

ELECTROCHEMICAL TREATMENT OF SEEPING LANDFILL WATERS IN NASAVRKY

ELEKTROCHEMICKÉ ČIŠTĚNÍ PRŮSAKOVÝCH VOD ZE SKLÁDKY V NASAVRKÁCH

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Abstract:

The article deals with the decontamination of seeping landfill waters of the Nasavrky landfill, operated by the AVE CZ Nasavrky a.s. company, as carried out under laboratory conditions. The risk pollutant that was monitored in the analysis was phenol. Its degradation was monitored on the model and the real landfill leachate waters by means of direct electrochemical oxidation and Fenton reaction.

Keywords:

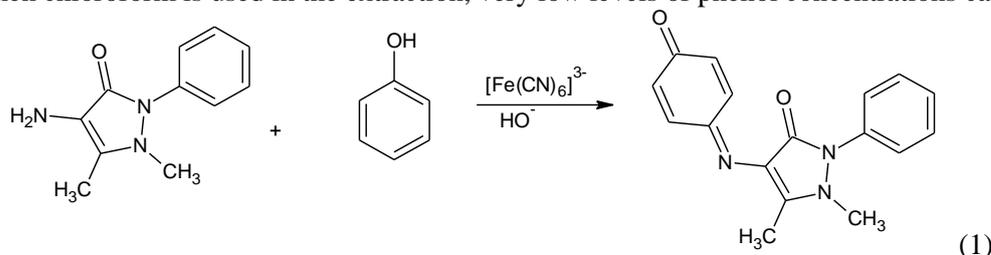
Phenol, seeping waters, electrochemical decontamination, BDD electrodes

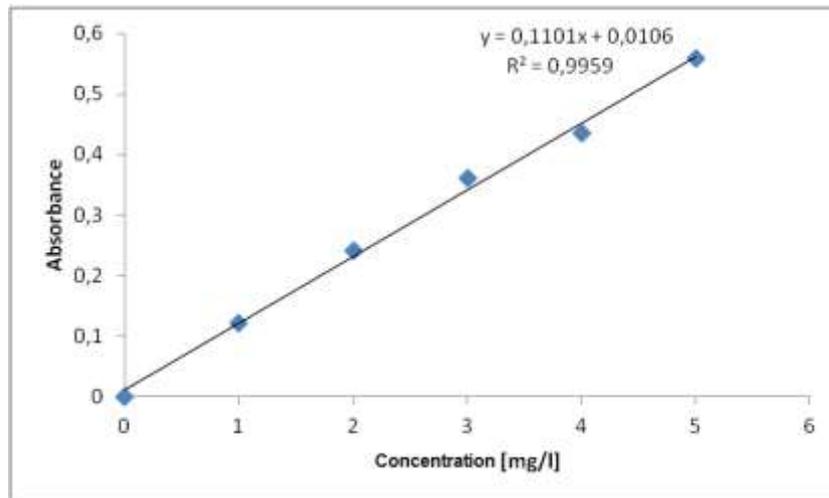
Introduction

The landfill is located in the vicinity of Nasavrky, approximately 440 metres from the southeastern edge of the village. The landfill is surrounded by fields and woodland. It is classified as a group C landfill – other refuse (S – OO), subgroup S – OO3. It is owned and operated by the AVE CZ Nasavrky a.s. company. The total land area of the premises is 7.5 hectares, out of which about 4.6 hectares are filled. According to 2011 and 2012 chemical analyses provided by AVE CZ a.s., the Nasavrky landfill has serious problems with phenols contained in seeping waters in concentrations of 0.1 – 5 mg l⁻¹. The analyses indicate that the level of CHSK fluctuates from 300 to 1100 mg.l⁻¹. The water also contains a high proportion of dissolved compound.

