

Purification of toxic wastewater

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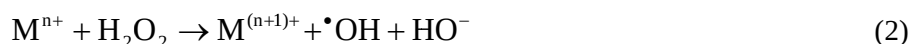
1 Introduction

New methods of toxic wastewater purification need to be found in industry as the traditional procedures are ineffective. This water contains mostly toxic, excitable, explosive or environmental unfriendly materials. Most of these substances are either very difficult or not biological degradable at all. The use of the AOPs¹ (Advanced Oxidation Processes) is the solution. All AOPs generate free hydroxyl radical. These radicals can be generated by chemical reaction, electrochemically or by using UV irradiation.

Fenton process² (1) and photo Fenton process (7) and its various modifications also belong to AOPs technologies.



Fenton process and its modifications can be divided into two groups. Reactions of the first group are classified by using metallic cations: frequently used Fe^{2+} also Cu^+ , Ti^{3+} , Cr^{2+} and others (2). All of these cations react analogously as in the classical Fenton reaction.



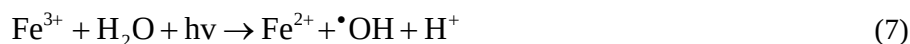
Fe^{3+} can be used, but reaction is much slower, due to Fe^{3+} reduction to Fe^{2+} .



Reactions of the second group are classified by oxidizing reagent. Degradation of this reagent produce hydroxyl radicals. Hydrogen peroxide, hypochlorous acid³ (4) or nitrous acid⁴ (5,6) can be used. Nitrous acid reacts with hydrogen peroxide at first. Then water and peroxonitrous acid (5) are produced.



Photochemical Fenton process (7,8), in comparison with classical Fenton process, uses UV irradiation and light. (180-400 nm).





Oxidizing reaction occurs under standard pressure in acidic background (pH = 3,0) and it is exothermic.

Fenton processes have many limitations. One of these limitations is an acidic background. In neutral or alkali background the reaction is much slower or does not work at all. The other limitation is with substances, which can be degraded by these reactions. Some substances are not oxidized by Fenton reaction, e.g. acetone⁷. The other disadvantage is the possibility of water toxicity increasing within the reaction. That is why it is necessary to know all the oxidation levels. Many times these levels are unpredictable mainly when more substances are present.

According to reasons written above, it was necessary to choose the proper model wastewater. That is why the phenol water was used. This water commonly used for these kind of the measurement as all oxidation levels of phenol are known.

The next possibility of Fe^{2+} batching is electrolytic anode dissolving^{5,6}. This process is controlled by Faraday law⁸:

$$\frac{m}{M} = \frac{I \cdot \tau}{|z| \cdot F} \quad (9)$$

The advantage of this application is that the amount of dissolved iron is exactly regulated. Moreover, the pollutants are oxidized at the anodic area.

The design of an apparatus for toxic wastewater is the aim of the experiments. Thanks to this apparatus the substances should be partly or fully degraded. After the degradation water could be treated by standard technological processes. The apparatus should not have a big trap circuit, due to apparatus low dimension.

2 Experimental

All measurements were carried out in transparent cylindrical vessel with flat bottom of inner diameter ($D=155\text{mm}$). The vessel was equipped by four radical plastic baffles ($b=20\text{mm}$; $h=2\text{mm}$). Pitched six blades impeller ($d=65\text{mm}$; $h=35\text{mm}$; CVS 69 1020) covered in Polyurex layer (mat V1605/0000) was used to homogenize the batch. Impeller speed was always 150 RPM. The pH values were measured by DULCOMETR (D1CAW0P20001G210G) with the probe DULCOTEST (PHEX 112 SE) and redox were measured by DULCOMETR (D1CAWOR20001G210G) with the probe DULCOTEST (RHEX-Pt-SE). DC source RFT 3217 (U 0÷30V; I 0÷10I). The temperature was measured by mercurial thermometer.

The chemicals were of G.R. purity. Model solution consisted of demineralized water and phenol ($c=0,5 \text{ g}\cdot\text{l}^{-1}$). The solution volume was 1,5l. Chemical oxygen demand⁹ (COD, in Czech CHSK) was measured. It was used for comparison of all measurement.

The reaction time of the experiment was 15 minutes due to the wastewater treatment technology. Longer reaction time would cause the undesirable trap circuit.

