Chemical and Electrochemical Coagulation of Wastewater from UCG

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Posted Date: 7 August 2024

doi: 10.20944/preprints202408.0474.v1

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Article

Chemical and Electrochemical Coagulation of Wastewater from UCG

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Abstract: This article compares chemical coagulation with electrocoagulation, two popular methods for the primary treatment of wastewater generated in the process of Underground Coal Gasification (UCG). The primary aim was to determine which method is more effective in the removal of cyanide and sulphide ions, metals and metalloids, as well as organic compounds. In both cases, experiments were conducted in batch 1 dm^3 reactors, and the coagulation/flocculation process was carried out using iron ions. Four types of coagulants were tested during the chemical coagulation study: $FeCl_2$, $FeSO_4$, $Fe_2(SO_4)_3$, and $FeCl_3$. In the electrocoagulation experiments, pure iron Armco steel was used to manufacture the sacrificial iron anode. Both processes were tested under a wide range of operating conditions (pH, time, Fe dose) to determine their maximum efficiency for treating UCG wastewater. It was found that, through electrocoagulation, a dose as low as 60 mg Fe/dm^3 leads to >60% cyanide reduction and >98% sulphide removal efficiency, while for chemical coagulation, even a dose of 307 mg Fe/dm^3 did not achieve more than 24% cyanide ion removal. Moreover, industrial chemical coagulants, especially when used in very high doses, can be a substantial source of cross-contamination with trace elements.

Keywords: chemical coagulation; electrocoagulation; iron; underground coal gasification; UCG

Highlights

- Physicochemical characteristics of wastewater produced in the UCG process of Polish bituminous coal.
- For chemical coagulation, the highest measured removal of cyanide ions reached 24%, while electrocoagulation removed close to 90%.
- High doses of commercial coagulants can lead to cross-contamination with heavy metals.
- Electrocoagulation proved to be an effective method for the removal of cyanide, sulphide, organics, and trace elements.

Introduction

Underground Coal Gasification (UCG) technology entails the conversion of coal directly within its seam into a useful gas. This gas can be utilized for chemical synthesis or as a source of energy for production of heat and power. While UCG is regarded as an economically viable and technically practical clean coal technology, several concerns still need to be addressed. One major issue pertains to environmental safety, specifically the generation of wastewater. This wastewater often carries a substantial amount of organic and inorganic contaminants, which may pose significant challenges for effective and safe waste management.

The characteristics of wastewater produced from Underground Coal Gasification (UCG) resemble those of coke wastewater, necessitating proper treatment due to its potential as an environmental pollutant. The formation and composition of this wastewater are influenced by several factors, including the type of coal used, process conditions such as pressure, temperature, gasification agent, reaction duration, and the configuration of the gas cleaning system [1]. The contaminants in UCG wastewater reflect the components present in the gasification system. Therefore, metals, cyanides (CN), sulphur compounds (S), and various organic pollutants like

 doi:10.20944/preprints202408.0474.v1

phenols, benzene, toluene, xylene (BTX), and polyaromatic hydrocarbons (PAH) are commonly detected [2,3]. Effectively treating this complex mixture poses significant technological and financial challenges.

Chemical coagulation is an essential process in industrial wastewater treatment, consisting of two main stages: coagulation and flocculation. During coagulation, coagulants such as Fe^{2+} and Fe^{3+} ions are added to neutralize the negative surface charge of colloidal particles, causing them to aggregate into larger microflocs. This step involves high-intensity mixing to ensure rapid dispersion of the coagulating agent and its subsequent interaction with contaminants. Subsequent flocculation is a step, where gentle mixing allows microflocs to grow into larger, stable macroflocs. Followingly macroflocs are separated from the water via sedimentation, centrifugation, flotation, or barrier filtration [4].

In wastewater treatment, ferrous sulphate (iron (II) sulphate) is one of the most commonly used coagulants because it usually allows for the formation of denser flocs than alum (aluminium sulphate). Furthermore, ferric chloride can be perceived as an alternative, because in many cases, it promotes even faster sedimentation [5]. Drawback of using iron chlorides may however be exacerbation of the problem of chloride corrosion [6].

Chemical coagulation is effective at removing a variety of contaminants, including suspended solids, organic compounds, colour, and some dissolved metals [7–10]. Iron-based coagulants are particularly notable for their ability to remove phosphates and heavy metals. This method is highly valued for its simplicity and effectiveness, especially in treating large volumes of water. It is commonly used in municipal water treatment, industrial wastewater management, mining operations, and chemical manufacturing. However, the process does produce a considerable amount of sludge, which requires proper handling and disposal [5]. Understanding and optimizing chemical coagulation is essential for enhancing wastewater treatment processes and efficiently addressing diverse contaminants. Unfortunately, because this process requires the use of coagulating and flocculating agents, as well as chemicals necessary for adjustment of pH and alkalinity, it can lead to secondary contamination of the treated stream. In extreme cases, this may render the overall purification strategy technically and environmentally unsound.

An alternative to the conventional chemical coagulation can be sought in electrocoagulation systems. Electrocoagulation (EC) is a versatile method for treating liquid effluents through five main mechanisms: coagulation and flocculation, chemical oxidation, pH adjustment, electroflotation, and microbial activity. The balance of these mechanisms depends on the process conditions and electrode material. Iron and aluminium are commonly used for coagulation and flocculation, with iron also effective for removing heavy metals and phosphate ions [11–13]. Other electrodes like stainless steel, zinc, titanium, or graphite are used in harsh conditions or for chemical oxidation and flotation [12,14–16].

Adaptability of electrocoagulation allows it to address various contaminants including Chemical Oxygen Demand (COD), heavy metals, organic compounds, oils, dyes, suspended solids, emulsified oils, phosphorus, nitrogen, pesticides, and pathogens [17–21]. Recent studies highlight EC's economic efficiency compared to other waste treatment methods. EC can remove multiple contaminants using different electrode setups and power input designs, making it suitable for municipal and residential wastewater treatment. Its applications extend to drinking water treatment, industrial effluents, metal machining, textiles, mining, oil and gas, petrochemicals, pharmaceuticals, semiconductors, electronics, food processing, dairy, agriculture, landfilling, and gemstone washing [22–34].

The major advantages of chemical- and electrocoagulation can thus be summarized as simple, compact, highly reliable, cost-effective, efficient, optimizable for a given contaminant. Conventionally chemical coagulation is the first treatment step when treating many industrial waters while electrocoagulation, despite its many merits, finds only specific applications. Both are not seen as a sole treatment process but rather as a first pretreatment step prior to biological and mechanical treatment or as a final polishing step before releasing the effluent into the environment.

 doi:10.20944/preprints202408.0474.v1

Interestingly even though the subject of chemical coagulation and electrocoagulation finds great attention, we still see limited number of papers presenting results of its integration with effluents generated in coal processing or in particular UCG technologies [35–37].

This research gap led to the conclusion that research dedicated to determining the characteristics and limitations of using chemical- and electrocoagulation as method for pretreatment of UCG wastewater will complement well future environmental and power engineering studies. Thus, in this work authors aim to compare the effectiveness of batch chemical coagulation and electrocoagulation processes applied to purification of raw wastewater produced in a pilot installation for researching the UCG process, located and run by GIG-PIB (Poland).

Materials and Methods

UCG Wastewater Characteristic

Wastewater from oxygen blown UCG of bituminous coal from the "Wesoła" Coal Mine was used in this study. Table 2 presented below collates basic physicochemical properties of the wastewater. Further details regarding the process and results of UCG experiments can be found in [38–40].

Table 1. Average physical and chemical characteristics of the UCG wastewater.

