

Original Research

Removing Phenols from Post-Processing Wastewater Originating from Underground Coal Gasification Using Coagulation-Flocculation and the H₂O₂/UV Process

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Abstract

Our paper presents the possibility of phenol removal from post-processing wastewater originating from an experimental simulation of the underground coal gasification process carried out in the Barbara Experimental Mine in Mikołów, Poland. The application of initial coagulation-flocculation processes with iron(II), iron(III), aluminium, titanium(IV), and zirconium(IV) and anionic flocculant has allowed phenols removal from 7.9% (pH 8, Zr⁴⁺ 400 mg/L) to 22.2% (for pH 8, Fe²⁺ 800 and 1,000 mg/L and for pH 8, Fe³⁺ 1,000 mg/L). The application of the coagulation-flocculation process and advanced oxidation in the H₂O₂/UV system resulted in a total reduction of phenolic concentrations in the treated wastewater by about 93% due to their reaction with OH• radicals, resulting from the UV rays impact on H₂O₂.

Keywords: phenols, wastewater, underground coal gasification, coagulants, advanced oxidation processes, AOPs

Introduction

Contamination of the natural environment, especially of surface waters with organic compounds, is connected to the constantly progressing process of industrialization in the world. Phenols and their compounds are toxic substances that are frequently present in industrial wastewater from petrochemical processes, chemical processing of coal, and the production of polymer resins,

pharmaceuticals, and more. Studies on effective methods of removal and degradation of phenolic compounds are important for protecting the natural environment against pollution [1]. In the wastewater originating from the refinery, phenols were found in the range 6-500 mg/L, in coke-plant effluents 28-3,900 mg/L, in wastewater from coal processing plants 9-6,800 mg/L, and in wastewater from the petrochemical industry 2.8-1,200 mg/L. In the case of wastewater from the production of pharmaceuticals, plastics, wood products, and paints, the concentration of phenols varied between 0.1 and 1,600 mg/L [2-3]. In wastewater from experimental

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coal gasification processes, the content of phenols was 11-3,090 mg/L and depended on the chemical composition of coal and the parameters of the gasification process [4-6]. Phenol is a toxic, carcinogenic, teratogenic, and potentially mutagenic compound and it is therefore one of the most important substances for which the U.S. Environmental Protection Agency (US EPA) has set a maximum emission limit of 0.5 mg/L [7-8]. For the same reasons, they determined a maximum phenols concentration in drinking water of 1µg/L. The conducted studies have shown that the use of chlorine to disinfect phenol-containing water leads to toxic 2-chlorophenol formation [9]. Phenols in concentrations over 2 mg/L are toxic to fish, and in concentrations from 10-100 mg/L cause the death of many aquatic organisms within 96 hours [10]. The removal of phenols from wastewater can be carried out by adsorption [11-12], extraction [13], reverse osmosis, and nanofiltration [14-15], perflation [16], and membrane distillation [17]. It is also possible to use chemical oxidation processes with ferrate(VI) and permanganate(VII) [18-19]. Wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) processes are also used.

In the second case, high temperature, high pressure, and catalyst additives are used [20]. Especially interesting and undertaken by many researchers seems to be the application of advanced oxidation processes (AOPs), which use hydroxyl radicals (OH•) formed in the reaction environment, which can react with most organic compounds, leading to their effective degradation. In addition to the classical Fenton method, its numerous modifications are used, such as: photo-Fenton or electro-Fenton processes, which usually lead to increased speed and final efficiency of the treatment process [21]. Among the methods of advanced oxidation, the H₂O₂/UV process is also used, whose advantage is that there is no need for the Fe(II) compounds presence to produce OH• and consequently avoid the formation of hydrated sediments of Fe(II) and Fe(III) hydroxides due to alkalisation of wastewater after the process is complete. The use of

the advanced H₂O₂/UV oxidation process allows for the degradation of many harmful substances such as steroid estrogens, 17β-estradiol, estriol, 17α-ethinylestradiol, phenolic xenoestrogens, and bisphenol A [22]. The purpose of the conducted research was to determine the removal effectiveness of brominated phenolic compounds present in wastewater from underground coal gasification by means of coagulation-flocculation and H₂O₂/UV processes. In the first step of the coagulation process, apart from the conventional coagulants, such as Fe(II), Fe(III) and Al salts, we also used Zr(IV), Ti(IV), and anionic flocculant. In the second stage, the H₂O₂/UV process degraded phenolic compounds remaining in coagulated and flocculated wastewater.