Methodology

The main aim of the work was to select and verify analytical methodology suitable for quantitative determination of current concentration of phenol in model and real seeping waters. It was decided to use a spectrophotometric determination of phenols with 4-aminoantipyrin, which is among the most decisive methods of determining phenols. Phenols react with 4-amino-2,3dimethyl-1-fenyl-3 prazilin-5-on (4-AAP) in the presence of K₃[Fe(CN)₆] in a slightly alkaline environment (pH 7.9). This gives rise to a colourful complex, whose absorption maximum is at 500 nm, cf. Figure (1) and Graph 1. This method is very sensitive and, when chloroform is used in the extraction, very low levels of phenol concentrations can be detected.





Graph 1: Phenol calibration curve measured under $t=25\text{ }^{\circ}\text{C}$, $\lambda = 500\text{ nm}$ against the background of phosphate buffer in a 10 mm quartz glass measuring cell.

The next aim was to find out whether phenol from the model and real landfill seeping waters may be electrochemically decontaminated by means of direct oxidation and, then, to verify the efficiency of such oxidation with respect to Fenton oxidation of model phenol waters. Because of the absence of cyanides in the real landfill water, the water was not tested for Fenton reaction. An additional aim was to test the electric, chemical and mechanical stability of BDD electrode prototypes provided for this purpose by Ing. Vojs from the Institute of Electronics and Photonics of the Slovak Technical University in Bratislava.

The direct oxidation of phenol occurred in a single-chamber, magnetically mixed and thermostat-tempered electrolyser with the volume of 125 ml on three different anodes. In all cases, the cathode consisted of a platinum electrode. The anodes were platinum, graphite and boron-doped diamond electrodes. The distance between the electrodes was 20 mm. The source was Manson *SDP 221* connected in a potentiostatic regime of $U = 10\text{ V}$. A two-electrode connection was used and the process was carried out under a constant pH, with electrodes positioned in the electrolyser together with the pH electrode governing the two-channel titrator TitraLab TIM 856 programmed as a two-way pH stat. The direct oxidation was performed at levels of pH 3 and 7.6. The samples of the reaction mixture were taken with a micro-pipette and the current phenol concentration was established after the procedure that involved 4-aminoantipyrin.

Platinum electrodes

The active surface area of the platinum electrode (1 cm^2) was formed by a polished Pt sheet with the width of 0.4 mm, welded with a Pt wire and smouldered to a Cu live wire with the cross-section of 0.75 mm^2 . The electrode was sealed in a glass tube and furnished with a plastic connector body, sealed with a 6 mm O-ring. This Pt electrode is a construction prototype produced in the electronic, glass-making and engineering workshop of the Faculty of Chemical Engineering, University of Pardubice, cf. Figure 1.



Figure 1: A platinum electrode with the surface of 1 cm^2

Graphite electrodes

Carbon electrodes, which are chemically inert, have a wide applicability thanks to their good conductivity. The active surface area of these electrodes is 22.6 cm^2 and it is easy to clean, e.g. with a sandpaper. The electrodes have a plastic connector sealed with a 6 mm O-ring identical with the connector of Pt electrodes.

The active part of the electrode is replaceable. It is made of carbon round with the purity of 99.9%, the diameter of 6.3 mm and the length of 130 mm (supplier: Alfa Aesar, USA), see Figure 2.



Figure 2: A graphite electrode

Boron-doped diamond electrodes

Boron-doped diamond electrodes are prepared by means of the chemical deposition of vapour. The BDD anode, supplied by Ing. Vojs for the test, had the active surface area of 1 cm², with the width of the BDD film of 1.3 μm, see Figure 3.



Figure 3: Boron-doped diamond electrode

Phenol degradation by means of Fenton reaction

Fenton reaction was carried out under three different pH levels – 2, 3 and 4. The molar proportions of hydrogen peroxide and iron sulphate used in the Fenton reaction was 10:1, 25:1 and 50:1. Where the reaction environment had the pH of 3 and 4 and the phenol solutions had the concentrations of 7 mg.l⁻¹ ($5.07 \cdot 10^{-5}$ mol.l⁻¹) and 12.4 mg.l⁻¹ ($8.98 \cdot 10^{-5}$ mol.l⁻¹), phenol was always degraded. With the environment having the pH of 2, the phenol solution had the concentration of 8.3 mg.l⁻¹ ($6.01 \cdot 10^{-5}$ mol.l⁻¹). However, with the proportion of hydrogen peroxide and iron disulphate of 10:1, there was no change and –even when hydrogen peroxide was subsequently added, increasing the proportion to 25:1 and 50:1 – phenol was not degraded.