Parameter	Value
pH, [-]	8.193
Conductivity, [mS/cm]	1600.5
Redox, [mV]	-113.3
COD, [mg O_2/l]	189.03
CN_{free}, [mg/dm^3]	0.971
S^{2-}, [mg/dm^3]	0.215
Trace elements	
Al [mg/kg]	2.520
As [mg/kg]	<0.02
Cd [mg/kg]	<0.02
Co [mg/kg]	<0.05
Cr [mg/kg]	<0.025
Cu [mg/kg]	<0.025
Fe [mg/kg]	0.179
Mn [mg/kg]	0.333
Mo [mg/kg]	<0.05
Ni [mg/kg]	0.492
Pb [mg/kg]	<0.05
Sb [mg/kg]	0.080
Ti [mg/kg]	<0.02
Zn [mg/kg]	0.213
Sum [mg/kg]	3.817
BTX	
Benzene [mg/dm^3]	0.210
Toluene [mg/dm^3]	0.080
Ethylbenzene [mg/dm^3]	0.004
m-xylene [mg/dm^3]	0.004
p-xlene [mg/dm^3]	0.010
Isopropylbenzene [mg/dm^3]	0.002
o-xylene [mg/dm^3]	0.010
Sum [mg/dm^3]	0.320

Mean values of 3 measurements.

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Herein investigated coagulation process is based on the use of iron ions, so the concentration of iron in UCG wastewater equal to 0.179 mg Fe/kg must be treated as a reference. Among trace elements, only the concentrations of Al, Ni, Mn, Fe, Zn, and Sb (listed in decreasing order of detected concentration) were determined above the lower limit of detection (LDL). Also, the wastewater was low in BTX and indicated concentrations of PAH <LDL. This influences high measurement error of testing applicability of coagulation methods for removal of organic pollutants.

Analytical Methods

Determination of pH, electrochemical conductivity, and redox potential

Determination of the pH of the wastewater, its electrochemical conductivity, and redox potential was carried out using a laboratory multifunction device CX505 produced by Elmetron. Dedicated electrodes were used to measure each of the parameters.

Determination of COD

The determination of COD was carried out spectrophotometrically using dedicated HACH-LCK 014 cuvette tests. In this method, oxidizable substances react with a solution of potassium dichromate in sulphuric acid in the presence of silver sulphate as a catalyst. The presence of chlorides is masked by mercury sulphate. The determination is based on the measurement of the intensity of the green colour caused in the solution by Cr3+ ions. Before analysis, the sample was diluted 10- and 25-fold. Then, 0.5 cm^3 of the diluted sample was introduced into the test cuvette and the samples were mineralized (digested) for 15 minutes at 170°C. After the mineralization was completed and the sample was cooled down, the colour intensity was measured at the wavelength of λ=605 nm using the DR6000 HACH Lange spectrophotometer.

Determination of the content of phenols

The content of phenols was determined as the so-called phenol index by the photometric method using dedicated HACH-LCK 354 cuvette tests. The method uses the reaction of phenols contained in the sample with 4-nitroaniline, which forms yellow complexes with phenols. 2 cm^3 of the diluted sample and 0.2 cm^3 of sodium nitrite solution were introduced into a test cuvette containing 4% hydrochloric acid. Then, after 2 minutes, the sodium carbonate solution was added to the cuvette. The colour intensity was measured after another 2 minutes at a wavelength of λ = 476 m using a DR6000 HACH Lange spectrophotometer.

Determination of the content of free cyanides

The content of free cyanides was determined by the photometric method using dedicated HACH-LCK 315 cuvette tests. In this technique, cyanide ions contained in the sample react with chlorine, and the resulting chlorinated cyanides, in the presence of barbituric acid, form violet complexes with pyridine. 1 cm^3 of the sample was introduced into a test cuvette containing potassium dihydrogen phosphate, chloramine B and sodium hydrogen phosphate, and 1,3-dimethylbarbituric acid was added. Then, after mixing, 1 cm^3 of pyridine solution was introduced into the cuvette and after 3 minutes the colour intensity was measured at the wavelength of λ = 588 m using the DR6000 HACH Lange spectrophotometer.

Determination of the content of ammonium nitrogen

The content of ammonium nitrogen was determined by the photometric method using dedicated HACH-LCK 302–305 cuvette tests. At an alkali environment (pH 12.6) ammonia reacts with hypochlorite and salicylic ions in presence of sodium nitroprusside (catalyst) to yield indophenol blue.

0.5 cm^3 of sample was introduced to the analytical cuvette containing hipochlorites and salicylic ions mixture. Next, nitroprusside was added, and the sample was left for 15 minutes, after which the intensity of solution colour was measured using DR6000 HACH Lange Spectrophotometer at wavelength λ = 550 nm.

Determination of the content of sulphides

The determination of sulphides was carried out spectrophotometrically using dedicated HACH-LCK 653 cuvette tests.

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In this method, sulphide ions contained in the sample react with p-aminodimethylaniline to form leucomethylene blue, which in the presence of iron (III) ions turns into methylene blue.

4 cm^3 of the sample was introduced into a test cuvette containing a 30% solution of sulphuric acid with the addition of p-aminodimethylaniline. Then 0.5 cm^3 of a solution of 3% sulphuric acid containing iron (III) ions was added. After 10 minutes, the colour intensity was measured at the wavelength of λ = 665 nm using the DR6000 HACH Lange spectrophotometer.

Determination of the content of total organic carbon (TOC)

The Vario MAX C analyser was used to determine the content of TOC. The technique is based on heat treatment of the sample and analysis of the post-reaction gases, which after purification - removal of corrosive and inhibiting components of the gas - are directed to the analyser equipped with a series of IR detectors. The TOC content is recalculated from the ratio of the resulting CO2 to the weight of the sample.

Determination of the content of cations and anions

The content of cations and anions was determined using a two-channel, capillary ion chromatograph Dionex ICS-5000. The method is based on the separation of negatively or positively charged ions using ion exchange chromatography. Analytical column IonPack AS-25 (250 mm×2 mm) together with protective column IonPack AG-25 were used for the separation of anions, while analytical column CS-16 (250 mm×3 mm) and a protective column CG-16 were used for the analysis of cations. The eluent flow was maintained at 0.250 cm^3/min for anions and 0.500 cm^3/min for cations. The column and detector compartments were maintained at 30°C and 20°C, respectively. The eluate leaving the column is continuously analysed by a conductivity detector. Chromatograms were recorded isocratically – 25 mM sodium hydroxide (for analysis of anions) and 25 mM methanesulfonic acid (for analysis of cations) were generated electrolytically in situ during the analysis. The measurement data is processed by the Chromeleon® 6.7 (Dionex) data management system.

Qualitative and quantitative analysis of trace elements

Samples were analysed according to ISO 11885 Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). Samples were digested in an Ethos One (Milestone, Italy) microwave digestion system using 2 cm^3 of sample and 6 cm^3 of Nitric acid (67 % from Sigma Aldrich) was added to each Teflon vessel. The vessels were heated at 200°C for 25 minutes in microwave oven. The concentrations of Al, As, Cd, Co, Cu, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Ti and Zn were determined using iCAP 6500 Duo (Thermo Scientific, USA). To calibrate the spectrometer, standard solutions were prepared from single-element solutions (SCP Science Company) with a standard concentration of 1,000–10,000 mg/dm^3.

Qualitative and quantitative analysis of Volatile Organic Compounds (VOC)

100 cm^3 of the sample was mixed with 25 cm^3 of hexane and mixed using a magnetic stirrer for 1 hour. Afterwards the separated organic phase was evaporated under reduced pressure and analysed by GC/FID.

The chromatographic analysis was performed using ThermoScientific Trace GC Ultra equipped with a capillary column ZB-WAXplus L=60m, ID=0.32mm, FT=0.25µm and a flame-ionization detector (FID).

