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REDUCTION OF HYDROCARBON CONTAMINATIONS IN THE CHEMICAL OXIDATION PROCESS

REDUKCJA ZANIECZYSZCZEŃ WĘGLOWODOROWYCH W PROCESIE UTLENIANIA CHEMICZNEGO

Abstract

Chemical oxidation methods have been recently applied for degrading toxic or hardly degradable pollutants in sewage. Among the frequently used oxidants, hydrogen peroxide is environmentally friendly. To increase the efficiency of oxidation, the reactions are activated with ions (Fe^{2+}), UV radiation or ozone. The mixture of hydrogen peroxide and iron(II) makes the so-called Fenton's reagent have a strong oxidizing quality. The results of laboratory experiments on hydrocarbons removal from contaminated water are presented in the paper. The efficiency of chemical oxidation with the use of hydrogen oxide and Fenton reactions for removing BTEX hydrocarbons (benzene, toluene, ethylbenzene, xylene) from contaminated water was compared.

Keywords: sewage treatment, chemical oxidation, Fenton's reaction, hydrocarbons

Streszczenie

Obecnie w coraz większym stopniu do degradacji zanieczyszczeń toksycznych lub trudno rozkładalnych zawartych w ściekach wykorzystuje się metody chemicznego utleniania. Wśród wielu stosowanych w praktyce utleniaczy bezpieczny dla środowiska jest nadtlenek wodoru. W celu zwiększenia efektywności procesu utleniania aktywuje się zachodzące reakcje jonami (Fe^{2+}), promieniami UV lub ozonem. Mieszanina nadtlenku wodoru i żelaza (II) tworzy tzw. odczynnik Fentona, reagent charakteryzujący się silnym oddziaływaniem utleniającym. W artykule przedstawiono wyniki badań laboratoryjnych usuwania węglowodorów z zanieczyszczonych wód. Dokonano również porównania efektywności oczyszczania skażonych wód węglowodorami z grupy BTEX (benzen, toluen, etylobenzen, ksylen) z zastosowaniem utleniania chemicznego z wykorzystaniem nadtlenku wodoru oraz z zastosowaniem reakcji Fentona.

Słowa kluczowe: oczyszczanie ścieków, utlenianie chemiczne, reakcja Fentona, węglowodory

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1. Introduction

Conventional methods of sewage treatment are not always effective or efficient, especially when hardly biodegradable substances are to be removed.

Sewage treatment creates serious technical and technological problems. Industrial waste is usually non-homogeneous, rich in organic matter and containing specific, frequently toxic components. Presently, the chemical oxidization method is applied more and more frequently for degrading toxic or hardly biodegradable substances present in industrial waste. Among many applied oxidants, hydrogen peroxide is used. It is environmentally friendly as it does not form dangerous by-products with the oxidized compounds. The only products of decomposition are water and oxygen. Efficient treatment of sewage with hydrogen peroxide frequently requires activating with ions Fe^{2+} (Fenton's reaction), ozone or UV radiation [2].

Literature data reveal that Fenton's reagent is one of the most efficient compositions based on hydrogen peroxide [2, 3]. This method can be effectively used for degrading various contaminations owing to the activity of hydroxyl radicals which can oxidize nearly all organic contaminations [2, 3], e.g. phenol ketone, alcohol, benzene, nitrobenzene, perchlorethylene, toluene, p-toluene, aniline, p-nitrophenol, humus compounds [2].

Oxidizing o-toluidine, urea and melamine resins in sewage with Fenton's reagents caused their degradation by 60%, 84% and 84%, respectively; p-methoxyaniline and aniline by 70–80%; ethers and ketones by 75%; colouring agents from textile industry by 95%, and atrazine – a hardly degradable and cancerous pesticide – nearly completely [2]. The investigations [2] revealed that the Fenton's reaction can be successfully applied for cleaning industrial sewage from chemical synthesis, e.g. production of maleic acid anhydrite, urea glues, alcohols; from pesticides production, e.g. from sewage containing: γHCH, α and β-HCH, DDT, DMDT, fenitrotion and chlorfenwinfos, textile production waste and removal of colouring agents from the waste [2].