Materials and Methods

Materials and Chemical Reagents

The research was carried out on a laboratory scale using post-processing wastewater originating from experimental simulation of the underground coal gasification process conducted in the Barbara Experimental Mine in Mikołów, Poland. Pre-filtered post-processing wastewater was collected in a 1,000-L closed tank to remove coal tar and other insoluble residues. 30 L of averaged wastewater was collected from the tank in order to carry out the present study. The selected physical and chemical parameters of the wastewater used are shown in Table 1. Ferrous(II) sulphate (FeSO₄·7H₂O, Chempur, Poland), iron ferric(III) chloride (FeCl₃·6H₂O, Chempur, Poland), aluminum sulphate (Al₂(SO₄)₃·18H₂O, Chempur, Poland), zirconium(IV) oxychloride (ZrOCl₂·8H₂O, POCH, Poland), and titanium(IV) chloride (1.197 mol/L in HCl) were used as coagulants. 30% NaOH and 20% HCl was used for pH adjustment, and sediment flocculation was carried out using a solution of 0.025% anionic flocculant (Furoflock CW277, Chemische Fabrik Wocklum GmbH & Co. KG, Germany). Filtration after flocculation and sedimentation of sludge was carried out using hard qualitative filters (POCH, Poland). 30% H₂O₂ (Chempur, Poland) was used for advanced oxidation in the H₂O₂/UV system, and Na₂SO₃ (POCH, Poland) was used to remove the remaining H₂O₂. All chemical reagents used in the tests were of analytical purity. Studies using advanced oxidation were carried out by means of a glass 0.6 L photoreactor equipped with a UV lamp (254 nm) of 11W power (PURITEC HNS, OSRAM) housed in a quartz glass casing. The use of a magnetic stirrer enabled mixing of wastewater irradiated at a constant speed of 250 rpm, and cooling allowed the tests to be carried out at a constant temperature of 19.0±1°C.

Analytical Methods

The pH-value of wastewater was determined with the use of WTWinolab pH/IONCond 750 and SenTix81

Table 1. Physicochemical parameters of post-processing wastewater originating from UCG.

Parameter	Unit	Value
pH	-	7.5
Electrical conductivity at 20°C	µS/cm	4,180
Absorbance (UV254, dilution 1:40)	-	0.437
Turbidity	NTU	171
Colour	mg Pt/L	3,320
Chemical oxygen demand (COD)	mg O ₂ /L	3,050
Total organic carbon (TOC)	mg/L	910
Total nitrogen	mg/L	580
Sulfides	mg/L	0.81
Phenols	mg/L	1,360

combination electrode according to PN-EN ISO 10523:2012, and the specific electrical conductivity using TetraCon325 electrode according to PN-EN 27888:1999. Turbidity was determined by the nephelometric method using a Cyberscan IR Turbidimeter TB1000 according to PN-ISO 7027:2003 and color using a SPEKOL 1200 spectrophotometer according to PN-ISO 7887:2012. Absorbance was determined using a Cary 50 UV/VIS spectrophotometer at 1:40 dilution of analysed wastewater (water for HPLC) and using quartz cuvettes with optical path length of 1 cm. Chemical oxygen demand (COD) was determined by spectrophotometric method using sealed tubes and a PF-11 spectrophotometer according to PN-ISO 15705:2005, and total organic carbon (TOC) content according to high temperature combustion at 680°C with IR detection using TOC-L_{CPH} by Shimadzu according to PN-EN 1484:1999. Sulphides concentration was determined by the spectrophotometric method using the test Visocolor Sulphides 0.1-0.8 mg/L (sulphides/*N,N*-dimethyl-1.4-phenylenediamine(III), Macherey-Nagel GmbH, Germany). Determination of phenols that are brominated in acidic medium at concentrations above 10 mg/L was carried out by bromometric titration method according to PN-72/C-04602/02. The concentration of the remaining H₂O₂ was determined by manganometric method according to PN-72/C-04602/02. The excess of H₂O₂ remaining after oxidation and alkalisation was removed using a stoichiometric amount of 10% Na₂SO₃.