The amount of 250 ml of the phenol solution was put into the electrolyser and 2.8 mg of iron sulphate were added ($1.47 \cdot 10^{-3}$ mol.l⁻¹). Subsequently, 30 per cent hydrogen peroxide was added, according to the proportions, in the amounts of 19 μl, 47,5 μl and 95 μl. With the lower proportions, the samples for the determination of current phenol concentrations were taken at ten-minute intervals. With the 50:1 proportion, samples were taken at five-minute intervals. Samples of 1 ml were taken, and, subsequently, we added the amount of 25 μl NH₄OH (0.5 mol.l⁻¹), 955 μl of buffer, 10 μl 4-AAP with the concentration of 0.0984 mol.l⁻¹ and 10 μl K₃[Fe(CN)₆] with the concentration of 0.243 mol.l⁻¹. After 15 minutes, the sample was measured for absorbency at 500 nm.

Results

a) Model water

Platinum anode, platinum cathode

With this measurement, there was repeatedly the highest decrease in phenol concentration from all the measurements carried out with pH = 3, cf. Graph 2. The phenol concentration in the solution after the termination of the measurement was 0.685 mg.l⁻¹ (0.007 mol.l⁻¹). Given the starting concentration of 7 mg.l⁻¹ ($5.07 \cdot 10^{-5}$ mol.l⁻¹), this represents 91 % efficiency of phenol degradation with the total charge of 6838 C. The velocity constant based on five repetitions was $1.49 \cdot 10^{-4} \pm 1,55 \cdot 10^{-6} \text{ s}^{-1}$ with the corresponding half-time decomposition of 4803 s. With the increase of pH to 7.6, phenol degradation was slower under the same conditions, cf. Graph 2. The measurement was terminated the next and the average phenol concentration in

the solution was 2.347 mg.l^{-1} (0.025 mol.l^{-1}). The efficiency of phenol degradation from the model waste water was 42.94 % and the charge used was 1761 C. The reaction velocity constant was $2.7410^{-5} \pm 3.38 \cdot 10^{-7} \text{ s}^{-1}$ and the half-time of phenol decomposition was 29858 s.

Graphite anode, platinum cathode

When the graphite anode was used at pH = 3, phenol degradation was slower than with platinum electrodes, cf. Graph 4. The disadvantage was the gradual burning of the graphite electrode and the destruction of the compactness of the electrode's surface. After five repetitions, the average efficiency of 76.43 % of phenol degradation was obtained. The reaction velocity constant was $k = 6.46 \cdot 10^{-5} \pm 3.05 \cdot 10^{-6} \text{ s}^{-1}$, $t_{1/2} = 11938 \text{ s}$, with the average consumption of 25415 C. At pH 7.6, phenol degradation in the model water occurred very quickly and five repetitions resulted in the residual concentration of 0.872 mg.l^{-1} (0.009 mol.l^{-1}), cf. Graph 5. The reaction occurred with the efficiency of 86.75 %, the average velocity constant was $1.23 \cdot 10^{-4} \pm 6.11 \cdot 10^{-6} \text{ s}^{-1}$ with the corresponding $t_{1/2} = 815 \text{ s}$.

Boron-doped diamond anode, platinum cathode

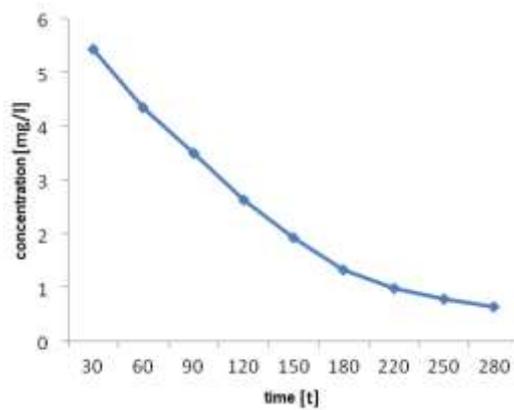
The conditions were set in the same way as in the previous measurements. However, regardless of the pH applied (whether 3 or 7.6), there was no phenol degradation at the BDD anode; instead, phenol was polymerized. The next day, the polymerized phenol was separated in the form of lumpy substance, cf. Figure 4. For this reason, the experiments could not be properly assessed.



