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Regeneration of process waters for their subsequent use in the viscose
and textile industry

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References

Abstract

The subject of study involved the treatment of real process wastewater from the production of rayon fibres. The goal of the work is to find a technological procedure, or to design a technology for reducing COD in process wastewater from the production of viscose fibres. During the annual monitoring of the production facility, we performed a mass balance of three problematic sources of process wastewater and analysed them repeatedly. All three sources showed high values of COD = 0.4-30 g/l, TOC = 0,09-7.1 g/l and the concentration of Zn^{2+} 0.09-0.5 g/l. At a total volume of 1.84 million m³, this represents a significant pollution source for the Elbe River. At lab scale, we tested a combination of filtration, microfiltration and oxidation using the Fenton, electro-Fenton and the indirect electrochemical oxidation methods, both on plate and newly developed macroporous BDD electrodes on a ceramic substrate, along with the final adsorption of Zn^{2+} emissions on the strongly acidic cation exchange resin Lewatit Mono plus S108. It was tested in Na⁺ and H⁺ cycles. Using an optimized technological sequence, we have achieved a COD reduction of up to 98 %, and TOC reduction of 85 % g/l. During the H⁺ cycle cation regeneration by sulfuric acid, Zn^{2+} emissions were converted to zinc sulphate that can be recycled in the spinning bath of the production process. The method was verified at a pilot scale.

Abstrakt

Předmětem vědecké práce je čištění reálných procesních odpadních vod z výroby vláken umělého hedvábí. Cílem práce je nalezení technologického postupu, případně navrzení technologie pro snížení CHSK v procesních odpadních vodách z výroby viskózního vlákna. Při ročním monitoringu výrobního zařízení byla provedena hmotnostní bilance tří problematických zdrojů procesních odpadních vod a opakovaně analyzována. Všechny tři zdroje vykazovaly vysoké hodnoty CHSK = 0,4-30 g/l, TOC = 0,09-7,1 g/l a koncentraci Zn^{2+} 0,09-0,5 g/l. V celkovém objemu 1,84 mil. m³ se jedná o významný zdroj znečištění řeky Labe. V laboratorním měřítku byly testovány kombinace filtrace, mikrofiltrace a oxidace pomocí metod Fenton, elektro-Fenton a nepřímé elektrochemické oxidace, a to jak na deskových, tak nově vyvinutých makroporézních BDD elektrodách na keramickém substrátu, spolu s finální adsorpcí emisí Zn^{2+} na silně kyselou katexovou pryskyřici Lewatit Mono plus S108. Byl testován v cyklech Na⁺ a H⁺. Pomocí optimalizované technologické sekvence jsme dosáhli snížení CHSK až o 98 % a snížení TOC o 85 % g/l. Během H⁺ cyklu regenerace kationtů kyselinou sírovou byly emise Zn^{2+} převedeny na síran zinečnatý, který lze recyklovat ve zvláknovací lázni výrobního procesu. Metoda byla ověřena v poloprodučním měřítku.

Keywords

industrial wastewater, spinning process, Fenton oxidation processes, electro – Fenton, regeneration of ion exchangers

Klíčová slova

průmyslové odpadní vody, zvláknovací proces, Fentonova oxidace, elektro – Fenton, regenerace iontoměníčů.

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Introduction

At the beginning of the 20th century, in places where there were no longer permanent settlements, a chemistry center was gradually established in Lovosice. The founder of the tradition of the chemical industry in Lovosice was Theodor Groger, who in 1900 had a chemical factory built in the fields between Lovosice and Terezín. The factory originally produced lubricating greases, oils and a considerable range of chemical products. The sulfuric acid and superphosphate factory was founded on January 29, 1903 by Adolf Schram. History of Glanzstoff – Bohemia s.r.o. dates back to the territory of the Czech Republic until 1921, when the company "První česká fabrika Glanzstoff a.s." was founded in Lovosice, closer to the city also on Tereziňská street, on 15 August 1921, the construction of the third chemical company Czech artificial silk factory (Glanzstoff Fabrik Elberfeld) began). The production of man-made fiber was started on March 6, 1923 with 665 employees [1]. In the 20s of the last centuries, together with the then "First Austrian factory Glanzstoff a.s.", it represented a production-sales community for textile viscose fibers, which were exclusively produced at the time [2].

Currently, Glanzstoff Bohemia s.r.o. part of the multinational concern Indorama Ventures Limited. The plant is a major producer of technical yarns, cords and fabrics for the rubber and composite industries and maintains a leading position in the production and processing of high strength viscose filament yarns for technical applications. The production of textile fiber is limited only to special applications, for example, fibers enriched with flame retardants, which are used to make fireproof suits for integrated emergency services. Due to the nominal production capacity of 12,000 t/year man-made yarn, 30,000 t/year TCF (Tire Cord Fabrics) and 7,300 tons/year SEC (Single-End-Cord), production quality and distribution network, it is an important system supplier at the global level [3].

Glanzstoff Bohemia s.r.o. takes its responsibility towards society and future generations very seriously. The basic premise of the production activity is the use of the best available technology and technique, the fulfillment of the limits of the integrated permit, legal limits and standards. Fulfilling the principles of sustainable development is a matter of course. As a chemical enterprise dealing with hazardous substances, the company carefully observes the safety measures given by the legislation, and in many ways even beyond it. Above all, from the point of view of threats to aquatic ecosystems and, of course, threats to human health. Thanks to investments in greening, production at GBO has become one of the most environmentally friendly of all viscose fiber production in the world. In order to maintain this state in the future, it is necessary to plan other projects leading to a reduction in the impact on the environment. Research tasks are solved in cooperation between witness workplaces, the aim of which is further reduction of emissions, reduction of harmful substances in waste water, ecological use of waste, energy savings, better monitoring and others.

Glanzstoff Bohemia s.r.o. does not have its own resources for water management. All technological water and utility water is purchased within the industrial zone from Lovochemie

a.s. It also does not have its own wastewater treatment plant, so their treatment is contractually provided at the Lovochemie a.s. wastewater treatment plant.