Fenton's reagent was also proved to be useful for destabilizing oil emulsions. The main advantage of Fenton's reaction is the separation of oil and water phase, as well as an effective decrease of the Chemical Oxygen Demand (COD) index by ca. 88–90% [2, 4].

Fenton's reagent may be also applied for removing phosphorus compounds from food industry waste [14]. The organic phosphorus was proved to be nearly completely removed from the waste (ca. 100%); besides, good results were obtained by removing organic substances, manifesting themselves in the lowered COD value. Organic phosphorus can be removed from fat waste by decomposing compound organic substances, in the course of which phosphorus is liberated and precipitated. In the case of Fenton's reagent, the liberation and precipitation processes take place concurrently [14].

Investigations were also conducted on cleaning coloured and phenol waste employing modified Fenton's reagent with steel cuttings as an alternative source of iron ions. Owing to the possibility of wider practical applicability of this method, the process was carried out in a flow reactor. The cleaning effect for both waste fluids in most of the operation of the column was equal or higher than 99% (99.1 to 99.9% for coloured waste, and 99.0 to 99.7% for phenol waste, respectively) [6].

Fenton's reaction was also used for decomposition of the oxidizing ethyl-t-butyl ether (ETBE) in water petrol extracts. This is the only possible way of removing ethyl-t-butyl ether from water contaminated with petrol containing this component [11, 12]. Oxygen

components of petrol, including ethyl-tert-butyl ether (ETBE) and methyl-tert-butyl ether (MTBE) are easier to dissolve in water than hydrocarbons and are very weakly biodegradable. When they are close to refineries, gas stations or in failure situations, they migrate to groundwater or water reservoirs creating a potential environmental hazard. The effectiveness of cleaning water extract of petrol containing ETBE as a function of the amount of catalyst and the duration of the oxidizing process was determined in [11, 12]. Owing to the possibility of using the method for cleaning groundwater, the experiments were made at an ambient temperature.

Because of its strong oxidizing qualities, Fenton's reagent can be used for degrading organic contaminations both in sewage sediments produced during the biological treatment of sewage and containing a considerable amount of organic matter, pathogenic organisms and those which are produced in, e.g. chemical or food production processes.

Fenton's reagent causes a considerable reduction of organic matter in sediments, also increasing physical properties, the structure of sediments, their sedimentary properties and dehydration qualities. Using the reagent for sediments neutralization, the heavy metals content, e.g. Zn, Cd and Ni can be reduced. In this way the oxygen sediment stabilization process can also be intensified [1].
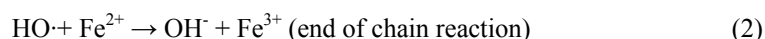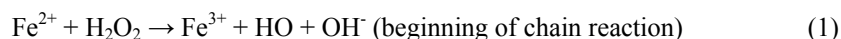
Owing to the availability of reagents, the simplicity of the procedure and apparatuses, Fenton's reagent is a promising method of sewage treatment.
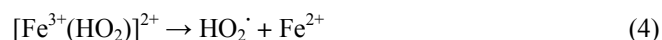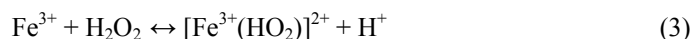
2. Mechanism of reaction

Hydrogen peroxide and iron(II) compounds form the so-called Fenton's reagent, which has a very strong oxidizing character.

The course of processes connected with H_2O_2 decomposition with the participation of iron(II) is complex, and the scheme of the mechanism was presented in, e.g. [13].