Qualitative and quantitative analysis of the Polyaromatic Hydrocarbons (PAH)

270 cm^3 of the sample was treated using Solid Phase Extraction technique (SPE) and Supelclean LC-18 SPE 500mg 6 cm^3 cartridges. The following steps of the SPE were performed. The cartridge was activated using methanol (2 steps x 2 cm^3 each) followed by rinsing with deionized water (3 x 1 cm^3). Subsequently, the sample was fed through the cartridge. Elution of the analytes was performed in two steps: 1) using acetone (2 x 2 cm^3) and 2) using benzene (2 x 2 cm^3). The thus obtained organic phase was analysed by GC/FICD.

The chromatographic analysis was performed using Trace GC ThermoFinnigan equipped with a capillary column ZB-6 L=60m, ID=0.32mm, FT=0.25µm and a flame-ionization detector (FID).

Introduction of cyanides and sulphides to the UCG wastewater

 doi:10.20944/preprints202408.0474.v1

In solutions not specifically prepared or treated to stabilise their cyanide or sulphide content, these contaminants tend to exhibit unstable behaviour, resulting in changes in their speciation and concentrations over time. Based on experience, wastewaters generated in coal gasification systems can contain more than 15 mg/dm^3 of cyanides and 40 mg/dm^3 of sulphides. However, in the case of the tested stream of UCG wastewater, due to the time gap between the gasification experiments and coagulation studies, the samples contained only traces of these contaminants. Specifically, the sulphide concentration did not exceed LDL (<0.1 mg/dm^3), while the cyanide concentration was measured to be 1 mg/dm^3. Therefore, it was decided to artificially introduce the aforementioned concentrations of cyanides and sulphides into the UCG wastewater before the coagulation experiments.

At the pH of the treated UCG wastewater, i.e., 8–9, sulphides mainly exist in the solution in the form of undissociated, soluble H_2S (gas) and HS^-. During electrocoagulation, the pH increases, leading to an increase in the amount of available free sulphide ions. On the other hand, chemical coagulants containing iron ions have an acidic pH, which may lead to the emission of gaseous hydrogen sulphide. To avoid the need to artificially increase the pH of the UCG wastewater, sulphides were added to the solution only in the case of EC experiments. Cyanides are known to form complexes over time and react with heavy metals, but they can also undergo oxidation with hydrocarbons available in the solution. Due to the much less volatile nature of cyanides, they were introduced for both chemical and electrochemical coagulation.

During both chemical- and electrocoagulation tests cyanides were added separately just before each of the conducted experimental series, and before division to individual objects. Table 2 presents the variability of cyanide concentrations in the objects subjected to chemical coagulation.

Table 2. Summary of measured concentrations of CN^- ions in UCG wastewater – chemical coagulation.

	Mean	Min	Max	St. dev.
CN^-	14.65	13.70	15.80	0.79

During the electrocoagulation trials, both cyanides and sulphides were introduced into the wastewater. The concentration of cyanides was maintained at a level similar to chemical coagulation tests, while the amount of sulphides introduced was 40 mg/dm^3. Table 3 presents the variability of cyanide and sulphide concentrations in the objects subjected to electrocoagulation.

Table 3. Summary of measured concentrations of CN^- and S^{2-} ions in UCG wastewater – electrocoagulation.

	Mean	Min	Max	St. dev.
Concentration of CN^- in tested samples	14.19	13.40	15.30	0.71
Concentration of S^{2-} in tested samples	37.92	29.85	45.15	5.39

During the batch electrocoagulation tests, the procedure for measuring sulphides in wastewater was refined. Despite introducing an identical mass of Na_2S, the observed data spread is associated with the continuous removal of sulphide from the solution and the emission of small amounts of gaseous H_2S. Further sources of variability are attributed to the heterogeneous hydration of the salt and the very small quantities of the added reagent. For this reason, the results on the effectiveness of sulphide removal presented below were compared using the average values shown in Table 3.

Feedstocks

Coagulants

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Four main types of iron-based coagulants were used in this study, namely acidic solutions of iron (II) and iron (III) sulphates and chlorides.

The table below presents a comparison of the basic characteristics of herein utilized coagulants. The last column represents the total Fe concentration in the coagulants, as the sum of all valences.

Table 4. Table summarizing the basic properties of the coagulants used.

Trade name	Chemical specie	Density, kg/dm^3	Total Fe content, % w/w
PIX-100	$FeCl_2$	1.2659	9.76
PIX-100 COP	$FeSO_4$	1.0552	1.75
PIX-113	$Fe_2(SO_4)_3$	1.5262	11.39
PIX-116	$FeCl_3$	1.3143	10.26

Electrodes

Anode was manufactured from flat plate or Armco pure iron steel (<99.5% Fe grade 04 J according to PN 89/H-84023/02, C_{max}=0.035%, Mn_{max}=0.25%, Si_{max}=0.02%, P_{max}=0.025%, S_{max}=0.030%, Cr_{max}=0.10%, Ni_{max}=0.10%, Cu_{max}=0.10%, Al_{max}=0.02%-0.07%). Cathode made of stainless steel (AISI 304).

Chemical Reagents:

For pH adjustments, commercially available 50% sodium hydroxide solution with analytical grade purity was utilized. Introduction of the desired amounts of cyanide and sulphide ions into the solution was carried out using potassium cyanide (KCN) and hydrated sodium sulphide (Na_2S). Thermo Scientific and Warchem Sp. z o.o. were the manufacturers of these reagents, respectively. Due to the hygroscopic nature of Na_2S, the actual state of its hydration was determined during the execution of the tests – described below.

Chemical Coagulation Setup

Sample notation:

Samples taken prior or after treatments, as well as characteristic parameters collected during the study, are described using a coding method presented in Table 5.

Table 5. Coding of samples – chemical coagulation tests.

notation of the tests and samples	coagulant_dose [mg Fe/dm^3]_pH before coagulation
example	PIX100_10_6,3

Test procedure

Jar tests were conducted during experiments on the chemical coagulation process of UCG wastewater. The main goal of coagulation was to maximise the removal of organic compounds, metalloids, and cyanides. The setup consisted of four identical sets of beakers with a capacity of 2 litres each. The beakers were placed on magnetic stirrers, and the type and length of the stir bars used were selected to enable both high turbulence and slow, gentle mixing required for proper coagulation during the different stages of the procedure. As a result, 40 mm rods with a diameter of 5 mm were found to perform best. No additional flocculant (e.g., polymeric) was added to enhance clarification.

Coagulation procedure

- pH correction
- Measurement of basic parameters of raw wastewater: pH, conductivity, redox
- Introducing 1,000 cm^3 of wastewater into each of the beakers
- Measurement of preset doses of coagulant and their introduction into syringes
- Start of the mixing and coagulation program

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- Measurement of basic parameters in the effluent after sedimentation is finished
- Sampling and lab analyses of the supernatant of the treated wastewater

Mixing program

1. Initiation of mixing; 1200 rpm for 1 min; very intensive mixing
2. Coagulant injection
3. 700 rpm for 5 min; medium intensity mixing
4. 400 rpm for 5 min
5. 200 rpm for 10 min; minimal intensity mixing, minimal agitation of the liquid
6. Cessation of mixing
7. Sedimentation – 120 min

Preliminary tests on the effect of coagulant dosage on the change in solution pH

pH corrections necessary to maintain the optimal working range for each specific coagulant were determined experimentally for each object (type of coagulant and dosage). In general, it was observed that the optimal pH range in which iron sulphates and chlorides achieved their maximum effectiveness fell within the range of 4–9. pH corrections were made only when the resulting pH of the solution fell outside the optimal range (when no signs of coagulation-flocculation were observed). For none of the samples was an external source of alkalinity added.

Electrocoagulation setup

In this study, the batch electrocoagulation tests were performed using an adapted version of the Jar Tests presented above. The experiments were carried out in a system consisting of two beakers of 2 dm^3 each, an electrode support stand, and a Twintex TP-2305 dual-channel power supply (30 V DC, 2x5 A). Both electrodes had an area of 20 cm^2 each and were spaced 2 cm apart during all experiments. Since the currents used in this study were very small (<0.5 A), to increase the resolution of the measurement, an additional measurement system consisting of a set of multimeters was used in addition to the measurement indicated by the power source. The measurements thus had a resolution of 1 mA/mV and a precision of 0.03%. The beakers were thermostated in a water bath at (19.7 ± 0.3°C).