Before every CHSK was measured, the solution was always alkalized. The results treated this way were than exacter due to the separated Fe^{2+} . These ions were precipitated and filtrated. The redundant hydrogen peroxide was decayed in alkali background.

Electrode pairs were made of dissolved iron anode and a cathode cell made from titanium.

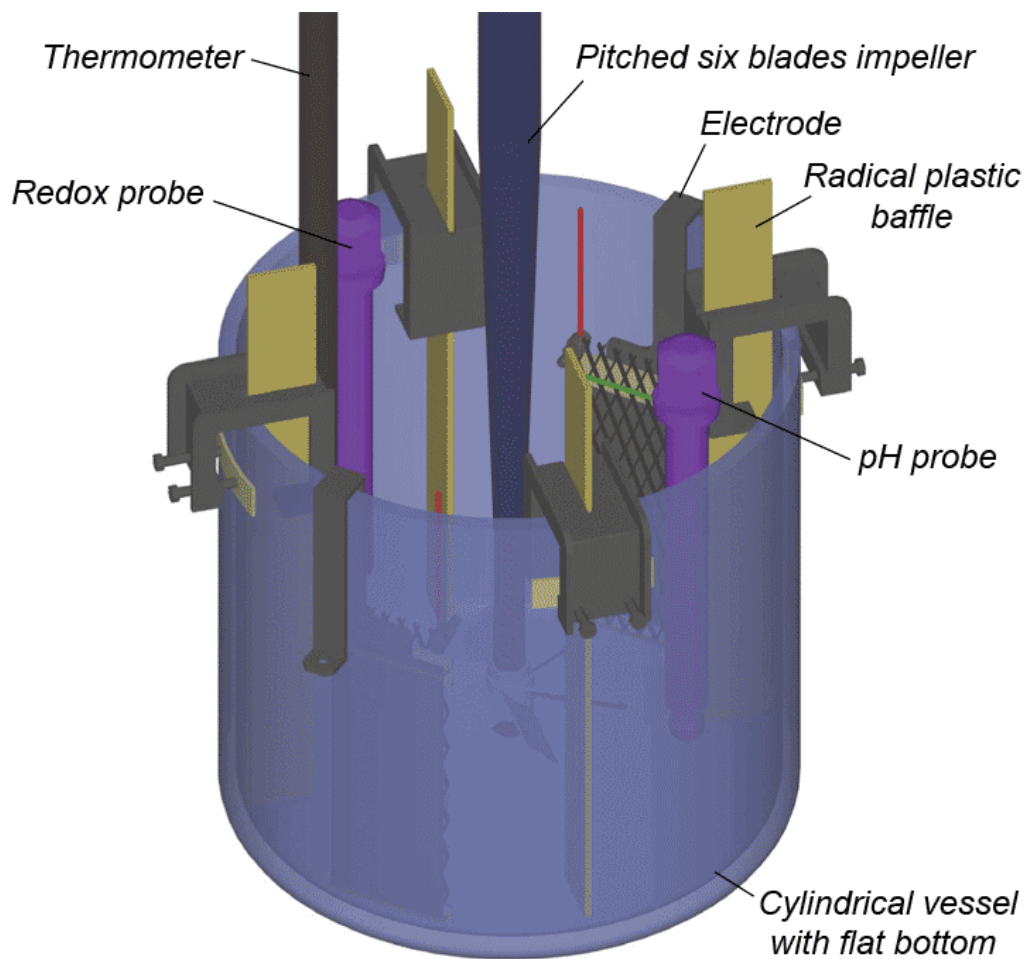


Fig. 1: Layout of experiments

2.1 Fenton process

Ferrous sulfate heptahydrate ($c=0,87 \text{ g}\cdot\text{l}^{-1}$) was added into the model wastewater as the source of Fe^{2+} . After that the sulfuric acid (25%) was added to gain value pH 3. The Source of free hydroxyl radicals is hydrogen peroxide (30%). It is supposed that the hydrogen peroxide is wholly consumed after 15 minutes and the reaction is finished. After the reaction the model water is alkalized by water solution of calcium hydroxide ($c=100 \text{ g}\cdot\text{l}^{-1}$). Better filterability is reached by adding a water solution of flocculant PK Sokoflok 16 ($c=0,1 \text{ g}\cdot\text{l}^{-1}$).