Fe^{2+} ions initiate and catalyze H_2O_2 decomposition, and as a result hydroxyl radicals are formed. The radicals trigger out a complex reaction in the water environment.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO + OH^- \text{ (beginning of chain reaction)} \qquad (1)$$

$$HO\cdot + Fe^{2+} \rightarrow OH^- + Fe^{3+} \text{ (end of chain reaction)} \qquad (2)$$

Thus produced iron(III) ions are a catalyst in the decomposition of hydrogen peroxide into oxygen and water. In the course of the reaction iron(III) and hydroxyl radicals are also formed. The reactions lead to the formation of Fe^{2+} ions from Fe^{3+} ions.

$$Fe^{3+} + H_2O_2 \leftrightarrow [Fe^{3+}(HO_2)]^{2+} + H^+ \qquad (3)$$

$$[Fe^{3+}(HO_2)]^{2+} \rightarrow HO_2\dot{} + Fe^{2+} \qquad (4)$$

The reaction of hydrogen peroxide and iron(III) (reactions 3 and 4) is defined as similar to Fenton's reaction [7, 18].

A number of Fenton's methods are known. These modifications frequently lie in introducing Fe^{3+} ions instead of Fe^{2+} and exceeding H_2O_2 in comparison to the amount of

iron used. In Fe^{3+}/H_2O_2 system Fe^{2+} ions are reproduced and $OH\cdot$ (as well as other radicals participating in the oxidization and reduction of organic compounds) are generated. The reactivity of contaminations and oxidants and reducers generated in reactions initiated in the Fe^{3+}/H_2O_2 system conditions the effectiveness of the process

$$Fe^{2+} + HO_2\cdot \rightarrow Fe^{3+} + HO_2^- \tag{5}$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \tag{6}$$

$$OH\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot \tag{7}$$

The course of the H_2O_2 reaction reveals that the so-called $OH\cdot$ sweeper (reaction 7) and initiator (reaction 1) may occur.

Hydroxyl radical may oxidize organic compounds (RH) by severing protons and creating alkyl radicals ($R\cdot$), which are highly reactive and may undergo further oxidization [9, 16, 19]

$$RH + OH\cdot \rightarrow H_2O + R\cdot \rightarrow \text{further oxidization} \tag{8}$$
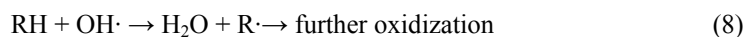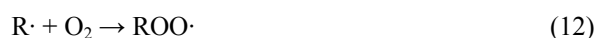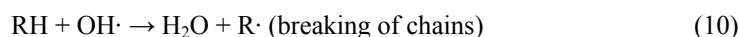
The general notation of Fenton's reaction was simplified by Walling [17], who also accounted for water dissociation

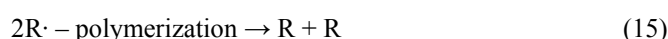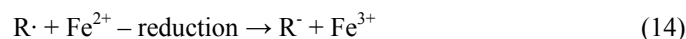$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \tag{9}$$
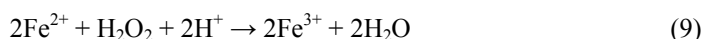
This notation suggests that H_2O_2 decomposition may take place if H^+ ions are present. This means that a low-pH environment will be advantageous for the generation of the maximum number of hydroxyl radicals.

In the presence of organic matter (RH), excess of iron(II) and low pH, the hydroxyl radicals may be attached to aromatic or heterocyclic compounds.

They may also sever the hydrogen atom, thus triggering out a chain reaction of radicals oxidization [10, 17]

$$RH + OH\cdot \rightarrow H_2O + R\cdot \text{ (breaking of chains)} \tag{10}$$

$$R\cdot + H_2O_2 \rightarrow ROH + OH\cdot \tag{11}$$

$$R\cdot + O_2 \rightarrow ROO\cdot \tag{12}$$

Free organic radicals produced in the course of reaction 10 may be oxidized by iron(III), reduced by iron(II) or polymerized according to the following reactions [15]

$$R\cdot + Fe^{3+} - \text{oxidization} \rightarrow R^+ + Fe^{2+} \tag{13}$$

$$R\cdot + Fe^{2+} - \text{reduction} \rightarrow R^- + Fe^{3+} \tag{14}$$

$$2R\cdot - \text{polymerization} \rightarrow R + R \tag{15}$$
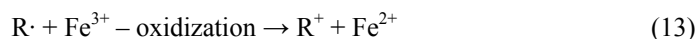
The succession of reactions (1), (2), (10) and (13) creates a scheme of Fenton's chain reaction.