The production of viscose fiber produces waste water polluted with inorganic and organic substances: zinc salts, organic substances increasing COD, dissolved inorganic salts, undissolved substances, carbon disulfide and sulfan. Wastewater is pre-treated before it leaves the company premises. In recent years, large sums have been invested in technological elements and in wastewater pretreatment equipment. This led to a reduction in the pollutant content of the wastewater and a 60% reduction in the total volume of wastewater. Furthermore, the technology of zinc regeneration by the method of sorption on an ion exchanger and subsequent elution with sodium sulfate was introduced. The obtained zinc is reused as a raw material. In 2002, the calcination process was introduced, where the extracted sodium sulfate is freed from crystalline water and sold as a product. This reduced the content of dissolved inorganic salts in the wastewater entering the treatment plant by approximately 80%.

However, these steps lead to a significant proportional increase in COD values in industrial wastewater. According to the integrated permit, Glanzstoff Bohemia s.r.o. must comply with the internal emission limits given by the sewage regulations of Lovochemie a.s. when transferring waste water. Although the limits at the outlet of the WWTP are a matter of Lovochemie a.s., Glanzstoff –Bohemia s.r.o. carefully monitors indicators that are affected by pollutants from its wastewater (such as zinc, carbon disulfide, sulfides, COD-Cr, etc.), and does not disclaim responsibility for any limits exceeded.

Based on the above, the Glanzstoff Bohemia company's research plan was created, which should reveal the most significant wastewater streams in terms of COD contribution in wastewater and at the same time find a technological solution for its removal.

1 Theoretical Part

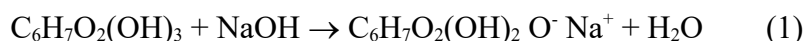
The basis of viscose fiber production is cellulose produced by sulfate technology, in the case of the Glanzstoff Bohemia plant in Lovosice, from soft woods (spruce wood) with a high content of α -cellulose (96-98%). Viscose fiber is essentially regenerated cellulose hydrate and its production can be divided into four steps.

- Mercerization of pulp, the goal of which is the production of alkali cellulose.
- Pulping, which increases the surface area of the alkali cellulose, and thus leads to a faster penetration of CS_2 within the sulphidation.
- A pre-ripening process in which the molecular weight is reduced by the action of oxygen. Cellulose is broken down into smaller, spinnable particles.
- Sulfidation, during which cellulose is esterified and xanthogenate is formed. This is further dissolved in NaOH, resulting in liquid viscose, which is further prepared by physical processes (spreading, filtration, homogenization, degassing, heating) for subsequent regeneration on spinning machines.

Regeneration of viscose takes place in an acidic spinning bath containing H_2SO_4 on special spinning machines. In the case of the plant in Glanzstoff Bohemia, these are KVKH machines with endless fiber winding and continuous sequence of fiber treatment steps after spinning. The technology of stretching and washing the fiber (or washing) from the remnants of the spinning bath is gradually included on the machines. Next, annealing in a solution of methyl orange, as a fiber pH indicator. Aeration in an oil bath for subsequent textile technological steps. The last technological step on the machines is drying the fiber through condensation pots, so-called dryers. Furthermore, the viscose fiber in Glanzstoff Bohemia is processed using standard technological procedures of the textile industry. Which are scanning, or twisting, i.e. rewinding and connecting non-standard windings. Then weaving.

1.1 Production of Viscose

Viscose in its xanthogenized form is the starting material for the production of viscose fiber. In the first stage of processing, so-called soaking takes place. The cellulose is crushed and mixed with caustic soda. This process can be expressed by the following mechanism [8].

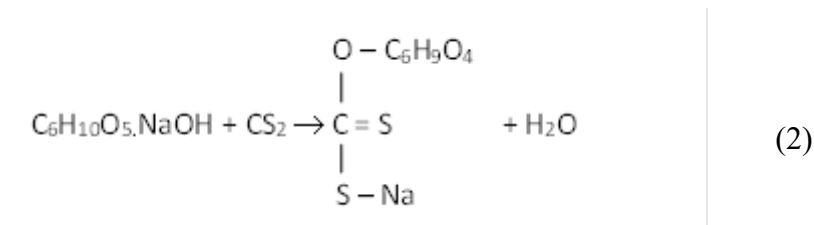


During this process, the cellulose gains volume and heat of reaction is released. Cellulose takes up water and caustic soda, which are partly stored in the expanding cellulose lattice. This stage of production is called alkalization, and its duration depends both on the starting raw material and the desired final product, as well as on the temperature and concentration of caustic soda. The intermediate product of this production step is called alkali cellulose.

After alkalization, the excess lye is squeezed out and the alkali cellulose goes on to pre-ripening. Pre-ripening takes place in aging boxes for about 30 hours. Oxidative degradation of cellulose chains (exothermic reaction) reduces the degree of polymerization (chain length).

Pre-ripening, guaranteeing the optimization of further processing, is dependent on the starting material, the desired final product and the alkalinization.

Sufficiently mature alkali cellulose is further sulphided in the technology with carbon disulfide, an exothermic reaction, so-called xanthogenation, xanthogenate is formed. The formation of cellulose xanthogenate by the action of carbon disulfide can be expressed by the following mechanism [8].



The xanthogenate further dissolves in water and caustic soda to form viscose. The dissolution must be as perfect as possible, otherwise subsequent filters, which capture larger solid particles, will become clogged. For perfect spinnability, it is necessary to ensure the appropriate maturity of the viscose and then high homogeneity. Therefore, the technologies of homogenization, filtration, heating and degassing are included before the spinning process. The perfectly prepared viscose is then spun in a spinning bath on special spinning machines.

1.2 Spinnig Bath

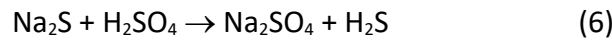
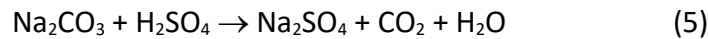
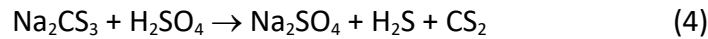
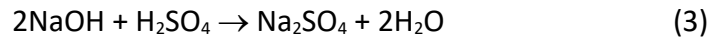
The spinning process of xanthogenized viscose takes place in an acid bath, which contains the following major components: water, sulfuric acid (H_2SO_4) in a concentration of around 80 g/l, zinc sulfate (Zn_2SO_4) in a concentration of around 60 g/l, sodium sulfate (Na_2SO_4) and surface-active substances. Technologically monitored parameters are density, which is formed by the ratio of water and sodium sulfate, concentration of sulfuric acid, concentration of zinc sulfate, temperature and turbidity, or transparency (purity) of the bath. Sodium sulfate precipitates dissolved sodium cellulose xanthate. Sulfuric acid converts xanthate to cellulose, carbon disulfide and sodium sulfate. Zinc sulfate aids the spinning process and affects the strength of the produced viscose fiber. The spinning bath needs to be continuously regenerated, which in practice means the removal of excess substances created by the spinning process, which are water, sodium sulfate and degraded surfactants. On the contrary, to supply input raw materials so that the spinning bath always has the same input parameters for a perfect spinning process.