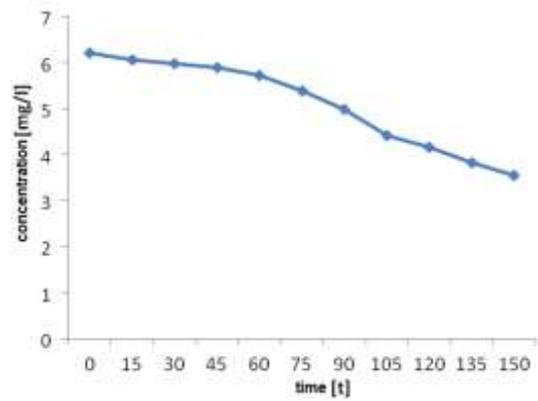
Figure 4: Polymerized phenol separated in the form of lumpy substance

Phenol degradation by means of Fenton reaction

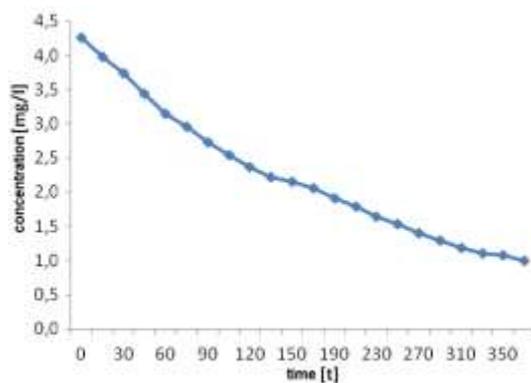
Fenton reaction was carried out with the model water at three levels of pH: 2, 3, and 4, cf. Graphs 7 and 8. For each pH, three different molar proportions of hydrogen peroxide and Fe^{2+} were used – 10:1; 25:1 and 50:1. Each experiment was reproduced three times and the values given were averaged. At pH = 2, there was no indirect oxidation of phenol, not even after increasing the proportion of hydrogen peroxide and Fe^{2+} . The starting concentration of phenol in the solution remained 12.4 mg.l^{-1} ($8.98 \cdot 10^{-5} \text{ mol.l}^{-1}$) until the next day, i.e. essentially without any change. By contrast, at pH 4, Fenton reaction had the highest efficiency of phenol degradation from the solution. In case of the proportion of hydrogen peroxide and Fe^{2+} of 10:1, the average velocity constant was $6.13 \cdot 10^{-4} \pm 1.43 \cdot 10^{-5} \text{ s}^{-1}$ with the corresponding average half-time of decomposition of 2716 s. In case of the proportion of 25:1, the figure was $3.63 \cdot 10^{-4} \pm 1.17 \cdot 10^{-5} \text{ s}^{-1}$ with the half-time of decomposition of 3341s. In case of the proportion of 50:1, the figure was $8.51 \cdot 10^{-4} \pm 2.61 \cdot 10^{-5} \text{ s}^{-1}$ with the half-time of decomposition of 1012 s. At pH 3, a reduction in the speed of phenol oxidation was observed. At pH 3 and the proportion of hydrogen peroxide and Fe^{2+} of 10:1, the average velocity constant was $1.49 \cdot 10^{-4} \pm 5.47 \cdot 10^{-6} \text{ s}^{-1}$ with the corresponding average half-time of decomposition of 6037 s. In case of the proportion of 25:1, the figure was $2.67 \cdot 10^{-4} \pm 3.03 \cdot 10^{-5} \text{ s}^{-1}$ with the half-time of decomposition of 4381 s. In case of the proportion of 50:1, the figure was $3.81 \cdot 10^{-4} \pm 2.86 \cdot 10^{-5} \text{ s}^{-1}$ with the half-time of decomposition of 3160 s.