The analysis of equations describing the reaction reveals that this mechanism is influenced by: hydroxyl radicals, iron(II), organic radicals, iron(III) and their reactions, which *ad extremum* may result in an inefficient decomposition of hydrogen peroxide, thus limiting the efficiency of oxidization of organic components. The maximum efficiency of the degrading process depends on the stoichiometric relations between Fe^{2+}, RH and Fe^{3+}. The course of decomposition is faster when $Fe^{2+}/H_2O_2 \geq 2$ [4].

Exceeding the optimum amount of H_2O_2 and Fe^{2+} may result in lowering the cleaning effect. This would be due to the reaction of H_2O_2 and/or Fe^{2+} and the produced OH· radicals. In such a case H_2O_2 and Fe^{2+} would act as the so-called "radical sweepers" (reaction 7).

Optimum conditions for Fenton reagent have been observed for pH 3–5. Lowering the effectiveness of contaminations removal in the above conditions is probably caused by H_2O_2 decomposition. At pH<3, the H^+ ion concentration is too high, causing that the hydrogen ion becomes the main acceptor of OH· radicals [3].

3. Methodology of experiments

The oxidization reaction was used in laboratory experiments for lowering the oil--products content dissolved in water solution. Among the oil-products contaminating the water environment, BTEX hydrocarbons (benzene, toluene, ethylbenzene, xylenes) are most water soluble.

For evaluating the effectiveness of BTEX removal from sewage by the oxidization method, the model sewage was prepared. It consisted of benzene, toluene, xylene and ethylbenzene, which were left over for 3 days to let them completely dissolve in the water medium.

Hydrocarbon compounds were oxidized with 30% hydrogen peroxide in the presence of a catalyst $FeSO_4 \cdot 7H_2O$ (Fenton's reaction). The reaction was carried out at a constant water temperature of $21^{\circ}C$ and constant pH equal to 3.5. Specific stages forecasted selecting optimum quantities of the catalyst and hydrogen peroxide for removing maximum quantities of contaminations from the sewage.

For the experiment's sake, samples of the solution were taken (100 cm^3 each) and reagents were added, leaving each sample for the time in which the full reaction could take place.

Lowering the total BTEX content was assumed to be the main criterion of contaminants removal. BTEX was determined with the gas chromatography methods with Head-Space extraction, in compliance with the standard PN ISO 11423-1. The measurements were performed on the Trace Ultra Thermo gas chromatograph with the DSQ-II mass spectrometer on the Rxi™-1ms Restek chromatography column (100% polydimethyl oxosilane; 0.25 µm film thickness, 30 m column length, 0.25 mm column diameter).

4. Discussion of results

The concentration of contaminations in water to be cleaned, as well as the results of investigations of BTEX oxidization with the use of Fenton's reaction are presented in Table 1.

Table 1

The Effectiveness of BTEX removal from water employing Fenton's reaction

Amount of introduced Fe^{2+} ions [mg]	Amount of admixed H_2O_2 [cm^3]	Analyzed component [$\mu g/dm^3$]					$\sum$ BTEX [$\mu g/dm^3$]
		benzene	toluene	etylobenzene	o-xylene	p,m-xylene	
Input sample		892.285	857.747	394.782	119.382	1,063.720	3,327.916
0.4	2	491.158	322.903	87.442	29.433	421.733	1,352.669
0.8	2	20.137	15.699	13.462	17.145	17.489	83.932
2.0	5	18.582	14.302	12.902	–	13.766	59.552
10.0	5	18.577	14.297	12.897	–	13.745	59.516
20.0	10	18.576	14.297	12.897	–	13.743	59.513
20.0	20	18.575	14.297	12.897	–	13.743	59.512
20.0	30	18.575	14.297	12.897	–	13.743	59.512
60.0	10	18.575	14.297	14.897	–	13.743	59.512
60.0	20	18.575	14.297	14.897	–	13.743	59.512
60.0	30	18.575	14.297	14.897	–	13.743	59.512

All measurements were made after the reaction was over. The reaction time for specific samples ranged from 1 to 48 hrs, depending on the amount of reagents used.