1.3 Spinning process

Viscose spinning is one of the most important parts of the technological process production of viscose fibers. The essence of spinning is based on extrusion pre-treated, homogenized viscose through the small openings of the spinning nozzles into the spinning bath. Harmful

gases (carbon disulfide, hydrogen sulfide) are released during coagulation, which is a major drawback of viscose fiber production. The subsequent withdrawal of the fibers from the spinning nozzles creates a negative pressure inside the fiber, which results in the collapse of the original circular cross-section of the fibers into their characteristic cloud-like shape. Along with spinning, fiber elongation takes place, during which fiber orientation and strength increase. The spinning of viscose fibers depends not only on the composition and properties of the solution and the spinning bath, but also on the immersion of the spinning nozzle in the bath. The deeper the spinning nozzle is immersed in the bath, the longer the path in the spinning bath. The normal immersion of the nozzles is between 20 and 30 cm, so the fiber remains in the bath, at normal withdrawal speeds, from 0.1 to 0.2 seconds [5] [6].

In addition to the main process of cellulose regeneration, several important secondary chemical reactions take place [7]:



It follows from this that the products from secondary chemical reactions must be extracted in the spinning bath regeneration technology and, due to the continuous washing of the fiber, also eliminated from the resulting waste water.

1.4 Industrial wastewater

Apart from Zn^{2+} ion emissions, the nature of industrial wastewater pollution in Glanzstoff Bohemia is similar to organic pollution from pulp and paper mills, where a combination of physical-chemical-biological treatment is often used, consisting of a combination of primary settling, coagulation-flocculation clarification and adsorption on activated carbon [4][9–10]. The presence of Zn^{2+} ion complicates water purification and zinc recycling. Older works usually used precipitation with milk of lime to form $\text{Zn}(\text{OH})_2$, or less efficient cathexes, membrane processes, electrodialysis or electrolysis [11–14]. The processes of electrodeposition on copper cathodes and nanofiltration were relatively effective in these wastewaters [16][17]. The precipitation process is still used even at the Glanzstoff Bohemia s.r.o. plant, where only the neutralization of acidic waste water with milk of lime is applied. A simple solution for industrial wastewater GBO contains a patent [17], which consists in the application of NaOH, where $\text{Zn}(\text{OH})_2$ is converted back to ZnSO_4 in the spinning bath by waste sulfuric acid. In the case of GBO, this solution is unfortunately out of the question for technological and economic reasons, as it is not technically possible to filter, recrystallize and dissolve the precipitated $\text{Zn}(\text{OH})_2$ directly in the plant. For a higher efficiency of the precipitation process, $\text{pH} \approx 9.5\text{--}10.5$ is required, when $\text{Zn}(\text{OH})_2(\text{s})$ predominates. In the pH range between 5–9.5, zinc is present mainly in the form of $\text{Zn}_5(\text{OH})_6\text{CO}_3)_2(\text{s})$, and at lower pH then $\text{ZnCO}_3(\text{s})$ predominates [3]. At the below-mentioned flow rates and volumes of

wastewater, the annual losses of the company amount to approx. 44.3 t of metallic zinc, or 121.5 t of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$, used as input raw material in the spinning and plasticizing bath.

1.5 Advanced oxidation processes

Water is essential for life, and although it is very abundant on Earth, its total volume is mainly made up of water resources that are not directly usable by humans. Salty waters of oceans and seas (97.2% of the total weight of water), or glaciers (2.15%). Only about 0.65% of the total weight of water can be directly used by humans [18]. Moreover, the distribution of water on land is geographically uneven and some areas are arid and desert. A significant part of water resources is more or less polluted due to human activity or due to natural phenomena. Therefore, there is a fundamental need for companies to develop effective and environmentally friendly methods of treating contaminated water, reducing or completely eliminating pollutants and recycling municipal and industrial water. Advanced oxidation processes (AOP) are among the methods of treating or pre-treating polluted waters. Precisely defined [19] as water treatment processes carried out at room temperature and normal pressure and based on the in situ generation of a strong oxidizing agent, such as hydroxyl radicals $\bullet\text{OH}$, in sufficient concentration to be effective to decontaminate waters. Recently, AOPs have been the subject of increased attention from scientists, as shown by a large number of basic and applied research papers [20]. They represent promising, efficient, environmentally friendly methods of removing POPs from water. AOP methods are based on the in-situ formation of $\bullet\text{OH}$ radicals using various chemical, photochemical, sonochemical or electrochemical reactions. The oldest and most widely used chemical AOP is the Fenton method, which uses a mixture of soluble ferric salt and H_2O_2 , known as Fenton's reagent [21] [22]. However, the overall oxidation efficiency can be significantly improved by using ultraviolet (UV) light irradiation (photo-Fenton method) or sunlight (solar photo-Fenton method) [22]. Another interesting improvement is based on the combination of the Fenton technique with electrochemical reactions. In fact, there are a number of electrochemical advanced oxidation processes (EAOP) [23][24]. Advanced oxidation processes (AOP) on an industrial scale represent important, perspective, effective and ecological methods developed primarily for the removal of persistent organic pollutants (POPs) from wastewater and effective decontamination through the action of hydroxyl radicals. The following overview of the main types of AOP [20] based on chemical, photochemical and electrochemical reactions represents a list of possible theoretical solutions for the pretreatment of industrial wastewater Glanzstoff Bohemia, for their subsequent recycling. The principles, performances, advantages and disadvantages of the application of these AOPs for the degradation and destruction of POPs in the aquatic environment were chosen based on the available results of international studies [18][25] [26].