Methodology of Research

A three-step study was conducted on a laboratory scale. In the first stage, the concentration of the following ions: Fe(II), Fe(III), Al, Ti(IV), and Zr(IV) was tested in the aqueous solution with pH 2-10. For this purpose, sample solutions (acidified with concentrated HCl) of each metal used as coagulants with concentration of 100 mg/L were prepared. Then the pH was adjusted to a selected value in the range 2-10 with 30% NaOH. After stabilizing the pH, it was filtered through a syringe filter to separate the precipitated sludge and the concentration of metal in the filtrate was determined. The purpose of this stage of the study was to determine the pH value in which the solubility of the precipitated metal hydroxides is the smallest and hence the effectiveness of the coagulant should be the greatest. In the second stage of the study, coagulation of post-processing wastewater was carried out with each coagulant in the amount of 200 mg of Fe²⁺, Fe³⁺, Al³⁺, Ti⁴⁺, or Zr⁴⁺/L at pH 6.5, 7.5, 8.5, and 9.5. Coagulant was added to the measured amount of wastewater in an appropriate amount so that metal ion concentration was 200 mg/L. Then the pH was adjusted to a selected value, 0.025% of anionic flocculant solution in the amount equivalent to 4 ml/L was added, and phenols, COD, UV₂₅₄ absorbance, color, and turbidity in the filtrate were determined. Subsequently, according to the presented methodology, for constant pH value of 8 and variable doses of coagulants, tests were carried out for the concentration of each metal ion 400-1,000 mg/L (for Al³⁺ 200-800 mg/L

due to the formation of large amounts of precipitate). In the third stage of initial coagulation-flocculation with Al₂SO₄·18H₂O as the most effective coagulant (400 mg Al³⁺/L, pH 7.5-8.0), purification was carried out by the method of advanced H₂O₂/UV oxidation. At this stage, the influence of H₂O₂ concentration and exposure time on the phenolic content in oxidized wastewater (pH, UV lamp power, mixing speed, and process temperature adopted as constant) were studied. The pH 3 value at which oxidation was performed was based on the findings of the paper [23]. The effectiveness of post-processing wastewater was studied by means of coagulation-flocculation and combined coagulation-flocculation and advanced H₂O₂/UV oxidation.

Results and Discussions

Table 1 shows the results of the post-processing wastewater from the Underground Coal Gasification (UCG) process, which was characterized by slightly alkaline pH (7.5), trace amounts of sulphides (0.81 mg/L), and slight turbidity (171 NTU). The tested wastewater was intensely brown colored (3320 mg Pt/L) and characterized by high concentrations of organic compounds (COD, TOC, N_{total}), including phenols (1360 mg/L). The effectiveness of coagulants used for the treatment of industrial and municipal wastewater depends on, among other factors, the pH at which the coagulation process is carried out. Conducting coagulation process at pH in which the solubility of the precipitated hydrated metal hydroxides is the smallest usually determines the significant efficiency of the process. Fig. 1 shows the dependence of metal ion concentrations (Fe²⁺, Fe³⁺, Al³⁺, Ti⁴⁺, and Zr⁴⁺) remaining in sedimentation water from the pH at which the coagulation process was performed (the initial concentration of each metal was 100 mg/L). The smallest concentrations of metal ions in the sediment solution over the entire pH range were obtained for Ti⁴⁺ and Zr⁴⁺ ions (in the ranges from 0.007-1.20 mg/L and 0.05-1.05 mg/L, respectively). The lowest concentrations of Fe²⁺ ions were observed in pH range 7-10 (1.4 mg/L and 0.021 mg/L, respectively). In the case of Fe³⁺ ions, the lowest concentrations were recorded

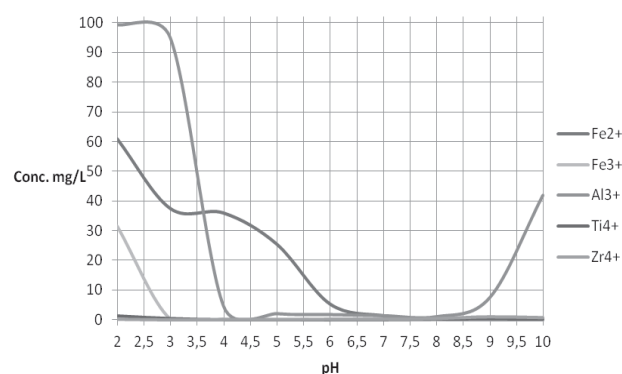


Fig. 1. Effect of pH on metal ion concentrations.