2.2 Electrochemical Fenton process

Dissolved iron anode is the source of Fe^{2+} for this reaction. This process was controlled by Faraday law (9), the amount of dissolved Fe^{2+} was directly proportional to current. The current value was chosen 1 A for all measurements. Fe^{2+} ($m=0,261 \text{ g}$) is dissolved within this time. This amount is equal to Fe^{2+} in heptahydrate used in Fenton reaction. One (I) or two (II) pairs of electrodes are used.

The conductivity of the model wastewater increased by adding inorganic salts, such as chloride or sulphate. The pH value still have to be 3 as at the beginning of the reaction. Hydrogen peroxide (30%) is the source of free hydroxyl radicals again.

After the reaction the model water is alkalized by water solution of calcium hydroxide ($c=100 \text{ g}\cdot\text{l}^{-1}$) or stronger sodium hydroxide ($4M$). Better filterability is reached by adding water solution of flocculant PK Sokoflok 16 ($c=0,1 \text{ g}\cdot\text{l}^{-1}$).

2.2.1 Regime of dosage hydrogen peroxide

The measurement was carried out with two electrodes. The Conductivity of model wastewater is raised by adding potassium chloride ($c=1,0 \text{ g}\cdot\text{l}^{-1}$). Then the pH was modified to value 3 by sulfuric acid (25%). Hydrogen peroxide (30%) is batched in two regimes:

- c(0) – Hydrogen peroxide was added at the beginning of the process ($\tau=0s$) and then the electrodes were connected immediately. The current value was constant during the process.
- c(5) – hydrogen peroxide was added after five minutes of the process. The current value was constant during the process.

After reaction the model water was alkalized by water solution of calcium hydroxide ($c=100 \text{ g}\cdot\text{l}^{-1}$) and water solution of flocculant PK Sokoflok 16 ($c=0,1 \text{ g}\cdot\text{l}^{-1}$) was added for better filterability.

2.2.2 One and two pairs of electrodes

When one pair of electrode was used, the anode and cathode were placed at the opposite side, i.e. $14cm$ far away. When two pairs of electrode were used, the distance between the anode and cathode of one pair was $1,8mm$. Each pair of electrodes was placed at the opposite side of the vessel perimeter.

Potassium chloride ($c=1,0 \text{ g}\cdot\text{l}^{-1}$) was used to raise the conductivity of solution. Then the pH was modified to value 3 by the sulphuric acid (25%). Hydrogen peroxide was added at the beginning of the reaction ($\tau=0s$) and then the electrodes were connected immediately. This took 15 minutes, i.e. regime c(0). Calcium hydroxide ($c=100 \text{ g}\cdot\text{l}^{-1}$) solution caused the alkalization. Water solution of flocculant PK Sokoflok 16 ($c=0,1 \text{ g}\cdot\text{l}^{-1}$) was added for better filterability.

2.2.3 Electrolyte

Calcium chloride was used in addition to potassium chloride. The amount of calcium chloride equals to the constant concentration of dissolved chloride ions in the model wastewater.

The other possibility was using the sulphate instead of chloride. The constant concentration of the dissolved ions had to be held in all. These sulphates were used: NaSO_4 , $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3\cdot 16\text{H}_2\text{O}$

3 Results and discussion

The CHSK was measured by Kubel's method due to the technical reasons. The time of the boiling was shortened from 10 minutes to 5 minutes.

The pH and redox values were measured too. These quantities were important to know due to the next wastewater treatment.

3.1 Fenton process

Results of this measurement are also the comparison values to other measurements which carried out were under different conditions.