2 Experimental Part

2.1 Characteristics of viscose industry wastewater

Viscose, or staple fiber, is mainly used for the production of textiles and clothing due to its advantages in comfort and moisture absorption. The world's largest producer of viscose with an annual capacity of approximately 4 million tons is China, where the textile and clothing industry has a long-standing tradition and its share of the market for medium and high-class fabrics is still increasing [27]. This is especially true in the two main categories of clothing, namely shirts and suits, where viscose staple is processed, the production of which increased from 2.8 million tons in 2011 to 3.4 million tons in 2018 [27][28]. A significant environmental problem related to the production of viscose fibers is the consumption of water, based on a ton of production, and the limited possibilities for its recycling. The work [27] mentions that, according to statistics, approximately 65 tons of fresh water are used to produce one ton of viscose staple, and approximately another 110 tons of fresh water are needed to dye and finish one ton of textiles. The consumption of alkali, carbon disulfide, sulfuric acid and other chemicals used in the production process is approximately 3.3 tons/ton of viscose fibers. A significant part of these chemicals passes into the washing water and together with it escapes into the environment. As part of the initial phase of the research, all water flows of all production processes were mapped. Sampling points were selected and analyzes of important parameters were carried out. Subsequently, the Block Flow Diagram was processed. Based on the performed analyses, see Fig. 1, waters with an important contribution to the quality of industrial wastewater were further selected within POP.

tests 1 (12.9.2018)	COD	IDS	TDS	insoluble particles	pH	hardness (Ca+Mg)	Zinc	sulfate	chlorides	conductivity
	mg/l	mg/l	mg/l	mg/l		°dH	mg/l	mg/l	mg/l	mS/cm
1	<25	231	276	0,5	10,1	5,8	n.d.	48,5	38,1	0,37
2A	28	198	248	0,8	10	5,8	n.d.	44,5	38,1	0,37
2B	204	69600	125300	65,2	8	2730	n.d.	117	53600	102
2C	33	8540	9750	4,2	9,9	56,6	n.d.	55,5	5300	15,4
3	38	239	248	0,2	10	5,9	n.d.	49,5	36,7	0,36
4	43	232	232	0,1	10,1	1,8	0,004	43,8	36,7	0,39
5	<25	463	504	0,1	10,2	<0,5	0,007	130	81,8	0,79
6		15	17	0	9,6	<0,5	n.d.	<5	3,5	0,03
7	158	977	1660	16,1	3,1	9,2	98,1	906	70,6	4,3
8	<25	263	288	2,3	7,8	7,6	0,018	31,1	56,4	0,41
9	145	959	1568	9	3,2	3,6	33,1	860	70,6	4,2
10	48	276	286		7,8	7,6	1,5	40,8	49,4	0,42
tests 2 (6.11.2018)	COD	IDS	TDS	insoluble particles	pH	hardness (Ca+Mg)	Zinc	sulfate	chlorides	conductivity
	mg/l	mg/l	mg/l	mg/l		°dH	mg/l	mg/l	mg/l	mS/cm
1	<20	221	290	0	9,2	6,2	n.d.	64	44,3	0,43
2A	<20	266	328	0,2	8,5	5,6	n.d.	58	49,5	0,42
2B	1320	72100	127900	43,8	6,7	2810	n.d.	47	54500	107
2C	22	1250	1660	0,2	9,7	3,4	n.d.	58	567	0,6
3	<20	221	277	0,4	8,8	6,2	n.d.	68	46	0,42
4	<20	255	262	0,2	9,3	<0,5	n.d.	56	46	0,45
5	<20	609	643	0,2	9	<0,5	n.d.	199	103	1,03
6	<20	5	12	0	9,7	<0,5	n.d.	<5	10,6	0,06
7	<20	335	337	17,4	6,7	0,96	0,03	39	49,5	0,48
8	<20	310	331	6,6	7,1	9	1,04	39	46	0,48
9	287	1070	1805	3,6	2,4	9,5	112	796	177	4,47
10	321	1060	1730	7,4	2,5	9,5	115	919	177	4,52
11	243	922	1600	0,4	2,3	1,12	19,7	772	230	4,82
12	<20	203	283	0,6	6,8	6,2	6	64	47,8	0,43
13	80	2110	2660	2	7,5	53,9	6,6	743	379	3,27
14										
15	258	530	616	80,6	11	5,6	6	112	39	1,09
16	<20	225	276	0,6	6	5,6	2,5	60	47,8	0,43

Figure 1: Results of analyzes of defined GBO wastewater collection points

2.2 Waste water from regeneration and flushing

Another important source of wastewater, hereinafter referred to as WWW2, is the rinsing water from the regenerative washing of the sand filters through which the technological water WWW1 passes. Sand filters are used in production to filter the spinning bath before its regeneration. It is thus used to capture gross impurities, but does not change the parameters WWW2 is contaminated with zinc sulphate, sulfuric acid, residues of cellulose, hemicellulose and surfactants. Washing water WWW2 is degassed from dissolved carbon disulfide and

hydrogen sulphide before entering the ion exchanger (CS_2 and H_2S is catalytically oxidized by SULFOX technology) and is then filtered on sand filters. From the technological nature of the source of these waters, it is clear that WW2 are produced discontinuously in periodically following 4 h cycles during counter current washing of sand filters A and B, Fig. 1. This follows after approx. 80 h of continuous filtering process WW1. The annual water volume of WW2 is approx. 400 m^3 , CHSKcr is in the range of 5-10,000 mg/l, which corresponds to the concentration of organic carbon (TOC) in the range of 1-3,500 mg/l. The ratio $\text{BOD}_5/\text{CHD}=0.29$ indicates more difficult biological degradability. Zn^{2+} emissions occur in concentrations of 100-200 mg/l.

2.3 Washing waters from corrective regeneration

Remedial regeneration washing waters are the third significant source of technological waste water in the GBO plant, they are strongly alkaline WW3 washing waters from the remedial regeneration of alternating cathexis filters, see Fig. 1. These are filled with strongly acidic cathexis Lewatit MonoPlus S108, working in the Na^+ cycle. The usual cathexis regeneration cycles take place after approx. 10 h by washing with a 10-14 percent solution of waste sodium sulfate from the sodium sulfate calcinate production plant. After approximately 2 weeks, the surface of the cathexis filling is clogged with insoluble residues of viscous fibers and sludge to the extent that it is necessary to regenerate the cathexis with a 1 mol/l sodium hydroxide solution (after passing through the cathexis filling WW3). This solution, however, is prepared from water already loaded with organic pollution from the mentioned technology. This reduces the efficiency of Na^+ ion regeneration and thus the capacity of the Lewatit MonoPlus S108 cathexis. The volume of WW3 during the regeneration cycle is approx. 20 m^3 , the annual volume of these waters is therefore approx. 500 m^3 . For WW3, the characteristic COD values are in the range of 12-30,000 mg/l, and the organic carbon TOC concentration in the range of 2,500-6,000 mg/l corresponds to these values. The found ratio of $\text{BOD}_5/\text{COD}=0.21$ indicates difficult biological degradability. Zn^{2+} emissions reach concentrations of 90-500 mg/l in WW3.