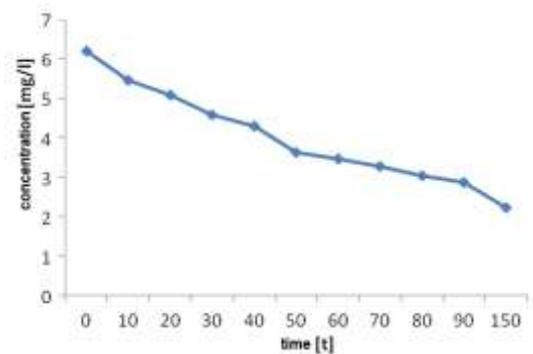
Graph 2: The dependence of phenol concentration on time during direct oxidation (Pt/Pt), $U = 9,99V$, pH 3, $t = 25\text{ }^{\circ}C$, $\lambda = 500\text{ nm}$ against the background of phosphate buffer in a 10 mm quartz glass cuvette.



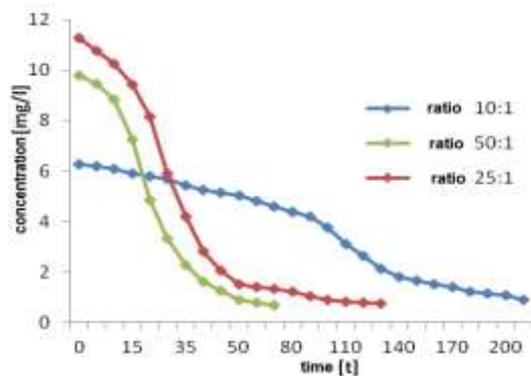
Graph 3: The dependence of phenol concentration on time during direct oxidation (Pt/Pt), $U = 9,99V$, pH 7,6, $t = 25\text{ }^{\circ}C$, $\lambda = 500\text{ nm}$ against the background of phosphate buffer in a 10 mm quartz glass cuvette.



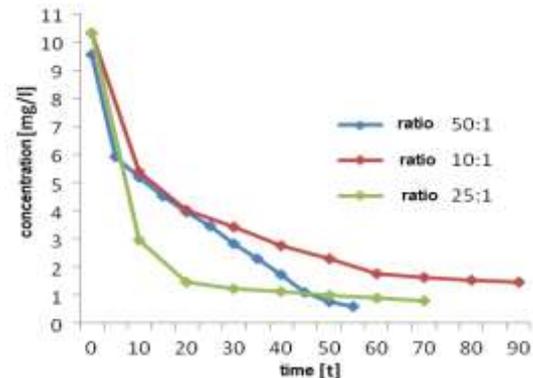
Graph 4: The dependence of phenol concentration on time during direct oxidation (Pt/graphite), $U = 9,99V$, pH 3, $t = 25\text{ }^{\circ}C$, $\lambda = 500\text{ nm}$ against the background of phosphate buffer in a 10 mm quartz glass cuvette.



Graph 5: The dependence of phenol concentration on time during direct oxidation (Pt/graphite), $U = 9,99V$, pH 7,6, $t = 25\text{ }^{\circ}C$, $\lambda = 500\text{ nm}$ against the background of phosphate buffer in a 10 mm quartz glass cuvette.



Graph 6: The dependence of phenol concentration on time during Fenton reaction, pH 3, $t = 25\text{ }^{\circ}C$, $\lambda = 500\text{ nm}$ against the background of phosphate buffer in a 10 mm quartz glass cuvette.



Graph 7: The dependence of phenol concentration on time during Fenton reaction, pH 4, $t = 25\text{ }^{\circ}C$, $\lambda = 500\text{ nm}$ against the background of phosphate buffer in a 10 mm quartz glass cuvette.

b) Phenol degradation from real landfill water by means of direct oxidation

The characterization of waste water from the Nasavrky landfill is summarized in Table 1 and 2.