Table 2. Physicochemical parameters of post-processing wastewater after the coagulation-flocculation process (pH 6.5-9.5, concentration of coagulant calculated on metal 200 mg/L).

pH	Phenols, mg/L	COD, mg O ₂ /L	Absorbance, UV ₂₅₄ (dilution 1:40)	Colour, mg Pt/L	Turbidity, NTU
Fe ²⁺ , 200 mg/L					
6.5	1146	2872	0.725	>5000	260
7.5	1190	2816	0.588	>5000	300
8.5	1148	2836	0.264	1030	15
9.5	1105	2856	0.396	1040	15
Fe ³⁺ , 200 mg/L					
6.5	1190	2856	0.353	2230	73
7.5	1190	2862	0.348	2070	58
8.5	1190	2864	0.313	1710	34
9.5	1190	2808	0.353	2020	37
Al ³⁺ , 200 mg/L					
6.5	1146	2740	0.257	870	15
7.5	1105	2720	0.259	830	14
8.5	1105	2720	0.261	820	16
9.5	1190	2800	0.273	930	19
Ti ⁴⁺ , 200 mg/L					
6.5	1169	2896	0.354	1340	36
7.5	1184	2808	0.301	1090	28
8.5	1126	2828	0.297	1080	16
9.5	1126	2852	0.385	1530	33
Zr ⁴⁺ , 200 mg/L					
6.5	1169	2968	0.354	1140	53
7.5	1169	3028	0.386	2070	77
8.5	1169	2952	0.442	3170	193
9.5	1169	2916	0.431	3000	191

for pH > 3 and were 0.2-0.0065 mg/L, whereas at pH 2 the concentration of Fe³⁺ in sediment solution was 31.5 mg/L.

For aluminum coagulant, the lowest concentrations of Al³⁺ ions were found in pH range 4-9, while at pH 10 the concentration of Al³⁺ was 42 mg/L. The conducted study showed that for pH between 6.25 and 8.75, the concentration of metal ions in sedimentation water was below 5 mg/L, and at pH above 8.75 a significant increase in Al³⁺ concentration was observed. As a consequence, a preliminary study of the effectiveness of the coagulation-flocculation of post-processing wastewater was conducted at pH 6.5, 7.5, 8.5 and 9.5 using a dose of each coagulant corresponding to 200 mg/L Fe²⁺, Fe³⁺, Al³⁺, Ti⁴⁺, and Zr⁴⁺. The impact of coagulation pH at constant metal concentration on phenolic content was studied, as well as COD, UV₂₅₄ color, and turbidity (Table 2).

The use of the mentioned coagulants caused a slight decrease in phenolic concentrations to 1,105-1,190 mg/L for Fe²⁺ and Al³⁺ and 1,126-1,184 mg/L for Ti⁴⁺. In the case of using salts containing Fe³⁺ and Zr⁴⁺ ions for coagulation, the phenolic concentration values were unchanged in the tested pH ranges and amounted to 1,190 and 1,169 mg/L, respectively. The coagulation-flocculation process enabled the removal from 12.5-18.8% of the initial amount of phenols equal to 1,360 mg/L. For comparison, other authors in the case of wastewater from the landfill leachate for highly extreme doses of coagulant and cationic flocculant (13.2 g/L 40% FeCl₃ and 62 ml/L of flocculant) obtained 98% phenol removal. The initial concentrations of phenol were 241.8 mg/L [24]. The largest reduction in COD (8.2-10.8%) was achieved after coagulation of Al³⁺ ions, while at extreme pH values (6.5 or 9.5), COD value was

Table 3. Physicochemical parameters of post-processing wastewater after the coagulation-flocculation process (pH 8, concentration of coagulant calculated on metal 200-1,000 mg/L).

Dose of coagulant calculated to metal (mg/L)	Phenols (mg/L)	COD (mg O ₂ /L)	Absorbance (UV ₂₅₄ , dilution 1:40)	Colour (mg Pt/L)	Turbidity (NTU)
Fe ²⁺ , pH 8					
400	1100	2704	0.274	1425	58
600	1067	2712	0.266	1590	78
800	1058	2732	0.278	3420	311
1000	1058	2688	0.287	>5000	>400
Fe ³⁺ , pH 8					
400	1143	2724	0.267	810	15
600	1143	2756	0.256	660	10
800	1101	2756	0.254	1840	<10
1000	1058	2672	0.254	1240	<10
Al ³⁺ , pH 8					
200	1101	2616	0.253	550	<10
400	1143	2612	0.253	580	<10
600	1143	2640	0.251	520	<10
800	1143	2812	0.267	580	<10
Ti ⁴⁺ , pH 8					
400	1083	2704	0.247	500	<10
600	1083	2696	0.244	480	<10
800	1083	2720	0.246	1030	<10
1000	1083	2812	0.245	1130	<10
Zr ⁴⁺ , pH 8					
400	1253	2768	0.351	1030	23
600	1211	2800	0.337	910	22
800	1126	2792	0.319	830	12
1000	1083	2680	0.283	980	18

