification phenol concentration decreased about 25-26% and COD values about 26-27%. Only for the case shown in Figure 3b, when temperature was really low, did biotreatment efficiency amount to 18% for phenols and 17% for COD. It was also observed that, beside temperature, many factors (e.g. quality and quantity of used biopreparat and bacteria medium, oxygen concentration, mixing rate, etc.) have a great influence on time and effectiveness of purification. They were examined earlier on a laboratory scale [2] and then, after optimization, applied in our processes.

In conclusion, we can state that our gas-work biotreatment method became very effective and successful and can

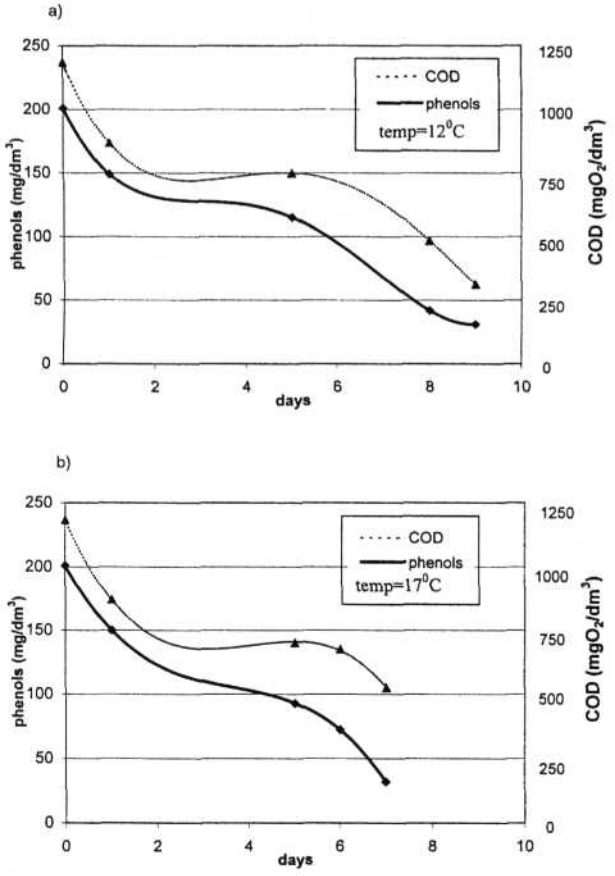

Fig. 3. Decomposition of some organic pollutants during biodegradation of sewage in winter (a - from 22 XI to 7 XII; b - from 7 I to 14 II); t - average air temperature.

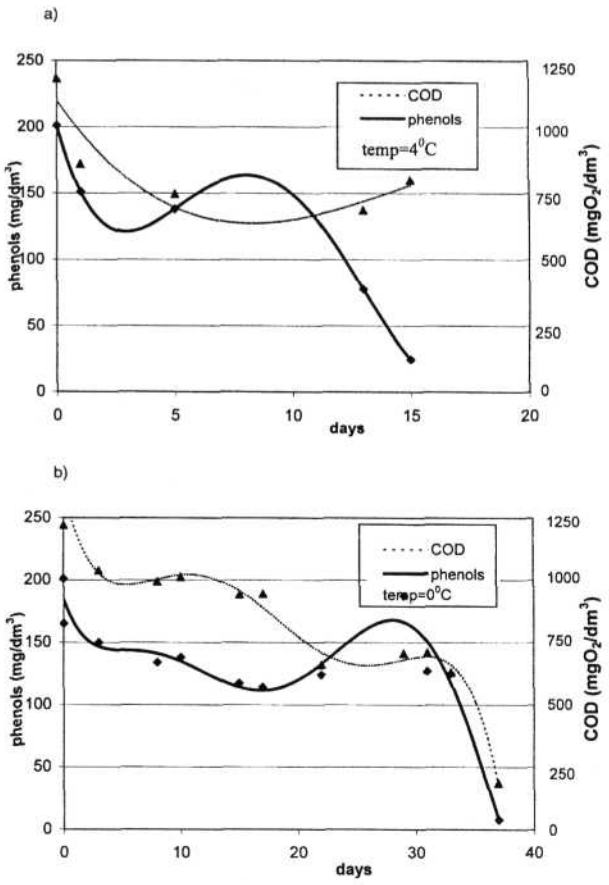

Fig. 4. Decomposition of some organic pollutants during biodegradation of sewage in spring (a - from 20 IV to 28 IV; b - from 11 V to 17 V); t - average air temperature.

be scaled up for industrial purposes. The obtained pollutant (organic and inorganic) reduction allowed us to dispose of purified sewage in the municipal sewage system. The elaborated HPLC method [221 allows for qualitative and quantitative determination not only of phenols, but also of PAHs.

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