2.4 Lewatit Mono Plus S108 cathex regeneration

The aim of the research part is to determine the useful capacity of the ionex Lewatit Mono Plus S108 for the capture of Zn^{2+} ions and to verify the possibilities of its regeneration with sulfuric acid. The initial analyzes of wastewater and used production technologies showed that the most ineffective option for reducing COD in wastewater leaving the Glanzstoff Bohemia production process is the optimization of the regeneration process of the ion exchange cartridge used to capture zinc ions in the stream of used washing water, where their concentrations exceed the value of 100 mg /l.

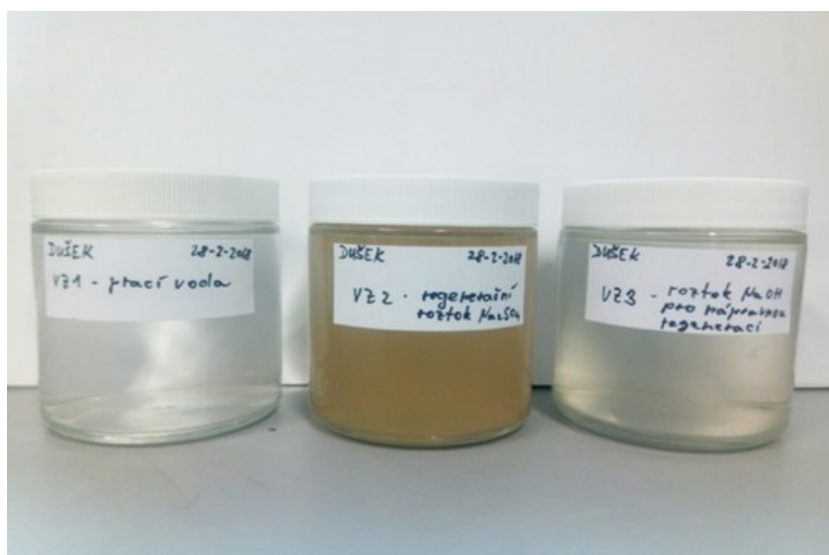


Figure 2: From left to right: samples of purified wastewater VZ1, sodium sulfate used for regeneration of ion exchanger VZ2 and sodium hydroxide with sodium and zinc sulfate residues used for remedial regeneration of acid cathexis VZ3.

Before the design of the next procedure, samples VZ1, VZ2 and VZ3 were subjected to initial analysis in order to obtain the relevant characteristics of washing water, regeneration and remedial regeneration solution. For this reason, pH and electrolytic conductivity values were measured. The quantitative representation of the organic matrix was determined by a combination of COD_{Cr} and TOC parameters. Simultaneously with the total organic carbon (TOC) parameter, total carbon (TC) and inorganic carbon (IC) were also determined, corresponding to the presence of carbonates and bicarbonates, respectively. The total content of TN nitrogen present was determined to clarify the character of the organic matrix.

sample	pH	Con	COD_{Cr}	TC	TOC	IC	TN	S	Na	Zn
		[mS/cm]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]
VZ1	2,17	4,66	458	117,36	114,24	6,45	3,12	450,7	280	109,6
VZ2	3,79	97,1	2150	908,2	903,31	34,0	5,10	29270	36710	2698
VZ3	12,56	183,3	410	119,27	112,23	7,14	2,76	4589	26235	2,098

Table 1: Summary of the results of the input analyzes of samples of washing water VZ1, regeneration solution Na_2SO_4 VZ2 and remedial regeneration sodium hydroxide solution VZ3.

2.4.1 Conclusion from the results of the input analysis and further procedure

The results of the input analysis show that the acidic ($\text{pH} = 2.17$) wash water purified on the ion exchanger is slightly organically polluted ($\text{COD} = 458 \text{ mg/l}$, $\text{TOC} = 114.24 \text{ mg/l}$) contains approx. 110 mg/l (1.676 mmol/l) zinc in the form of 270.65 mg/l (1.676 mmol/l) zinc sulfate and 280 mg/l (11.773 mmol/l) sodium, which corresponds to 836.2 mg/l sodium sulfate (5.887 mmol/l). Since the concentration of sulfur found in the washing water was 450.7 mg/l ($14,056 \text{ mmol/l}$), after subtracting the molar amount attributable to sulfates, there is still approx. 208.2 mg/l (6.49 mmol/l) of sulfur. It is a question whether it occurs in the form of sodium or zinc sulfide or in the form of carbon disulfide. Since sulfides would be subject to hydrolysis and decomposition in an aqueous acidic environment to release hydrogen sulfide, I consider the presence of remaining sulfur in the form of 247 mg/l (3.245 mmol/l) CS_2 to be more likely. Regarding the analysis of the data obtained from the analysis of the regeneration solution containing sodium sulfate, it can be stated that it is a slightly acidic solution with $\text{pH} = 3.79$ and conductivity $\kappa = 97.1 \text{ mS/cm}$, which contains a significant amount of cellulose and hemicellulose ($\text{COD} = 2150 \text{ mg/l}$, $\text{TOC} = 903 \text{ mg/l}$). Quantitative determination of sodium zinc and sulfur concentration using ICP-AES analysis found 2.698 g/l zinc (41.266 mmol/l), which corresponds to a zinc sulphate concentration of 6.662 g/l (41.266 mmol/l). The found sodium concentration of 36.71 g/mol (1.597 mol/l) corresponds to a sodium sulphate concentration of 113.406 g/l (0.798 mol/l), which represents a strongly supersaturated solution from which the undissolved portion of Na_2SO_4 will gradually be excreted, which corresponds to reality. It follows from the sulphur balance that in the regeneration solution its concentration is 29.270 g/l (0.913 mol/l) and after subtracting the substance amount of sulphates, its residual concentration is 2.359 g/l (73.567 mmol/l). Due to the acidic nature of the solution, I am inclined to believe that, despite the low boiling point, it may represent carbon disulfide, slightly soluble in water, or hydrogen sulphide, which is much more soluble.