the highest (2,740 and 2,800 mg O₂/L, respectively). The use of aluminum coagulant also caused a significant decrease in UV₂₅₄ (37.4-41.2%), color (72.0-75.3%), and turbidity (88.9-91.2%). In the case of using for coagulation Fe²⁺ ions at pH 6.5 and 7.5, the color of treated wastewater intensified (>5,000 mg Pt/L) and turbidity (260 and 300 NTU, respectively) increased. For Fe³⁺, Ti⁴⁺, and Zr⁴⁺ ions, UV₂₅₄ value, colour, and turbidity were higher in the studied pH range than for Al³⁺ ions. In addition, in the case of Al³⁺, large, well-sedimented sludge flocs (for pH 6.5, 7.5 and 8.5) were obtained in the flocculation process. In the next step, the efficiency test of the coagulation-flocculation process was carried out at pH 8 and using the increasing doses of each coagulant corresponding to 400, 600, 800, and 1,000 mg/L of Fe²⁺, Fe³⁺, Ti⁴⁺, and Zr⁴⁺ (for Al³⁺ 200-800 mg/L). The influence of

coagulant (metal ions) dose at constant pH on phenolic content and additionally on the change in the value of COD, UV₂₅₄, color, and turbidity was studied.

The results of our studies are shown in Table 3. The lowest phenol concentrations (1,058-1,067 mg/L) were observed after using Fe²⁺ (600, 800, and 1,000 mg/L), but as the coagulant dose increased, unacceptable increase in UV₂₅₄ (max. >0.287), color (max. >500 mg Pt/L), and turbidity (max. >400 NTU) took place. The increase in the color value of wastewater was also noted after using high doses of coagulant containing Fe³⁺ (1,840 and 1,240 mg Pt/L for 800 and 1,000 mg Fe³⁺/L, respectively). Slightly higher values of phenolic concentrations (1083 mg/L) were obtained when Ti⁴⁺ ions were used for the coagulation process, which corresponded to a decrease in UV₂₅₄ (0.244-0.247) and turbidity (<10 NTU) for all doses. Unfortunately,

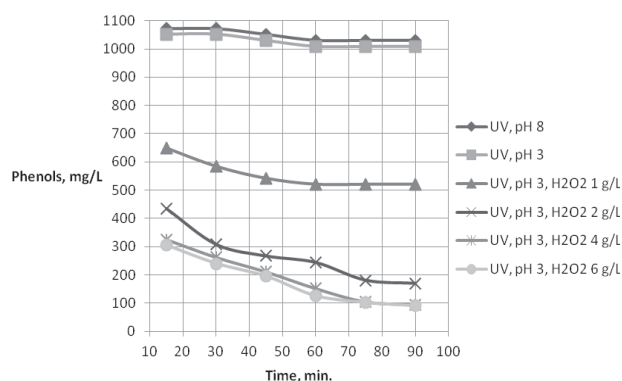


Fig. 2. Effect of time and H₂O₂ dose on phenol concentrations.

increasing the coagulant dose also caused an increase in the color value of the treated wastewater (max. 1,130 mg Pt/L, 1,000 mg Ti⁴⁺/L), and was associated with high consumption of NaOH for alkalisation of wastewater resulting from the need to use significantly acidified TiCl₄ solution to inhibit hydrolysis of Ti⁴⁺ ions. When coagulant containing Al³⁺ ions was used, significant color reductions (82.5-84.3%) and turbidity (<10 NTU for each Al³⁺ dose) were achieved. In addition, the use of aluminium coagulant was associated with the need for a slight pH adjustment and the formation of a considerable amount of precipitate; however, it consisted of flocks characterized by large size and fast sedimentation.