Using the lowest dose of catalyst $FeSO_4 x7H_2O$, from which 0.4 mg Fe^{2+} ions and 2 cm^3 H_2O_2 were introduced to the cleaned water, it was possible to remove nearly 60% of the total BTEX content as compared to the state before cleaning. When the ions content was doubled (0.8 mg Fe^{2+}), at the same amount of H_2O_2 a definitely higher degree of BTEX reduction was obtained (97.5%). In both cases the time needed for completing the reactions was long (ca. 40 hrs).

By using 2.0 mg Fe^{2+} and 5 cm^3 H_2O_2 the reaction was accelerated to ca. 8 hrs and the $\sum$ BTEX was reduced to 59.552 $\mu g/dm^3$. Further increasing Fe^{2+} ions and H_2O_2 did not improve the effectiveness of the process, but definitely shortened the time of water cleaning to 1 hr at 60.0 mg Fe^{2+} and 30 cm^3 H_2O_2.

The reaction time for samples with the below reagents quantities was the following:
3.5 hrs for 20.0 mg Fe^{2+} and 10 cm^3 H_2O_2; 2.5 hrs for – 20.0 mg Fe^{2+} and 30 cm^3 H_2O_2; and also 2.5 hrs for 60.0 mg Fe^{2+} and 10 cm^3 H_2O_2.

From among the removed hydrocarbons only for o-xylene the full decomposition and removal were obtained for 2.0 mg Fe^{2+} and 5 cm^3 H_2O_2.

The effectiveness of BTEX removal from model sewage with Fenton's reaction was compared to the effectiveness of the cleaning process of the same solution employing only H_2O_2. Samples of 100 cm^3 each were collected and 10 and 30 cm^3 H_2O_2 were admixed and left over for 8 hours. The results are presented in Tab. 2.

Table 2

The effectiveness of BTEX removal from water employing oxidization with H_2O_2

Amount of admixed H_2O_2 [cm^3]	Analyzed component [$\mu g/dm^3$]					$\sum$ BTEX [$\mu g/dm^3$]
	benzene	toluene	etylobenzene	o-xylene	p,m-xylene	
Input sample	892.285	857.747	394.782	119.382	1,063.720	3,327.916
10	231.462	202.464	48.997	22.496	242.905	748.324
30	212.266	183.091	43.611	21.832	210.497	671.297

The analysis of the obtained results reveals that cleaning water from BTEX with H_2O_2 enables lowering their content from 3,327.916 $\mu g/dm^3$ to the level of 671.297 $\mu g/dm^3$ for 10 cm^3, and the tripled quantity of H_2O_2 improved the result by only 3%.

5. Concluding remarks

The following conclusions were drawn on the basis of the performed experiments:
– the effectiveness of BTEX removal from water solutions with Fenton's method is conditioned by the amount of the used catalyst and hydrogen peroxide. Another important parameter is the time of reaction till the reagents are exhausted,
– for efficient cleaning of 100 cm^3 of model solution containing 3,327.916 $\mu g/dm^3$ BTEX the minimum quantity of the catalyst in the form of Fe^{2+} ions is 0.8 mg, and 30% hydrogen peroxide is 2 cm^3, respectively,
– by introducing 2.0 mg of Fe^{2+} and 5 cm^3 of H_2O_2 the BTEX contaminations in water solution were reduced by 98.2% and did not improve even at 10 and 30-time higher Fe^{2+} ion content and 6-time higher H_2O_2 content, respectively. The only difference was observed for the duration of reaction in the successive experiments from 1 to 48 hours.

Using only hydrogen peroxide for removing BTEX from water solutions is less effective and more costly than Fenton's reaction. Several times more hydrogen peroxide has to be used than in the case of a reaction in the presence of a catalyst. Even so, the final result is definitely worse.

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