2.5 Etape I Determination of the usable capacity of Ionex for Zn^{2+} capture and the possibility of its regeneration with sulfuric acid

The tested ionex Lewatit Mono Plus S108 is a strongly acidic cathex based on sulfonated styrene-divinylbenzene copolymer, with sulfonic acid groups converted to sodium salt. Katex has a density of 1300 kg/m^3 , the bulk density ranges from 800 to 850 kg/m^3 . Katex is stable in the pH range of 0 - 14 , storable at -20 to $+40 \text{ }^\circ\text{C}$ and operationally applicable in the temperature range of 0 to $+120 \text{ }^\circ\text{C}$. The total capacity indicated by the manufacturer reaches 2.2 molar equivalents per litre. Katex is highly monodisperse (the uniformity coefficient is 1.05 ± 0.05) with an average ball size of $0.64 \pm 0.05 \text{ mm}$. The manufacturer recommends counter current regeneration of the cathex by applying 100 g of HCl per 1 l of cathex or by applying sulfuric acid in an amount of 150 g/l of cathex or using NaCl in an amount of 90 g/l of cathex. In the case of hydrochloric acid, the manufacturer recommends its application in a concentration of 4 - 6 wt. \% of the solution, when regenerating with sulfuric acid, a concentration of 1.5 - 3.0 wt. \% and when applying NaCl solution then 8 - 10 wt. \% .



Figure 3: Batch arrangement of experiments to determine the total capacity of the strong acid cathexis Lewatit Mono Plus S108



Figure 4: Column arrangement of experiments to determine the total capacity of the strongly acidic cathexis Lewatit Mono Plus S108

2.5.1 Conclusions for etape I

Batch experiments both on the model solution and with real washing water VZ1 demonstrated the possibility of increasing the useful capacity of the Lewatit Mono Plus S108 acid cathexis, when in the case of the model solution the average useful capacity of Lewatit Mono Plus S108 was 1.78 ± 0.025 eg/l. In the case of application of washing water VZ2, the average usable capacity was 1.789 ± 0.031 , i.e. practically identical within the experimental error. If a sodium sulphate regeneration solution contaminated with zinc sulphate and an organic matrix was used for regeneration, the useful capacity of ionex was reduced to 1.324 ± 0.014 eg/l and 1.31 ± 0.035 eg/l for washing water VZ1, respectively.

This assumption was independently confirmed during column experiments, which also unequivocally demonstrated the possibility of increasing the capacity of the Lewatit Mono Plus S108 acid cathexis by approx. 26%, if the previously used regeneration solution VZ2 of sodium sulphate, which is permanently contaminated with zinc sulphate in the amount of 6.7 g/l and cellulose and hemicellulose residues (COD = 2150 mg/l, TOC= 903 mg/l) replace 3 wt. % sulfuric acid. The total capacity of Lewatit Mono Plus S108 with the transition from the Na^+ cycle for the regeneration of VZ2 to the H^+ cycle with regeneration using 3 wt. % of sulfuric acid managed to increase from 1.294 ± 0.032 eg/l to 1.783 ± 0.037 eg/l According to the cathexis manufacturer's recommendations, the amount of regenerating agent can be reduced by switching from the Na^+ cycle to the H^+ cycle from 3.4 equivalents of Na^+/L to 3.0 equivalents of H^+/L (1.5 moles of H_2SO_4 per 1 liter of cathex). Optimization of the regeneration medium – sulfuric acid was not carried out. The amount recommended by the manufacturer was enough to restore the ionex capacity.

2.6 Etape II Sorption tests of ionex, comparison of Na⁺ and H⁺ cycles

When planning the tests, it was based on the delivered data of the working modes (sorption, regeneration) of cathexis filters. The laboratory tests were designed to correspond on a reduced scale to the existing Zn sorption/regeneration operation. The volume of ionex and the volumes and flow rates of the liquid phases were equivalently reduced within the laboratory tests, but proportionally they corresponded to real operating conditions and can therefore be interpreted on real operating conditions. Work and regeneration cycle times were maintained.

The scale of the laboratory tests was chosen to be 1: 3,333,333 compared to real conditions, so the laboratory tests took place on a scale 3,333,333 times smaller than the existing operation. According to the supplied information, it was therefore not possible to change the washing water flow rates or the length of the sorption time. These parameters were therefore maintained within the laboratory tests, the flow of washing water was equivalently reduced to correspond to the reduced volume of the ionex filling in the laboratory column. The following Table 8 shows the current operating conditions and the conditions chosen in the laboratory tests.

2.6.1 Conclusion Etape II

The conducted experiments prove that the Na₂SO₄ used for regeneration in the current operation is unsuitable for these purposes, as this solution is highly contaminated and causes fouling of the ionex with organic substances. The tests carried out further show that a much more suitable way of regenerating Zn is to operate cathexes in the H cycle and perform H₂SO₄ regeneration. The H₂SO₄ solution is not contaminated, and its use does not reduce the effectiveness of Zn sorption. With sorption in the H-cycle, there is also a high probability that there will be no need to perform corrective regeneration, or the frequency of performing corrective regenerations would be significantly reduced. The question, however, is choosing the right regeneration mode so that not too much H₂SO₄ is consumed, but that the regeneration is sufficiently effective, i.e. all the absorbed amount of Zn is washed out of the ionex.

Measured Zn concentrations at the outlet of the column in operation during sorption can be distorted in several ways. If there is an incomplete flushing of the Na₂SO₄ regeneration solution from the ionex bed, there may be an increase in the concentration of Zn at the outlet of the column, when, due to the flow of washing water, the remnants of the regeneration solution are washed out and also because the remaining solution reduces the capacity of the ionex. Fluctuations in the concentration of Zn at the outlet of the column are further caused by a change in the flow of washing water through the column, while an increase in the flow will cause a higher concentration of Zn, because the sorption equilibrium will not be established and Zn will begin to penetrate the column, and on the contrary, a decrease in the flow through the column will reduce the concentration of Zn at the outlet of the column.