The characteristics of Fe dissolution were investigated at both constant and variable current. It was found that in the constant-current mode, higher control precision and the ability to more closely maintain the controlled parameters were observed. This mode was also easier to control. On average, a 7.6% lower loss of electrode mass was observed than was calculated using the Faraday equation. Working in a closed system, a steady increase in the pH of the wastewater was observed as the dose of Fe introduced increased.

Sample notation

Samples taken prior or after treatments, as well as characteristic parameters collected during the study, were described using a coding method presented in

Table 6. Coding of samples – electrocoagulation tests.

test and sample notation	el_dose [mg Fe/dm^3]_current [mA]_time [min]_pH before the process
example	el_d60_i58_t60_pH8,5

Calculation of removal efficiency / reduction of the value of component *i*,

$$\eta_i = 1 - \frac{c_{i\_outlet}}{c_{i\_inlet}} \ [\%] \qquad \text{Eq. (1)}$$

where:

c_{i_inlet} – concentration of component *i* at the inlet to the reactor [mg/dm^3]

c_{i_outlet} – concentration of component *i* at the outlet from the reactor [mg/dm^3]

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The effectiveness of treatments was determined here based on the removal efficiency, while cyanides, heavy metals, and organic pollutants (BTX) were the main analysed variables. Additionally, such parameters as redox or COD were used here as secondary evaluation measures.

Results and Discussion

Chemical Coagulation of UCG Wastewater

$FeCl_2$ as a source of Fe ions – PIX-100

Table 7 collates the results of using $FeCl_2$ as a source of Fe ions. None of the tested coagulant doses (123–309 mg Fe/dm^3) resulted in a reduction in the concentration of cyanide ions greater than 24%. With increasing doses of the coagulant, an increase in the values of redox potential, COD, and conductivity of the wastewater was observed. In chemical coagulation, this observation is attributed to the introduction of an excess of iron, chloride, and sulphate ions, as well as secondary contaminants brought into the wastewater with the coagulant itself. This notion will be further explored in the following paragraphs.

Table 7. Chemical coagulation of UCG wastewater using $FeCl_2$.

	PIX100_1,0_7,9	PIX100_1,5_7,9	PIX100_2,0_7,9	PIX100_2,5_7,9
Fe dose, mg Fe/dm^3	123.55	185.33	247.10	308.88
pH after introduction of the coagulant, -	5.88	5.73	5.41	3.70
Conductivity, mS/cm	2.003 (-25.15%)	2.241 (-40.02%)	2.573 (-60.76%)	2.894 (-80.82%)
Redox, mV	24 (-121.18%)	36 (-131.76%)	52 (-145.88%)	152 (-234.12%)
CN^-, mg/dm^3	10.8 (21.17%)	10.4 (24.09%)	11.1 (18.98%)	10.7 (21.9%)
COD, mg/dm^3	186.2 (2.62%)	194.2 (-1.57%)	204.2 (-6.8%)	216.2 (-13.08%)

Average of measured value (N=3) (removal/reduction eff.) – negative value indicates an increase in the specific property. The concentration of cyanide measured in the effluent prior to treatment was equal to 13.7 mg/dm^3.

$FeSO_4$ as a source of Fe ions – PIX-100 COP

In the case of PIX-100 COP, much lower doses of coagulant were introduced into the treated UCG wastewater stream (37–92 mg Fe/dm^3). This action was aimed to indicate the effectiveness of cyanide reduction using very low doses of divalent iron.

Table 8 indicates that already a dose of approximately 74 mg Fe/dm^3 led to a 19.6% reduction of cyanide. Similarly to PIX-100, increasing the dosage resulted in an increase in the redox value and the conductivity of the wastewater. However, contrary to PIX-100, lower doses of PIX100 COP caused a slight (5–6%) decrease in the COD.

Table 8. Chemical coagulation of UCG wastewater using $FeSO_4$.

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	PIX100 COP_2,0_8,2	PIX100 COP_3,0_8,2	PIX100 COP_4,0_8,2	PIX100 COP_5,0_8,2
Fe dose, mg Fe/dm^3	36.93	55.40	73.86	92.33
pH after introduction of the coagulant, -	7.10	6.74	6.44	6.43
Conductivity, mS/cm	1.6931 (-5.79%)	1.7402 (-8.73%)	1.7625 (-10.12%)	1.7563 (-9.73%)
Redox, mV	-46 (-59.41%)	-25 (-77.94%)	-7 (-93.82%)	-7 (-93.82%)
CN^-, mg/dm^3	12.5 (15.54%)	12.3 (16.89%)	11.9 (19.59%)	11.9 (19.59%)
COD, mg/dm^3	181.2 (5.72%)	181.2 (5.72%)	180.2 (6.24%)	180.2 (6.24%)

The concentration of cyanide measured in the effluent prior to treatment was equal to 14.8 mg/dm^3.

$Fe_2(SO_4)_3$ as a source of Fe ions – PIX-113

PIX-113 was the first of the two coagulants used that was based on trivalent iron ions. Theoretically, an increase in ion charge should result in significantly higher effectiveness in neutralising negatively charged colloids. However, an undesirable effect is that when using equivalent doses of Fe, it is necessary to perform corrections to maintain the process within the optimal pH range. Corrections were applied to all tested samples where the dose exceeded 190 mg Fe/dm^3.

Similar to the coagulants based on Fe^{2+}, no improvement in cyanide removal efficiency was achieved. The maximum reduction value of 21% was recorded for a dose of 260 mg Fe/dm^3. Increasing the dose of PIX-113 resulted in an increase in the conductivity of the wastewater; however, the observed impact of the dose on the redox value was ambiguous. Similar to PIX-100 COP, a 5–6% decrease in the COD value of the wastewater was observed.

Table 9. Chemical coagulation of UCG wastewater using $Fe_2(SO_4)_3$.

	PIX113_0,7_8,3	PIX113_1,1_10,0	PIX113_1,5_10,0	PIX113_1,9_10,0
Fe dose, mg Fe/dm^3	121.68	191.22	260.75	330.28
pH after introduction of the coagulant, -	5.46	8.88	7.71	6.28
Conductivity, mS/cm	1.7646 (-10.25%)	2.383 (-48.89%)	2.696 (-68.45%)	2.847 (-77.88%)
Redox, mV	50 (-144.12%)	-149 (-31.47%)	-76 (-32.94%)	2 (-101.76%)
CN^-, mg/dm^3	12.1 (16.55%)	12.9 (18.35%)	12.5 (20.89%)	12.6 (20.25%)
COD, mg/dm^3	177.2 (7.32%)	175.2 (3.31%)	169.2 (6.62%)	169.2 (6.62%)

The concentration of cyanide measured in the effluent prior to treatment was equal to 15.8 mg/dm^3.

$FeCl_3$ as a source of Fe ions – PIX-116

The last of the tested coagulants was ferric chloride, which was expected to exhibit the highest coagulation activity. Corrections were performed on all tested samples.

For all assessed categories, the impact of using PIX-116 did not differ from the observations made for the other coagulants. At the lowest dose, a 5–7% lower efficiency in cyanide removal was observed, while an insignificant 1–2% higher efficiency in COD removal was also noted.

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Table 10. Chemical coagulation of UCG wastewater using $FeCl_3$.