For Al³⁺ doses in the range of 200-800 mg/L, similar concentrations of phenols, COD, UV₂₅₄, color, and turbidity were obtained. For this reason, it was assumed that the treated wastewater prior to H₂O₂/UV treatment would be coagulated with an average dose of aluminium coagulant, i.e., 400 mg Al³⁺/L at pH 8. Therefore 10 one-liter wastewater samples were coagulated, which after averaging by mixing exhibited pH 8 and contained 1,100 mg/L of phenols. That wastewater was exposed in a photoreactor and the results of the carried out studies are shown in Fig. 2. UV irradiation at pH 8 and 3 was associated with slight changes in phenolic concentrations, which varied between 1,073-1,030 and 1,052-1,009 m/L, respectively. Smaller values were reached after 90 min. of UV light exposure, then H₂O₂ was added at 1, 2, 4, and 6 g/L. At all doses, the highest rate of reduction of phenolic concentrations was observed up to 60 min. duration of the process, after which the value of phenolic concentration varied only

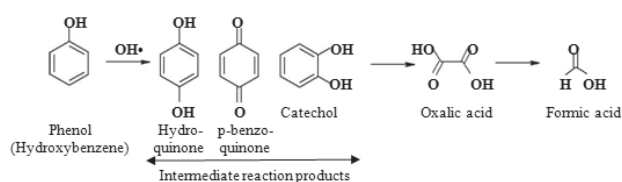


Fig. 3. Degradation of phenol (hydroxybenzene) in aqueous solution [23, 29-30].

slightly. The highest difference in phenol concentration in treated wastewater was for H₂O₂ doses of 1 and 2 g/L, while the difference was small when 4 and 6 g/L H₂O₂ was used. Therefore, the use of H₂O₂ doses greater than 4 g/L in the case of treated wastewater would be technically and economically unjustifiable. Therefore, for the purified wastewater we used the following optimum values for process parameters: pH 3, H₂O₂ concentration 4 g/L, exposure time 90 minutes, UV lamp power 11 W, mixing speed 250 rpm, and temperature 19±1°C. Use of the above parameters resulted in a decrease in phenols concentration from 1,100 mg/L (value after coagulation-flocculation) to 95 mg/L (reduction by 91%). Other authors using zeolite obtained 93-100% reduction of phenol. The degree of phenol removal was dependent on the zeolite dose. In this case phenol is only adsorbed and does not decompose [25]. The application of membrane technique can remove 88% of phenol, which was separated as a condensed permeate [26]. Other authors also studied the removal of phenol using biological processes in the aerobic bioreactor with glass beads. The phenol removal rate of 89% was achieved. The application of anaerobic wastewater stabilization pond for phenol removal obtained 90% of phenol reduction [27-28].

In the presented study, taking into account the initial concentration of phenols in the post-processing wastewater (1360 mg/L), the use of the coagulation-flocculation process (pH 8, 400 mg Al³⁺/L) allowed for a decrease in phenolic concentration to 1,100 mg/L (19.1%) and using the processes of coagulation-flocculation and advanced H₂O₂/UV oxidation, up to 95 mg/L (93%). The carried out studies show that phenol degradation in the post-processing wastewater took place in an acidic environment (pH 3), and the intensity of degradation increased with the increase in H₂O₂ dose to 6 g/L, which affected the amount of OH• radicals formed per unit time. Intermediate phenol products identified and characterized in the literature, such as hydroquinone, p-benzoquinone and catechol, indicate that OH• radicals are involved in phenol decomposition, as schematically shown in Fig. 3 [29-30].

Conclusions

Our paper presents results of research on phenol removal from wastewater originating from an experimental simulation of the underground coal gasification process conducted in the Barbara Experimental Mine in Mikołów, Poland. By means of the coagulation-flocculation process carried out with the use of coagulants containing Fe²⁺, Fe³⁺, Al³⁺, Ti⁴⁺, and Zr⁴⁺ salts, a slight decrease in phenolic concentrations ranging from 7.9% (pH 8, Zr⁴⁺ 400 mg/L) to 22.2% (for pH 8, Fe²⁺ 800 and 1,000 mg/L, and pH 8, Fe³⁺ 1,000 mg/L) was obtained. Applying combined coagulation-flocculation processes (Al³⁺ 400 mg/L, pH 8) and advanced H₂O₂/UV oxidation (pH 3, H₂O₂ 4 g/L, UV exposure time of 90 minutes, UV power

of 11 W, mixing speed 250 rpm, $19\pm 1^\circ\text{C}$), resulted in a total reduction of phenolic concentration in the treated wastewater by about 93% due to their reaction with $\text{OH}\cdot$ radical ions resulting from the impact of UV radiation on H_2O_2 .

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