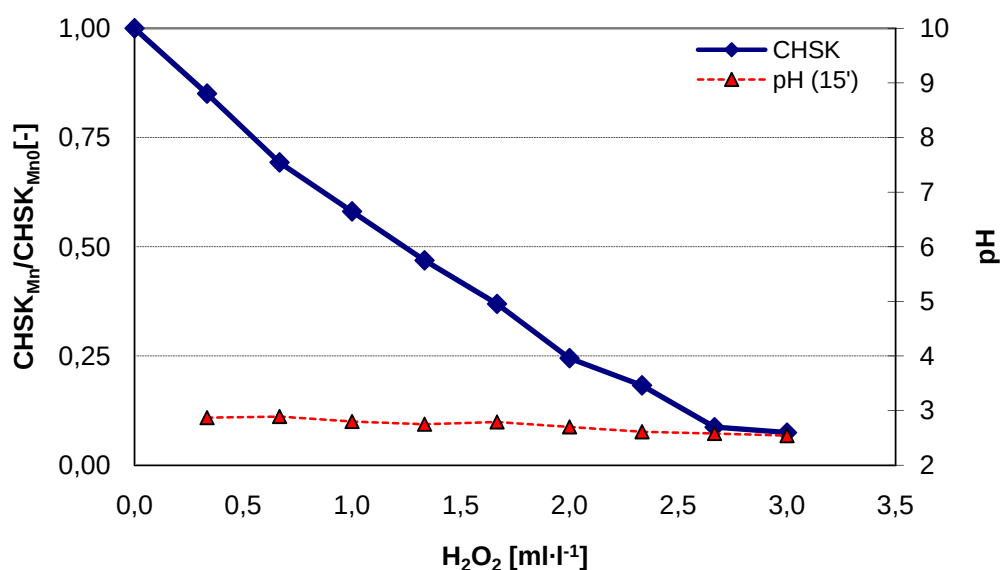


Fig. 2: Fenton process - Phenol ($0,50 \text{ g}\cdot\text{l}^{-1}$); H_2SO_4 ($\sim 0,2\text{ml}$, 25%); $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ($0,87 \text{ g}\cdot\text{l}^{-1}$); H_2O_2 (30%); $\text{Ca}(\text{OH})_2$ ($10\div 15\text{ml}$, $100 \text{ g}\cdot\text{l}^{-1}$); PK Sokoflok 16 (10ml , $0,1 \text{ g}\cdot\text{l}^{-1}$), reaction time: 15 minut.

3.2 The effect of hydrogen peroxide dosage

The effectivity of the process decreased when the hydrogen peroxide was added 5 minutes after the start of the process. It is caused by the electrolysis of the electrolyte, since the pH of the solution is rising during the electrolysis. This proved that the hydrogen peroxide dosage is very important for the process.

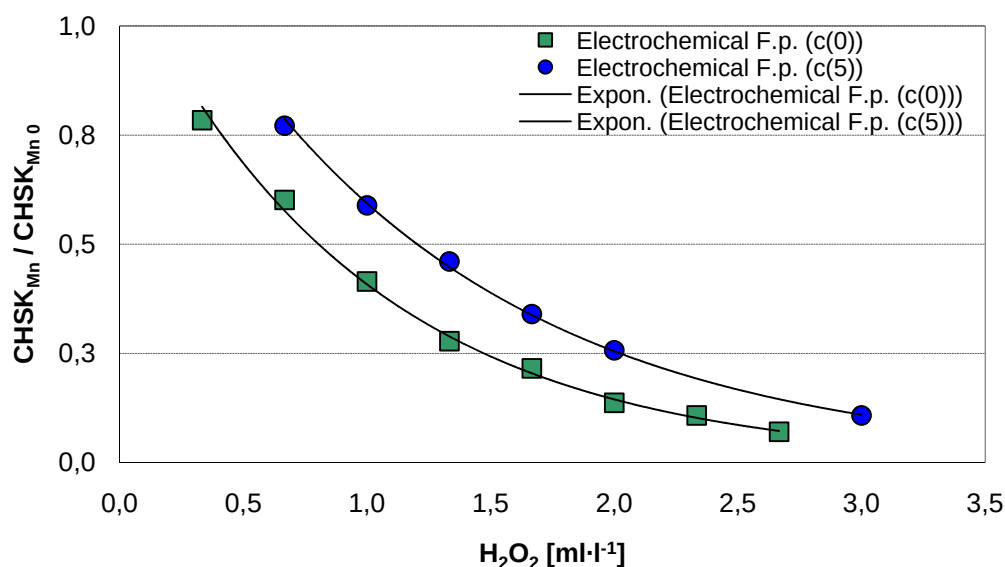


Fig. 3: The effect of H_2O_2 dosage - Phenol ($0,50\text{g}\cdot\text{l}^{-1}$); H_2SO_4 ($\sim 0,2\text{ml}$, 25%); KCl ($1,0\text{g}\cdot\text{l}^{-1}$); H_2O_2 (30%); $\text{Ca}(\text{OH})_2$ (15ml , $100\text{g}\cdot\text{l}^{-1}$); PK Sokoflok 16 (5ml , $0,1\text{g}\cdot\text{l}^{-1}$), reaction time: 15 minutes, two pairs of electrodes.