	PIX116_0,9_10	PIX116_1,3_10	PIX116_1,7_10	PIX116_2,1_10
Fe dose, mg Fe/dm³	121.36	175.30	229.24	283.18
pH after introduction of the coagulant, -	8.97	8.59	7.30	5.84
Conductivity, mS/cm	2.381 (-48.77%)	2.623 (-63.89%)	2.93 (-83.07%)	3.068 (-91.69%)
Redox, mV	-154 (-35.88%)	-132 (-16.47%)	-57 (-49.71%)	27 (-123.82%)
CN^-, mg/dm³	13.3 (12.5%)	12.6 (17.11%)	12.2 (19.74%)	12.2 (19.74%)
COD, mg/dm³	177.2 (6.83%)	173.2 (8.94%)	175.2 (7.89%)	174.2 (8.41%)

During this measurement series, the cyanide concentration in the effluent before coagulation was 15.2 mg/dm³.

Effect of coagulant on the removal of cyanide ions

For all tested doses and forms of Fe used in the chemical coagulation experiments, only a slight decrease in cyanide concentration was measured. The maximum reduction of 24% was achieved using the coagulant PIX-100 ($FeCl_2$) at a dose of 185 mg Fe/dm³.

The collected experimental data indicate that the upper limit of cyanide removal efficiency from UCG process wastewater using the tested chemical coagulants is confined to the range of 22–24%. Importantly, none of the tested configurations succeeded in reducing the cyanide concentration in the solution below the limit of 10 mg/dm³.

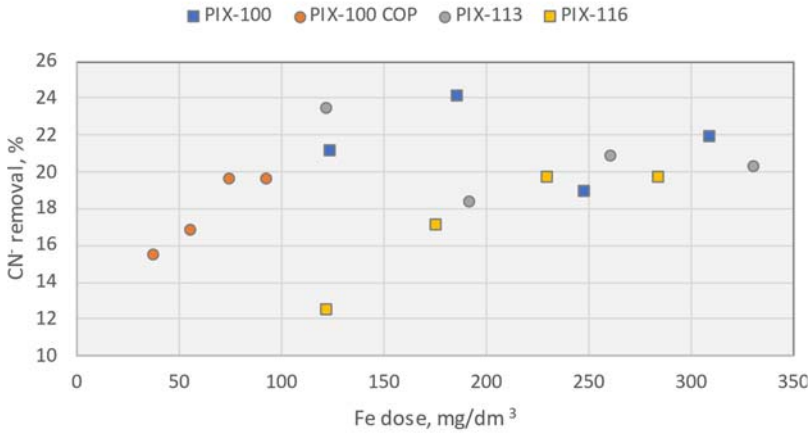

Figure 1. Effect of Fe dose on removal of free cyanide from UCG wastewater – chemical coagulation.

Effect of coagulant on the removal of metals and BTX

Analyses of heavy metal and BTX content in coagulated wastewater were carried out using the supernatant obtained after two hours of sedimentation. The samples were not subjected to filtration before analysis. Generally, the coagulation and flocculation processes were rapid and efficient, as evidenced by the iron content not exceeding the detection level in 3 of the 4 samples compared in Table 11. The table collates the results from all four tested coagulants at doses that resulted in the highest removal efficiency.

When analysing metals and metalloids, all tested coagulants reduced Al and Sb concentrations to below the detection limit (<LDL). Coagulants with sulphate as the counter ion demonstrated higher efficiency in removing trace elements. However, these coagulants also caused cross-contamination of the treated wastewater with Ni and Mn. Specifically, PIX-100 introduced Cu into the solution, and PIX-116 introduced Zn. These findings indicate that while pure reagents can achieve high efficiency

 doi:10.20944/preprints202408.0474.v1

in heavy metal removal, industrial or technical grade coagulants may produce effects contrary to the intended reduction of trace elements.

The coagulants were also analysed for their effect on the content of BTX and PAH in the UCG wastewater. Table 11 presents only the results for BTX, as all tested PAHs were measured to be <LDL. For BTX, it should be noted that the use of chemical coagulants led to inconclusive results. The observed small increases in the content of individual BTX compounds can be attributed to both the very low levels of measured values and the heterogeneity of the effluent. Overall, it appears that the coagulants had no positive effect on the removal of BTX.

Table 11. Summary of the removal efficiency for trace elements and BTX – most favourable configurations of the tested chemical coagulants.

	PIX100_1,5_7,9	PIX100 CPO_4,0_8,2	PIX113_1,5_10,0	PIX116_2,1_10,0
Fe dose, mg Fe/dm^3	185.33	73.86	260.75	283.18
CN^-, mg/dm^3	10.4 (24.09%)	11.9 (19.59%)	12.5 (20.89%)	12.2 (19.74%)
COD, mg/dm^3	194.2 (-1.57%)	180.2 (6.24%)	169.2 (6.62%)	174.2 (8.41%)
Trace elements				
Al, mg/kg	<0.125 (>95.04%)	<0.125 (>95.04%)	<0.125 (>95.04%)	<0.125 (>95.04%)
Fe, mg/kg	75.9 (-42302.23%)	<0.125 (>30.17%)	<0.125 (>30.17%)	<0.125 (>30.17%)
Mn, mg/kg	1.15 (-245.35%)	0.452 (-35.74%)	0.103 (69.07%)	1.63 (-389.49%)
Ni, mg/kg	0.545 (-10.77%)	0.526 (-6.91%)	0.546 (-10.98%)	0.566 (-15.04%)
Sb, mg/kg	>0.02 (>75%)	>0.02 (>75%)	>0.02 (>75%)	>0.02 (>75%)
Zn, mg/kg	0.871 (-308.92%)	0.079 (62.91%)	0.014 (93.43%)	3.7 (-1637.09%)
Sum of metals, mg/kg	78.677 (-1961.23%)	1.327 (65.23%)	0.933 (75.56%)	6.257 (-63.92%)
BTX				
Benzene, mg/dm^3	0.16 (23.81%)	0.75 (-257.14%)	0.06 (71.43%)	0.66 (-214.29%)
Toluene, mg/dm^3	0.13 (-62.5%)	0.15 (-87.5%)	-	-
Ethylobenzene, mg/dm^3	0.41 (-10150%)	0.18 (-4400%)	0.01 (-150%)	0.02 (-400%)
m-xylene, mg/dm^3	0.05 (-1150%)	0.02 (-400%)	-	-
p-xsylene, mg/dm^3	0.05 (-400%)	0.38 (-3700%)	0.01 (0%)	-
Isopropylbenzene, mg/dm^3	0.04 (-1900%)	0.06 (-2900%)	-	-
o-xylene, mg/dm^3	0.04 (-300%)	0.51 (-5000%)	0.01 (0%)	0.22 (-2100%)
Sum of BTX, mg/dm^3	0.88 (-700%)	2.05 (-1763.64%)	0.09 (18.18%)	1.11 (-909.09%)

Electrocoagulation of UCG wastewater

As previously introduced, general considerations lead to the conclusion that the processes of chemical and electrocoagulation, when performed using the same cation, differ mainly in their effect on pH (during electrocoagulation, pH increases). Consequently, electrocoagulation results in a significantly lower amount of cross-contaminants introduced. A drawback, particularly important

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from a technological perspective, is that compared to chemical methods, electrocoagulation leads to the formation of finer flocs and thus, even with longer sedimentation times, results in less effective spontaneous sedimentation. Similarly to chemical coagulation, the efficiency of batch electrocoagulation experiments was also assessed based on the removal efficiency of cyanides, sulphides, heavy metals, and organic compounds (BTX, PAH).

Effect the dose of Fe

The first set of electrocoagulation experiments was designed to determine the effect of the Fe dose. During these tests, the electrode dissolution time was kept constant at 60 minutes and the pH of the effluent was not adjusted.

The first two tests in this series were conducted using constant-voltage mode (where the current varied due to changes in the conductivity of the effluent), while the subsequent two tests were carried out in constant-current mode (with the voltage of the source adjusted to maintain a constant current flow). As no significant differences were observed between the modes, and the constant-current mode was easier to control, the remaining electrocoagulation experiments were conducted in constant-current mode. collates all data characterising the conditions of the tests as well as the measured parameters.