2.7 Etape III Stable ionex tests for sulfuric acid regeneration

The experimental work was divided into two parts within this stage. First, the sorption capacity of the ionex for Zn^{2+} ions was determined for real washing water and for a model Zn solution. Subsequently, experiments were carried out in order to verify and determine the resistance of cathexis to an acidic environment and changes in osmotic pressure. Furthermore, batch tests were carried out in order to determine the optimal concentration of H_2SO_4 for cathexis regeneration. In the next part of the experimental work, a total of 20 sorption column tests were performed, which simulated the real operation of cathexis filters on a reduced scale.

	TOC (mg/l)	Zn (mg/l)	COD _{Cr} (mg/l)		
Input of washing water	80,7	100,3	Input regeneration		<5
output sorption	TOC (mg/l)	Zn (mg/l)	Output regeneration	COD _{Cr} (mg/l)	COD _{Cr} /3ml ionex (mg)
T1A	59,7	0,47	T1A	34	0,5
T1B	59,1	0,42	T1B	222	2
T2A	59,6	0,22	T2A	243	3,3
T2B	57,2	0,21	T2B	487	4,4
T3A	59,9	0,33	T3A	383	5,2
T3B	60,7	0,47	T3B	714	6,4
T4A	64	0,35	T4A	515	7
T4B	63,7	0,17	T4B	1080	9,7
T5A	64	0,37	T5A	805	10,9
T5B	64,4	0,43	T5B	1471	13,2
T6A	64,7	0,33	T6A	1361	18,4
T6B	65,8	0,29	T6B	1602	14,4
T7A	67,6	0,36	T7A	1253	16,9
T7B	67,2	0,22	T7B	1916	17,2
T8A	64,2	0,31	T8A	1358	18,3
T8B	68,8	0,44	T8B	1951	17,6
T9A	64,2	0,14	T9A	1567	21,2
T9B	64,1	0,34	T9B	2056	18,5
T10A	62,3	0,24	T10A	1646	22,2
T10B	65,6	0,31	T10B	2221	20
T11A	66	0,22	T11A	1576	21,3
T11B	66,1	0,34	T11B	2335	21
T12A	62,5	0,3	T12A	1480	20
T12B	64,6	0,46	T12B	2038	18,3
T13A	65,2	0,24	T13A	1628	22
T13B	65,7	0,39	T13B	2221	20
T14A	66,6	0,37	T14A	1445	19,5
T14B	66,9	0,47	T14B	1751	15,8
T15A	68	0,2	T15A	1655	22,3
T15B	67	0,28	T15B	2317	20,9
T16A	68,2	0,27	T16A	1576	21,3
T16B	67,1	0,29	T16B	2274	20,5
T17A	67,8	0,16	T17A	1284	17,3
T17B	67,6	0,21	T17B	1768	15,9
T18A	71,2	0,27	T18A	1668	22,5
T18B	70,6	0,26	T18B	2256	20,3
T19A	70,4	0,2	T19A	1519	20,5
T19B	69,1	0,43	T19B	2252	20,3
T20A	71,2	0,22	T20A	1524	20,6
T20B	70,8	0,23	T20B	1995	18

Table 2: Determined values of TOC and COD_{Cr} in column outputs during sorption and regeneration.

2.7.1 Conclusion Etape III

Ionex in the chosen working mode of 10 hours of sorption and regeneration by one of the two methods described (ie 15% vol or 20% vol H_2SO_4) worked reliably during all 20 sorption cycles. During sorption, there was no Zn concentration breakthrough of more than 1.5 mg/l, even at the end of the sorption period. The average concentration of Zn in the purified washing water, i.e. at the exit from the column, was below 0.5 mg/l. No significant damage to the ionex grains was observed during the experiments. Ionex sorbs a small amount of TOC from the wash water, but this is subsequently washed out of the ionex during regeneration. During the 20 sorption cycles performed, the capacity of the ionex was not affected by the effect of adsorbed TOC, which would result in a decrease in Zn sorption efficiency. Ionex capacity, or the efficiency of Zn sorption was constant during all twenty sorption cycles performed, and there was no decrease in this efficiency even in the last cycles.

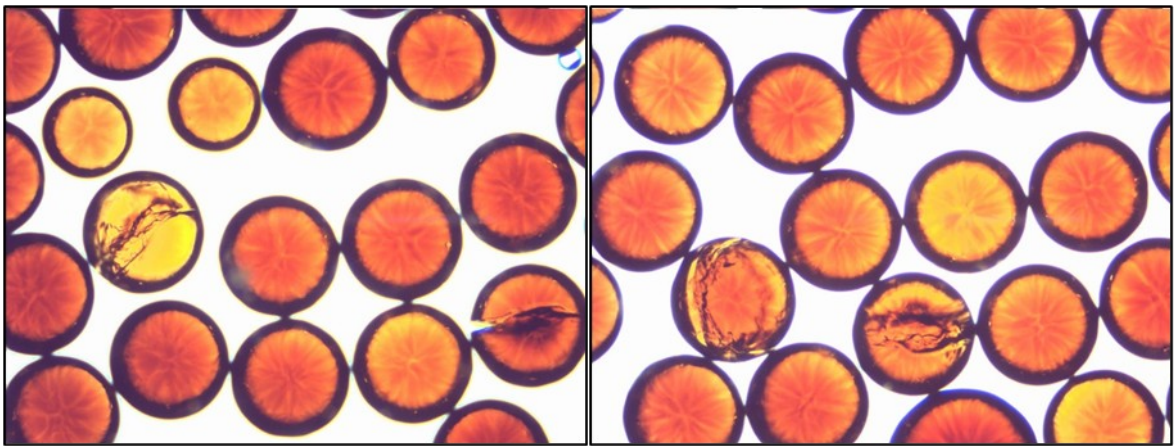


Figure 5: Example of damage to a new unused LEWATIT MonoPlus S 108 ionex.