3.3 One or two pairs of electrodes usage

The comparison of CHSK measurements shows that the usage of the two pairs (II) of electrodes is more convenient. When one pair of electrodes is used, the quadruple amount of

potassium chloride is necessary though the voltage is doubled. Moreover, all parts of the apparatus which were in contact with the wastewater, produced the significant amount of iron.

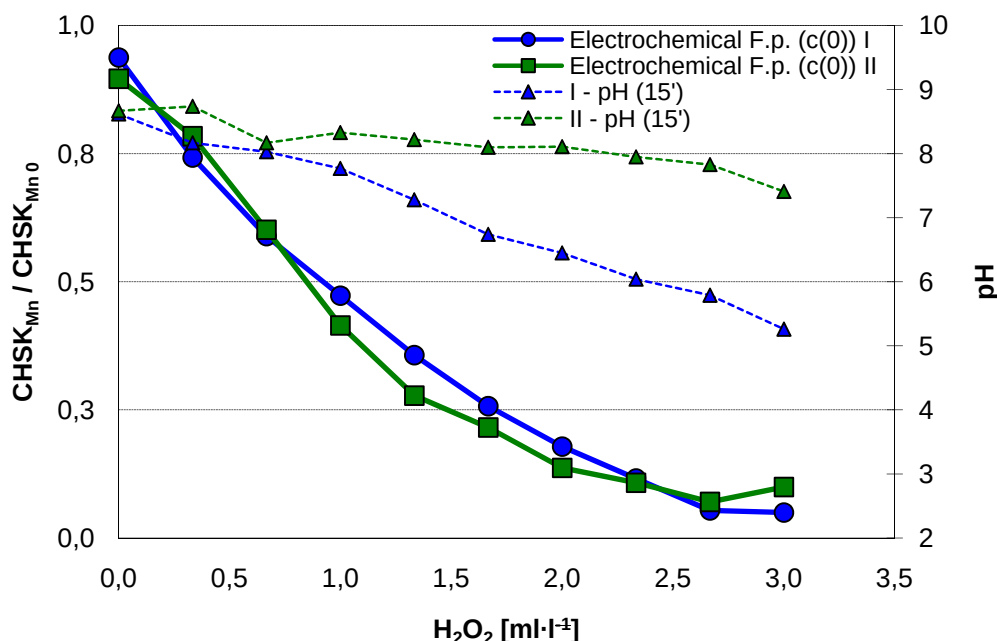


Fig. 4: One or two pairs of electrodes usage - Phenol ($0,50\text{g}\cdot\text{l}^{-1}$); H_2SO_4 ($0,2\div 0,6\text{ml}$, 25%); KCl ($1,0\text{g}\cdot\text{l}^{-1}$ (I), $4,0\text{g}\cdot\text{l}^{-1}$ (II)); H_2O_2 (30%); $\text{Ca}(\text{OH})_2$ ($15\div 50\text{ml}$, $100\text{g}\cdot\text{l}^{-1}$); PK Sokoflok 16 ($5\div 15\text{ml}$, $0,1\text{g}\cdot\text{l}^{-1}$), reaction time: 15 minutes, two pairs of electrodes.

3.3.1 Electrolyte

A) chloride:

Two chloride electrolyte were used: potassium chloride ($c=1,0\text{g}\cdot\text{l}^{-1}$) and calcium chloride ($c=0,74\text{g}\cdot\text{l}^{-1}$). The amount of dissolved chloride anions in the model wastewater must be strictly constant. CHSK measured values and pH were similar when these electrolytes were used.

This means that chlorides support conductivity very well. On the other hand the potassium chloride is unsuitable according to the technology of the wastewater treatment as Hydroxide potassium is produced due to electrolyte decay and this by-product does not coagulate. Then the filtration is very slow and sludge appears in the filtrate.

In contrast to potassium chloride the calcium chloride is consumed in fewer amount and it is good filterable. pH increase in alkali region which is common to both chlorides. It can be an advantage, the less amount of calcium hydroxide is necessary for the process to dissolve the redundant Fe^{2+} . But the effectivity of the process decreased. The constant current value is held during the whole purifying process thanks to the chlorides.

B) sulphate:

The other possibility was to replace chloride electrolyte by sulphate. Sodium sulphate ($c=5,5\text{g}\cdot\text{l}^{-1}$) was used as the first. Upper limitation of the voltage at electrodes was 30V.