Due to the increasing pH of the sample during electrocoagulation, both cyanides and sulphides were introduced to the UCG effluent prior to treatment. For cyanides, a clear effect of the coagulant dose on the reduction efficiency was observed. The highest cyanide removal efficiency achieved during this series of tests was 89%, indicating that a dose of 225 mg Fe/dm^3 reduced the concentration to less than 1 mg/dm^3. Even more substantial results were obtained for sulphide ions, where more than 98% reduction was observed for all tested process variables. The only slight difference occurred when electrocoagulation was performed at higher pH levels. Further details regarding these experiments are presented in subsequent sections of this work.

Table 12. Results of a study on the effect of Fe dose at constant anode dissolution time.

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	el_d60_i58_t60 _pH8,5	el_d120_i115_t60_p H8,5	el_d180_i172_t60_p H8,5	el_d240_i230_t60_p H8,5
Current [mA]	58	115	172	230
Voltage min–max [V]	2.79	4.51	6.46–7.25	7.82–8.97
Time [s]	3600	3600	3600	3600
Measured Fe dose /difference from Faraday's law, mg Fe/dm^3 / %	56.8 / 6.25%	110.6 / 7.93%	165.2 / 8.05%	226.2 / 5.85%
Parameters of the effluent after electrocoagulation				
pH, -	8.74	8.91	9.06	9.18
Conductivity, mS/cm	1.8339 (-14.58%)	1.7657 (-10.32%)	1.6886 (-5.5%)	1.5938 (0.42%)
Redox, mV	-142 (-25.29%)	-151 (-33.24%)	-160 (-41.18%)	-166 (-46.47%)
CN^-, mg/dm^3	3.74 (60.59%)	2.51 (73.55%)	1.48 (84.4%)	1.03 (89.15%)
S^{2-}, mg/dm^3	0.395 (98.96%)	0.405 (98.93%)	0.306 (99.19%)	0.217 (99.43%)
COD, mg/dm^3	247.2 (13.02%)	238.2 (16.19%)	227.2 (20.06%)	222.2 (21.82%)

During this series of experiments, the cyanide in the effluent before coagulation was 9.49 mg/dm^3 while as the baseline for the calculation of sulphide removal the value of 37.9 mg/dm^3 was used (Table 3).

Figure 2 clearly indicates that, through electrocoagulation, a dose of approximately 55–60 mg Fe/dm^3 can reduce the cyanide concentration by over 60%. This result alone is nearly three times better than what is observed in the case of chemical coagulation. Further increasing the dose to 230 mg Fe/dm^3 results in an increase in cyanide reduction to 90%.

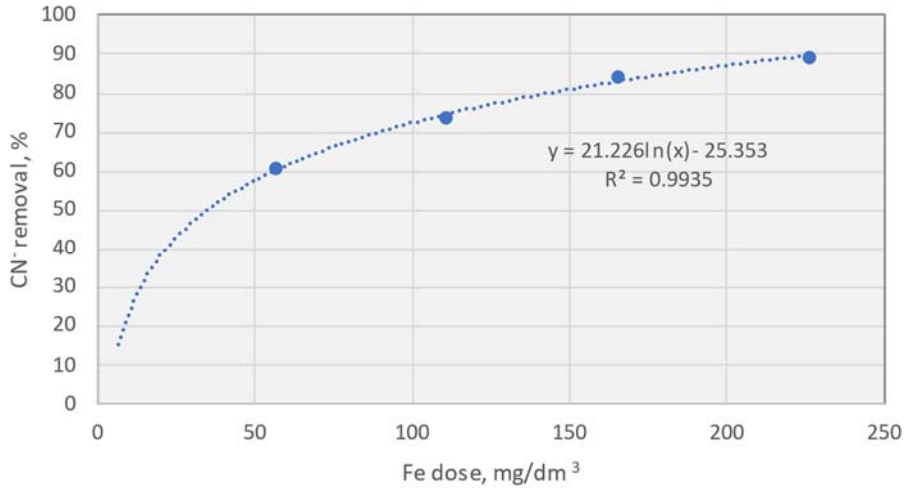

Figure 2. Effect of Fe dose on cyanide removal from UCG wastewater – electrocoagulation.

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An additional parameter demonstrating the beneficial effect of electrocoagulation on wastewater was the decrease in COD. However, in none of the tests did the COD decrease by more than 28%.

Similarly to chemical coagulation, the redox potential increased with low doses of Fe, while the conductivity of the solution increased across the full range of Fe doses tested. It is worth noting that, due to the mechanistic effect of the formation of very fine flocs, the change in conductivity is not straightforward.

Effect of the electrode dissolution time at a constant dose of Fe

Subsequently, a series of experiments was conducted to determine the effect of electrocoagulation time. This series of tests indicated that as the time of electrode dissolution increased, the resulting concentration of cyanides in the treated effluent also increased, leading to a decrease in removal efficiency. However, for cyanides, sulphides, and COD, clear and overlapping minima were observed, suggesting that for a dose of 104–115 mg Fe/dm^3, a process time of 60 minutes is optimal.

Table 13. Results of the anode dissolution time study at a constant dose of Fe.

	el_d120_i230_ t30_pH8,7	el_d120_i153_ t45_pH8,5	el_d120_i115_ t60_pH8,5	el_d120_i77_ t90_pH8,6	el_d120_i57_ t120_pH8,7
Current [mA]	230	153	115	77	57
Voltage min–max [V]	8.50–9.86	5.50–5.93	4.51	3.48–3.69	2.63–2.81
Time [s]	1800	2700	3600	5400	7200
Measured Fe dose / difference from Faraday's law, mg Fe/dm^3	104.2 / 13.26%	109 / 9.06%	110.6 / 7.93%	113.7 / 5.76%	114.9 / 3.51%
Parameters of the effluent after electrocoagulation					
pH, -	8.99	9.04	8.91	9.02	9.03
Conductivity, mS/cm	1.7945 (-12.12%)	1.7643 (-10.23%)	1.7657 (-10.32%)	1.7537 (-9.57%)	1.7891 (-11.78%)
Redox, mV	-156 (-37.65%)	-157 (-38.53%)	-151 (-33.24%)	-157 (-38.53%)	-158 (-39.41%)
CN^-, mg/dm^3	2.93 (69.13%)	3.38 (64.38%)	2.51 (73.55%)	3.62 (61.85%)	4.14 (56.38%)
S^{2-}, mg/dm^3	0.771 (97.97%)	0.563 (98.52%)	0.405 (98.93%)	0.595 (98.43%)	0.996 (97.37%)
COD, mg/dm^3	256.2 (26%)	254.2 (16.44%)	238.2 (16.19%)	261.2 (19.43%)	266.2 (23.11%)

Determination of main effects and interactions between time and dose

The electrocoagulation studies performed were further analysed to determine the existence of main effects as well as interactions between the controlled variables. For the case of time and dose, a positive interaction effect was found for cyanide removal from UCG wastewater. As expected, the dose had the dominant effect in this process. For COD, a negative effect of time and a positive effect of dose were observed. Notably, in this system, the interaction effect of dose and time had the most significant impact on COD reduction.

The following Figure 3, Figure 4 and Table 14 illustrate graphically and numerically the results of these analyses.