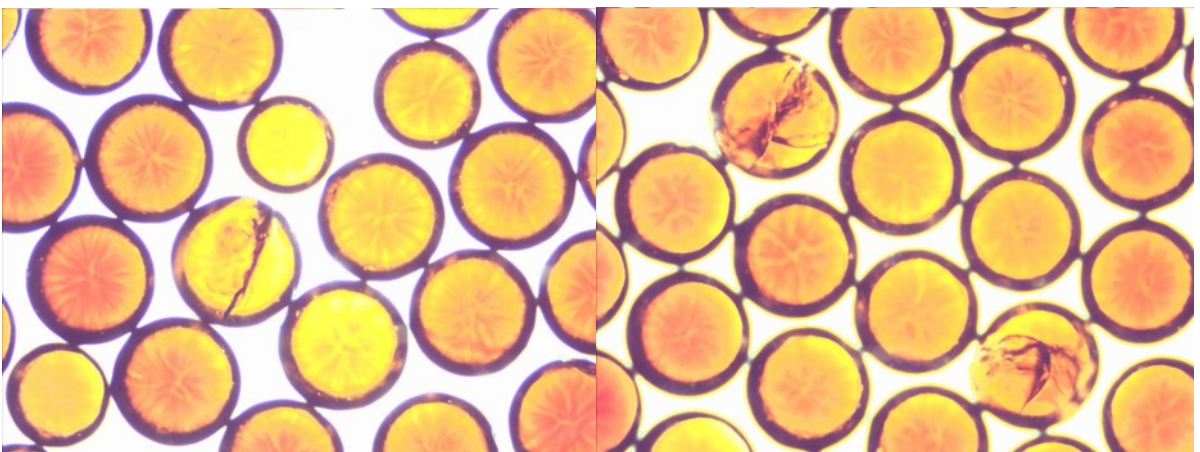


Figure 6: Example of ionex grain damage after 20 sorption cycles – column A regeneration 15% vol H_2SO_4 , column B regeneration 20% vol H_2SO_4 .

3 Results and Discussion

After annual monitoring and balancing of the flows of operational wastewater, we proposed filtration on a 10-15 μm filter for the three most problematic waters WW1-WWW3. This pre-treatment in laboratory and pilot tests reduced the COD value of WW1 by approx. 7-9%. With an annual flow of 1,796 million m^3 , this reduces organic pollution by 53-68 t, expressed in COD. Chemical and electrochemical oxidation of these waters is problematic due to the minimum eight-hour reaction time and flow rate of approximately 250 m^3/h . In laboratory and semi-operational conditions, a reduction of COD by 66-88% and TOC by 42-71% was achieved with these waters after eight hours. The capture of Zn^{2+} emissions was increased by increasing the sorption capacity of the cathexis thanks to a change in the method of its regeneration using waste sulfuric acid. The concentration of Zn^{2+} at the outlet of cathexis filters oscillated between 0.5-2.0 mg/L. By regenerating the cathex, zinc sulphate is produced that can be used in the spinning bath, while the concentration of the regenerating acid has dropped from 18 to 15% by volume.

WW2 and WW3 waters are generated discontinuously, which provides sufficient time for filtration and chemical oxidation. On a laboratory scale, we found and semi-operationally verified the technological sequence of cleaning these waters. The average COD value for WW2 was 10.740 ± 1.319 g/L and the average TOC was 2.459 ± 0.292 g/L. For WW2-1 filtration, COD decreased by 23.4-37.3% and TOC by 9.0-27.3%. At a volume of 40,000 m^3/year , this represents a COD reduction of 186.6 t. The subsequent Fenton oxidation increased the COD removal efficiency to the resulting 96.4-98.0%. On a corporate scale, this reduces COD by 414-421 t, using approx. 1420 t of 35% H_2O_2 at a cost of approx. €568,000.

The pre-purified WW2 could be freed of Zn^{2+} on a cathexis filter operating in the H^+ regeneration cycle, without the concentration of Zn^{2+} emissions exceeding 2 mg/l after 10 h of sorption.

For WW3, the average initial pollution was COD = 22.967 ± 3.981 g/l and TOC = 5.776 ± 0.869 g/l. After adjusting the pH to 2.8, we reduced the initial COD = 28.5 g/l by 49.9-50.2% and the initial TOC = 7.0 g/l decreased by 50.1-50.4% at WW3-1 by filtration. For the Glanzstoff Bohemia plant, with a volume of this water of 500 m^3 , this means a reduction of COD by approx. 5.7 t/year. Subsequent Fenton oxidation achieved a COD reduction of up to 97.5% (98.0% pilot test) after 8 h. In the balance of the plant, this represents the potential to reduce COD by approx. 11.2 tons/year. This requires 35.2 t of 35% hydrogen peroxide at a price of approx. €14,090 (the calculation is based on the currently valid prices). Approximately 40 t of zinc/year can be recycled on cathexis filters from WW1-3 pre-purified in this way, as ZnSO_4 at a cost of approximately €140,000. This partially offsets the cost of oxidizing WW2 and WW3 waters. The introduction of filter pre-treatment in the production operation represents, in the current state, the potential to reduce COD by approx. 245-260 tons/year. With the discontinuous oxidation of wastewater WW2 and WW3, organic pollution can be reduced by another approx. 233-240 tons/year. After the previous filter pre-treatment WW1-WWW3, this represents the potential to reduce total COD pollution in the Glanzstoff Bohemia s.r.o. plant. by about 500 tons (80%).

4 Conclusion

By evaluating all the facts related to industrial waste water originating from the production of viscose fibre. After the subsequent analysis of all streams of various polluting waters and subsequent research, which included the above-mentioned pretreatment methods, wastewater treatment. Furthermore, through tests with the inclusion of various waste water treatment technologies, it was evaluated that the most effective in terms of the cost of raw materials and energy associated with the reduction of the COD content appears to be a change in the regeneration technology of the ion exchangers that are used in the operation of the Spinning Bath for the reabsorption of zinc. Zinc is recycled here for its subsequent use in production as an input raw material. In current technology, the regeneration of ion exchangers is carried out with waste sodium sulphate in the so-called Na^+ cycle. The sodium sulphate for the production of the regeneration solution comes from the spinning bath, which contains a large amount of TOC/COD, and this is then transferred to the Katex filters and deposited on the ion exchangers. This material must then be washed into the waste water by remedial regeneration with a NaOH solution. The change in technology consists in the fact that we will replace the Na^+ regeneration system with an H^+ system using sulfuric acid, which is available as an input raw material for the production of viscose fibre, but also as a secondary product of catalytic oxidation in the treatment of waste air processed from the exhausts of individual production plants.

Following tests with the capacity of Lewatit mono plus in laboratory conditions and determination of all parameters of the proposed regeneration change, a semi-operational unit was designed. This semi-operational model was put into real operation at a scale of 1:40. The PiD wiring diagram is shown in Appendix 1. According to the test results, the technology will be further designed on an industrial scale, including operation parameters, concentrations and volume flows.

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