This sulphate is absolutely unsuitable. Sodium ions inhibit the coagulation of by-products during the reaction, that is why a big amount of calcium hydroxide water solution and flocculant water solution is needed. However, total coagulation is not reached and the filterability is lowered. And this causes significant inaccuracies in CHSK measuring.

The other electrolytes were calcium sulphate dihydrate ($c=6,67 \text{ g}\cdot\text{l}^{-1}$), cupric sulphate pentahydrate ($c=9,7 \text{ g}\cdot\text{l}^{-1}$) and aluminum sulphate hexadecahydrate ($c=8,1 \text{ g}\cdot\text{l}^{-1}$).

The pH value was always under 4,1 when sulphates were used as electrolyte except for calcium sulphate dihydrate.

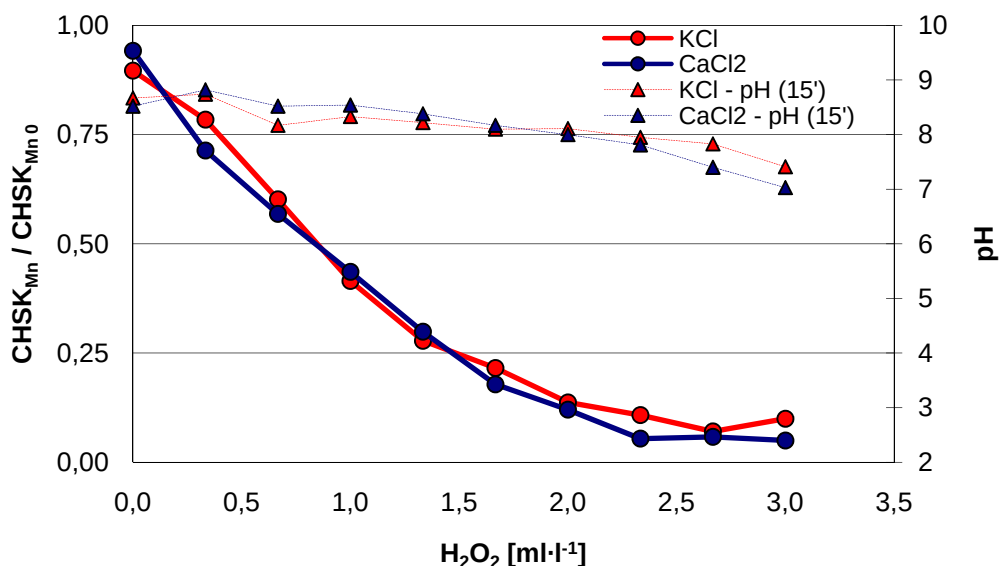


Fig. 5: Electrolyte - chloride - Phenol ($0,50 \text{ g}\cdot\text{l}^{-1}$); H_2SO_4 ($0,3\div 0,6 \text{ ml}$, 25%); KCl ($1,0 \text{ g}\cdot\text{l}^{-1}$); CaCl_2 ($0,74 \text{ g}\cdot\text{l}^{-1}$); H_2O_2 (30%); $\text{Ca}(\text{OH})_2$ ($10\div 15 \text{ ml}$, $100 \text{ g}\cdot\text{l}^{-1}$); PK Sokoflok 16 (10 ml , $0,1 \text{ g}\cdot\text{l}^{-1}$), reaction time: 15 minutes, two pairs of electrodes.