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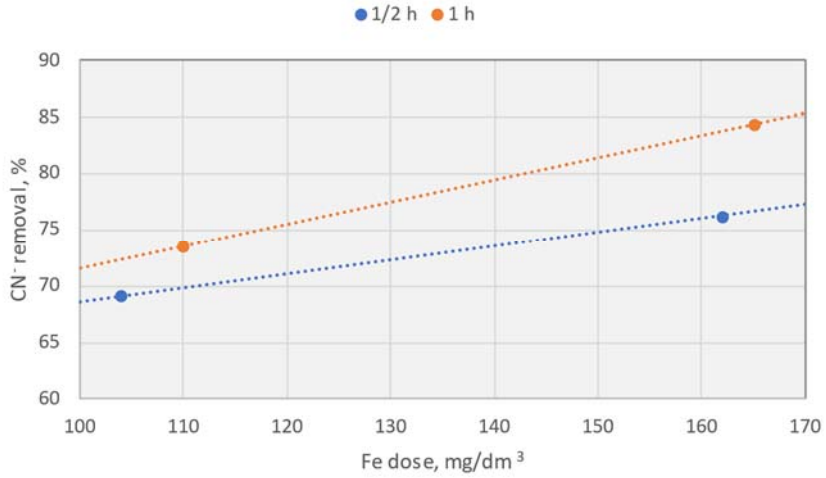

Figure 3. Interaction between time and dose of Fe on the efficiency of the removal of cyanide from UCG wastewater – electrocoagulation.

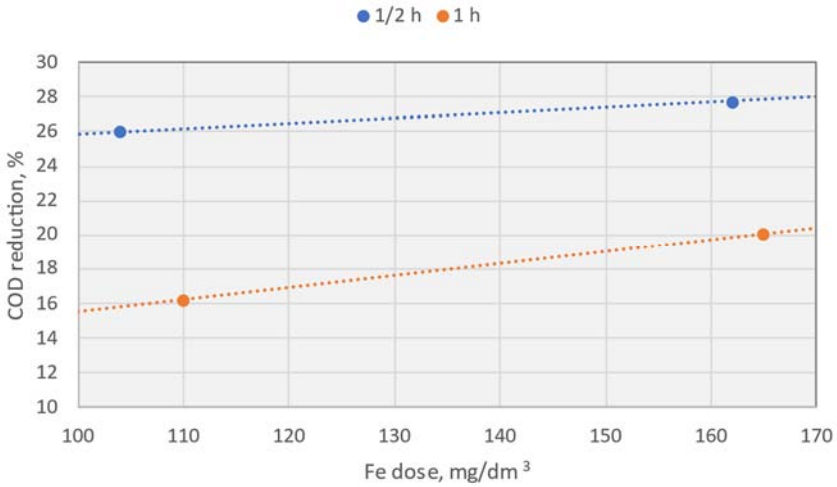

Figure 4. Interaction between time and dose of Fe on the efficiency of the removal of cyanide from UCG wastewater – electrocoagulation.

Table 14. Compilation of normalised values of main effects and interactions between time and dose of Fe on the efficiency of cyanide and COD reduction in UCG wastewater – electrocoagulation.

Effect	removal of CN	removal of COD
ME_{time}	4.42	-9.81
ME_{dose}	7.16	1.73
Interaction.Eff.	3.69	2.14

Effect of effluent pH

Furthermore, a series of studies was conducted to determine the effect of changing the pH of the treated wastewater. At higher pH levels, an increase in the amount of iron hydroxide flocs produced is expected; however, at the same time, the amount of free Fe ions available in solution decreases.

From the data presented in Table 15 it can be seen that at a final process pH of 11, the efficiency of sulphide and cyanide removal decreased from previously observed levels of approximately 89% and 99% to 48.5% and 89%, respectively. Thus, although producing more flocs can be crucial for

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separating suspended solids or grease from other effluents, in the case of UCG wastewater, this approach proves to be less effective.

Table 15. In influence of varying the pH of the electrocoagulated wastewater – at constant dose and time of Fe dissolution.

	el_d240_i230_t60_pH8,5	el_d240_i230_t60_pH9,5	el_d240_i230_t60_pH10,5	-
Current [mA]	230	230	230	-
Voltage min–max [V]	7.82–8.97	8.78–10.61	7.50–10.25	-
Time [s]	3600	3600	3600	-
Measured Fe dose / difference from Faraday's law, mg Fe/dm^3 / %	226.2 / 5.85%	213.7 / 11.05%	215.5 / 10.3%	-
Parameters of the effluent after electrocoagulation				
pH, -	9.18	10.07	11.01	-
Conductivity, mS/cm	1.5938 (0.42%)	1.7268 (-7.89%)	2.384 (-48.95%)	-
Redox, mV	-166 (-46.47%)	-219 (-93.24%)	-272 (-140%)	-
CN^-, mg/dm^3	1.03 (89.15%)	4.56 (51.95%)	4.89 (48.47%)	-
S^{2-}, mg/dm^3	0.217 (99.43%)	2.578 (93.2%)	4.038 (89.35%)	-
COD, mg/dm^3	222.2 (21.82%)	239.2 (26.22%)	244.2 (24.68%)	-

Efficiency of electrocoagulation on removal of metals and BTX from wastewater

During the batch electrocoagulation tests, the removal of elements such as aluminium, manganese, and zinc was primarily observed (reduction to below the limit of detection). However, electrode dissolution, along with the excess Fe introduced, was also associated with a slight increase in Ni and Sn content in the treated effluent. The maximum recorded concentrations of these elements were 0.77 mg/kg and 0.096 mg/kg, respectively.

Using the data as an example, it can be determined that doses of 225–325 mg Fe/dm^3 introduced into UCG wastewater resulted in a residual concentration of Fe in the treated effluent in the range of 2–3 mg Fe/kg. This is expected, as under basic conditions Fe primarily forms very poorly soluble hydroxides.

In the case of BTX, a 2–50% decrease in concentration was observed for benzene, toluene, and ethylbenzene. Compared to chemical coagulation, these results are also more promising and conclusive.

Table 16. Results on the efficiency of removal of trace elements and organic compounds – electrocoagulation.

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	el_d240_i230_t60_pH8,5	el_d240_i306_t45_pH8,5	el_d180_i345_t30_pH8,7	-
Current [mA]	230	306	345	-
Voltage min–max [V]	7.82–8.97	10.12–11.97	11.64–12.65	-
Time [s]	3600	2700	1800	-
Measured Fe dose / difference from Faraday's law, mg Fe/dm^3 / %	226.2 / 5.85%	227 / 5.31%	162.2 / 9.98%	-
Parameters of the effluent after electrocoagulation				
pH, -	9.18	9.22	9.16	-
Conductivity, mS/cm	1.5938 (0.42%)	1.6005 (0%)	1.7334 (-8.3%)	-
Redox, mV	-166 (-46.47%)	-168 (-48.24%)	-166 (-46.47%)	-
CN^-, mg/dm^3	1.03 (89.15%)	2.43 (74.39%)	2.25 (76.29%)	-
S^{2-}, mg/dm^3	0.217 (99.43%)	0.103 (99.73%)	0.647 (98.29%)	-
COD, mg/dm^3	222.2 (21.82%)	229.2 (24.65%)	250.2 (27.73%)	-
Trace elements				
Al, mg/kg	<0.125 (>95.04%)	<0.125 (>95.04%)	<0.125 (>95.04%)	-
Fe, mg/kg	1.94 (-983.8%)	2.55 (-1324.58%)	2.99 (-1570.39%)	-
Mn, mg/kg	<0.2 (>39.94%)	<0.2 (>39.94%)	<0.2 (>39.94%)	-
Ni, mg/kg	0.748 (-52.03%)	0.77 (-56.5%)	0.686 (-39.43%)	-
Sb, mg/kg	0.085 (-6.25%)	0.084 (-5%)	0.096 (-20%)	-
Zn, mg/kg	<0.02 (>90.61%)	<0.02 (>90.61%)	<0.02 (>90.61%)	-
Sum of metals, mg/kg	3.118 (18.31%)	3.749 (1.78%)	4.117 (-7.86%)	-
BTX				
Benzene, mg/dm^3	0.204 (2.86%)	0.1 (52.38%)	0.2 (4.76%)	-
Toluene, mg/dm^3	0.269 (-236.25%)	0.07 (12.5%)	0.04 (50%)	-
Ethylobenzene, mg/dm^3	0.01 (-150%)	0.002 (50%)	-	-
m-xylene, mg/dm^3	0.02 (-400%)	0.03 (-650%)	-	-
p-xsylene, mg/dm^3	0.02 (-100%)	0.01 (0%)	0.02 (-100%)	-
Isopropylbenzene, mg/dm^3	0.01 (-400%)	-	0.009 (-350%)	-
o-xylene, mg/dm^3	0.03 (-200%)	0.09 (-800%)	0.04 (-300%)	-

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Sum of BTX, mg/dm^3	0.563 (-411.82%)	0.302 (-174.55%)	0.309 (-180.91%)	-

Conclusions

The experimental results collected indicate the potential for using both chemical coagulation and electrocoagulation to treat wastewater from the UCG process. It should be noted that while the removal of sulphides, cyanides, trace elements, and BTX from the wastewater was demonstrated, the large number of experiments necessitates that the subsequent paragraphs summarise the findings and discuss their implications.