Table 1: Waste water characteristics

Specific conductance	10.99 mS.cm ⁻¹
Temperature	19.5 °C
pH	7.66
Phenol	2.7 mg.l ⁻¹ (2.87.10 ⁻⁵ mol.l ⁻¹)
COD	949 mg.l ⁻¹
Dissolved elements	6.33 g.l ⁻¹
Density	1.006 g.cm ⁻³

Table 2: Results of TOC measurement

Total carbon	940.5 mg.l ⁻¹
Inorganic carbon	612 mg.l ⁻¹
Total organic carbon	328.5 mg.l ⁻¹
Total nitrogen	277 mg.l ⁻¹

Platinum anode, platinum cathode

Five repetitions resulted in good reproducibility. Unlike the model waters, the solution in the electrolyser was yellow after the experiences and it clearly smelled of chlorine, which was most likely generated from the chlorides present. After the termination of measurements, phenol concentration in the solution was 1.103 mg.l⁻¹ (0.012 mol.l⁻¹), the resulting COD was 699 mg.l⁻¹ and the specific conductance was 8.57 mS.cm⁻¹. Phenol degradation from waste water occurred with the efficiency of 60.78 %. The charge used was 3075 C and the velocity constant was $4.73 \cdot 10^{-5} \pm 5.87 \cdot 10^{-6} \text{ s}^{-1}$ with the corresponding $t_{1/2} = 19271 \text{ s}$.

Graphite anode, platinum cathode

Even in this case good reproducibility was obtained after five repetitions. Unlike when the Pt anode was used, there was no observable generation of chlorine. The resulting COD was 254 mg.l⁻¹ under the specific conductance of 9.79 mS.cm⁻¹. Phenol degradation occurred with the efficiency of 76.51 %, the charge used was 3027 C. The average velocity constant was $7.67 \cdot 10^{-5} \pm 8.19 \cdot 10^{-6} \text{ s}^{-1}$.

Boron-doped diamond anode, platinum cathode

The conditions were set in the same way as with the previous measurements but the repetitions were not reproducible. As with the model waters, phenol was polymerized, with the formation of polymer suspension that was hard to filter. After the termination of the experiment, the average final COD after 24 hours was CHSK 409 mg.l⁻¹ and conductivity was 8.84 mS.cm⁻¹.

Discussion and conclusion

No problems occurred during direct phenol oxidation when inert platinum anodes were used, both in model and real landfill waters. However, when carbon anodes were used, phenol oxidation was accompanied by the simultaneous oxidation of anode surfaces. The smooth surface of the electrode thus eventually turned into a porous one and, as a result of the mixing of the reaction mixture, micro-particles of oxidized carbon were being gradually released into the solution from the electrode; these particles may have served as absorbent material disturbing the spectrophotometric determination of phenol using the reaction with 4-AAP, which resulted in the need of having to carry out a laborious filtration of each sample before its analysis. When the BDD anode was used, phenol was polymerized in all cases regardless of the pH value of the environment. In acid environment, the polymerized phenol was separated in the form of lumpy substance. In alkaline environment, the particles of polymerized phenol created a suspension that was gradually being

separated from the solution, it was very difficult to filter and it distorted the spectrophotometric evaluation of the remaining phenol unaffected by the reaction. In addition, the partially polymerized phenol created a sticky film on the anode, thereby reducing the active surface of the electrode and increasing electric resistance. Thus, the surface of the BDD anode had to be cleaned from time to time (mechanically or by means of changing the polarity of the electrodes). Another method of phenol degradation from model waste waters was Fenton reaction. The measurements were taken at three pH levels – 2, 3, and 4. The proportions of hydrogen peroxide and Fe^{2+} were always 10:1, 25:1 and 50:1. The degradation was best at pH 4. By contrast, there was no degradation at all at pH 2. As regards the practical applicability, there is a high efficiency of phenol degradation when carbon anodes are used: this resulted in 75 % and 86 % efficiency. On the other hand, the testing of BDD electrodes resulted in a certain degree of disappointment because we could not find such operating conditions – neither for model nor for real landfill waters – that would not lead to phenol polymerization before its electrochemical oxidation.

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