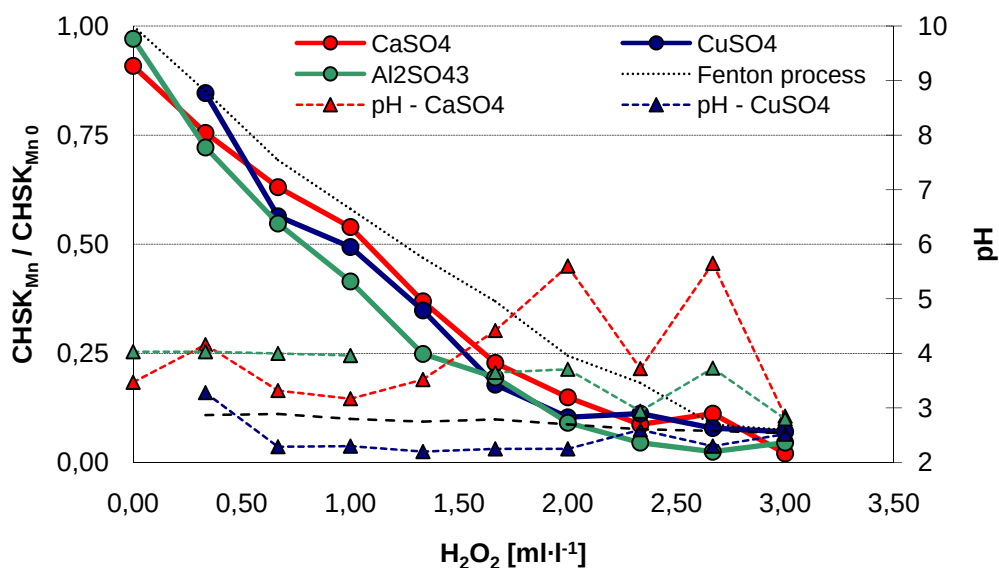


Fig. 6: Electrolyte - sulphate - Phenol ($0,50 \text{ g}\cdot\text{l}^{-1}$); H_2SO_4 ($\sim 0,3\div 0,6 \text{ ml}$, 25%); $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ($6,67 \text{ g}\cdot\text{l}^{-1}$); $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ ($9,7 \text{ g}\cdot\text{l}^{-1}$); $\text{Al}_2(\text{SO}_4)_3\cdot 16\text{H}_2\text{O}$ ($8,1 \text{ g}\cdot\text{l}^{-1}$); H_2O_2 (30%); $\text{Ca}(\text{OH})_2$ ($\sim 10\div 15 \text{ ml}$, $100 \text{ g}\cdot\text{l}^{-1}$); $\text{Ca}(\text{OH})_2$ ($25\div 30 \text{ ml}$, 4M); PK Sokoflok 16 ($10\div 15 \text{ ml}$, $0,1 \text{ g}\cdot\text{l}^{-1}$), reaction time: 15 minutes, two pairs of electrodes.

Calcium sulphate dihydrate – Bad dissociation limits the usage of this electrolyte. Dissociation is indirectly proportional to the temperature – this is reflected in the final pH. Filterability is good and the strong hydroxide is not necessary to use. Calcium hydroxide water solution ($c=100 \text{ g}\cdot\text{l}^{-1}$) was enough to alkalize the wastewater.

Cupric sulphate pentahydrate – It is the best electrolyte from the energetic point of view. The voltage applied at the beginning is higher than that at the end of measurement. But The pH value is lower than at the beginning, which was a disadvantage and the reason to use sodium hydroxide water solution (4M) instead of previously used calcium hydroxide water solution ($c=100\text{ g}\cdot\text{l}^{-1}$). The other disadvantage in this case was the production of Copper at the cathode.

Aluminum sulphate hexadecahydrate – in this case, CHSK is the lowest. Applied voltage is approximately a half a higher than by the voltage at the cupric sulphate. The usage of This electrolyte is the most effective. The advantage is that during the whole process the pH value of the solution is from 3 to 4. Moreover, aluminum ions are catalyzer when the phenol is degraded and cause better filterability. In comparison to other used sulphates this filtrate is slightly coloured.

The disadvantage is that the big amount of the sludge is produced and it settles badly. The concentrated sodium hydroxide water solution (4M) is necessary to alkalize the solution.

4 Conclusions

From our experiments the following conclusions might be drawn:

- ◆ Hydrogen peroxide added at the beginning of the process ($\tau=0s$) – effectivity lower by acidity rising when Fe^{2+} dissolved.
- ◆ Two pairs of electrodes better due to lower used concentration of electrolyte – cathode and anode closer to each other.
- ◆ Electrolyte:
 - chloride – small amount and good conductivity, the best usage of calcium chloride.
 - sulphate – constant pH value

The best usage of them is aluminium sulphate hexadecahydrate: pH always under value 4, almost colourless solution after filtration, the lowest CHSK.

Symbols

b	[mm]	baffle width
c	[g · l ⁻¹]	concentration
D	[mm]	vessel diameter
d	[mm]	impeller diameter
F	[C · mol ⁻¹]	Faraday's constant; $F=96485\text{ C}\cdot\text{mol}^{-1}$
h	[mm]	Impeller off-bottom clearance
h	[mm]	baffle thickness
I	[A]	current
M	[g · mol ⁻¹]	molar mass
m	[g]	mass
z	[1]	valence number of the substance
τ	[s]	time

Acknowledgements

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