Chemical Coagulation

Four commercially available coagulants, differing in the valency of the iron ion (II or III) and the counter ion (chlorides or sulphates), were characterised for their efficiency in the chemical coagulation of UCG wastewater. The following conclusions can be drawn from these experiments:

$FeCl_2$ – PIX100

- None of the tested coagulant doses achieved a reduction in cyanide concentration of more than 24%.
- The highest tested coagulant doses resulted in the greatest clarity of the solution and the fastest sedimentation.
- For PIX100, an increase in dose led to a clear increase in COD; for instance, at the highest tested dose of 307 mg Fe/dm^3, COD increased by 13%.

$FeSO_4$ – PIX100 COP

- A dose of 74 mg Fe/dm^3 resulted in a 19.6% reduction in cyanide content.
- Both redox potential and conductivity increased with increasing dose.
- COD decreased with increasing dose, with a 6% reduction achieved at the maximum tested dose of 92 mg Fe/dm^3.

$FeCl_3$ – PIX113

- Doses comparable to PIX100 required pH adjustment.
- At the maximum tested dose of 260 mg Fe/dm^3, the cyanide content was reduced by 21%.
- The effect on redox potential was ambiguous.
- COD reduction increased with dose, but at best, only a 5–6% decrease in COD was achieved.

$Fe_2(SO_4)_3$ – PIX116

- The behaviour was highly analogous to that observed for PIX113; however, at the lowest tested dose of 120 mg Fe/dm^3, a 5–7% lower cyanide removal efficiency was recorded.

General observations of the chemical coagulation process of UCG wastewater

- For all tested doses and forms of Fe used in the coagulation process, only a slight decrease in cyanide concentration was observed. The maximum reduction of 24% was achieved with PIX100 ($FeCl_2$) at a dose of 185 mg Fe/dm^3.
- The collected experimental data indicate that the upper limit of cyanide removal efficiency from UCG wastewater for all tested coagulants lies in the range of 20–24%.
- None of the tested process configurations were able to reduce the concentration of cyanides in the solution to below 10 mg/dm^3.
- The optimum pH range for the use of all tested coagulants was determined to be 4–9.
- For the maximum tested doses of coagulants, effective coagulation, flocculation and sedimentation were observed, resulting in residual Fe concentrations in the solution below the limit of detection (LDL).
- All tested coagulants led to a decrease in Al and Sb concentrations to below LDL; however, they also introduced secondary contamination with Ni and Mn. Additionally, PIX100 introduced Cu into the solution, while PIX116 introduced Zn.

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- Higher trace element removal efficiency was observed with the sulphate coagulants.
- None of the tested coagulants demonstrated a clear effect on BTX removal.

One of the risks associated with chemical coagulation for the removal of cyanide or sulphide is the need to apply very high doses of the coagulant. This not only introduces secondary pollutants but also counterions into the wastewater. It is important to note that the sulphates and chlorides introduced along with the iron can lead to concentrations that exceed permissible limits, necessitating further treatment before the effluent can be safely released.

Electrocoagulation

Compared to the chemical coagulation experiments described above, the electrocoagulation process exhibited several favourable characteristics.

Five sets of batch electrocoagulation experiments were conducted to determine the effects of Fe dose (current intensity as a function of time) and pH on the efficiency of reducing cyanide, sulphide, COD, redox potential, metals and metalloids, as well as organic compounds. It was found that both the dose and the interaction of dose and time had the greatest impact on the removal of cyanide and COD. These analyses can be summarised in the following points:

- A dose as low as 60 mg Fe/dm^3 led to over 60% cyanide reduction and more than 98% sulphide removal efficiency.
- The highest sulphide removal efficiency achieved was over 99.7% (with S^{2-} residual concentration equal to 0.103 mg/dm^3) at a dose of 240 mg Fe/dm^3.
- Performing electrocoagulation at a starting pH higher than 8.5 resulted in reduced removal efficiency for S^{2-} and CN^-, likely due to decreased availability of free Fe ions in solution.
- Increasing the dose of Fe from 60 mg/dm^3 to 240 mg/dm^3 improved cyanide removal efficiency from 60% to 90%, resulting in a residual concentration of 1.03 mg/dm^3.
- For COD, the highest removal efficiency achieved was only 26%.
- During batch electrocoagulation experiments, the treated wastewater became enriched with Ni and Sn, which may be related to the components of the electrodes used. Other trace elements remained at levels below the limit of detection (LDL).
- Electrocoagulation was effective in reducing Zn, Al, and Mn present in UCG wastewater. Notably, Mn was one of the contaminants introduced by chemical coagulants. Doses higher than 220 mg Fe/dm^3 led to the complete removal of Zn.
- Electrocoagulation resulted in an increase in Fe content in the solution, which was dose dependent. The maximum concentrations of Fe in the treated effluent were measured at 2–3 mg/dm^3. Given the production of insoluble iron hydroxides, effective flocculation and filtration should help manage this contamination effectively.
- In the case of BTX, a reduction of up to 50% in benzene, toluene, and ethylbenzene was observed. These results were clearer than those achieved with chemical coagulants, although the residual concentrations of organics in UCG wastewater were very low.

In the UCGwater PLUS project, the research on electrocoagulation was part of a larger research scheme aimed at demonstrating the potential of using a hybrid wastewater treatment system. This system combines electrocoagulation, wetlands, and solid-phase adsorption. Results from this part of the research are also documented in the literature [38,39,41,42].

Conceptualization, Mateusz Szul; Data curation, Mateusz Szul and Tomasz Billig; Formal analysis, Tomasz Billig; Funding acquisition, Mateusz Szul; Investigation, Mateusz Szul and Katarzyna Rychlewska; Methodology, Mateusz Szul, Katarzyna Rychlewska and Tomasz Iluk; Project administration, Mateusz Szul; Resources, Mateusz Szul and Katarzyna Rychlewska; Supervision, Mateusz Szul and Tomasz Iluk; Validation, Tomasz Iluk; Visualization, Mateusz Szul, Tomasz Iluk and Tomasz Billig; Writing – original draft, Mateusz Szul and Tomasz Billig; Writing – review & editing, Mateusz Szul and Tomasz Iluk.

Funding: The paper is the result of the UCGWATERplus project "Coal- and bio-based water remediation strategies for underground coal gasification and beyond", which is supported by the EU

Research Fund for Coal and Steel, under the Grant Agreement no. 101033964, and the Polish Ministry of Education and Science, under the contract no. 5185/FBWiS/2021/2.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

BTX benzene, toluene, xylene
COD chemical oxygen demand
EC electrocoagulation
GIG-PIB Główny Instytut Górnictwa – Państwowy Instytut Badawczy (Central Minining Institute – National Research Institute) – Katowice, Poland
ME main effect
PAH polyaromatic hydrocarbons
TOC total organic carbon
UCG underground coal gasification
WW wastewater

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