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Refinement of spent diethylene glycol

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ABSTRACT

The aim of these experiments was to verify our suggested purification process of the spent diethylene glycol solution acquired from the drying of natural gas. Diethylene glycol is commonly polluted by degradation products and/or other chemical types during the drying process. Continuous pollution compromises the glycol desiccation ability, increases energy demands on its dehydration in the distillation process and finally results in the replacement of exhausted glycol. Our suggested purification process is based on the dilution with demineralized water, coagulation with organic flocculants, precipitation at higher pH with caustic soda, active carbon treatment, microfiltration and electrodialysis desalination.

Keywords: Diethylene glycol; Electrodialysis; Purification

1. Introduction

Natural gas is widely used as a fuel in the industrial, commercial and residential sector. Because of its irregular use during the year, part of the gas has to be stored in underground storage facilities. Natural gas pumped from these storage areas must meet strict regulations regarding cleanliness, allowable concentration of contaminants, maximum water content and others before it is transported to the customer. Natural gas is saturated in the storage tank with water vapors from bearing waters. A dehydration process for the natural gas after the removal from the underground gas storage is, therefore, essential before its distribution. The absorption method utilizing absorption liquid, for example, triethylene glycol (TEG), diethylene glycol (DEG) or monoethylene glycol (MEG) is the most common way to dehydrate the gas. After the drying process watered glycols have to be regenerated. The regeneration is typically done by the distillation process, and the fresh glycol can be then reused for further drying.

The long-term chemical stability of glycols is often unsatisfactory. High temperatures used during the distillation leads to the formation of degradation products and subsequently the color of the glycol changes from a transparent yellow through brown to black. In addition to degradation products, black gel-like liquid also contains solids, oils, detergents and other additives gained during the whole process.

The determination of a system of methods which are able to improve cleaning processes of the spent glycol is desirable. Since second half of twentieth century, there were announced a lot of patents for the purification of ethylene glycol from various industrial sources typically from polymer industry [1–3]. These vary by different pretreatment for the removal or the modification of presented contaminants. Generally is utilized distillation, vacuum distillation or vacuum membrane distillation [4,5] with certain pretreatment or posttreatment of the spent glycol mixture. However, carrying out the distillation with mixture of water, glycol and other liquid residues increases process costs and cleaning demands of the distillation apparatus. Washabaugh and Collins [6] utilized reduction agents with water dilution followed by adsorption columns and filters. Adsorption

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columns could be also substituted by the addition of the active carbon [7] for the sorption of organic residues. Final distillation step can be replaced by a membrane technology like reverse osmosis [8] and sometimes also with ultrafiltration for the reverse osmosis pretreatment [9]. Kelly et al. [10] added ion-exchange columns after ultrafiltration instead of reverse osmosis for final salts removal. New modern techniques like pervaporation technology could be also used for DEG regeneration [11]. From this brief overview follows that the glycol purification demands a complex and versatile technology especially whenever membrane processes are implemented.

Our suggested purification process includes dilution, coagulation with organic flocculants, precipitation at higher pH by caustic soda, powdered active carbon treatment, microfiltration (MF) and electrodialysis (ED). The proper control of pH in each purification step is the most important parameter. This contribution deals only with pretreatment of spent DEG solution. The distillation of the resulting mixture of water and purified glycol is considered to be carried out as the final step of the whole technology.

The novelty of this contribution is the suggestion of the complex purification technology based on a proper pH control during certain steps. This technology should be suitable for purifying of various spent glycols.

2. Materials and methods

We have carried out experiments with raw spent DEG solution acquired after drying of the natural gas. The composition of the sample given by the customer is shown in Table 1. Subsequent analysis of the sample properties was made by MemBrain s.r.o., Czech Republic.

Table 1
Sample composition, general

Species	Value
Cl^-, mg/L	41,250
SO_4^{2-}, mg/L	<2
Ba^{2+}, mg/L	<0.001
Cr^{3+}, mg/L	0.07
Cu^{2+}, mg/L	0.14
Mn^{2+}, mg/L	20.7
Sr^{2+}, mg/L	12
Zn^{2+}, mg/L	24.5
Ca^{2+}, mg/L	559
Mg^{2+}, mg/L	41.9
Na^+, mg/L	8,720
K^+, mg/L	840
Conductivity, mS/cm	2.03
pH	3.86
Turbidity, NTU	9.25
Total solids (TS), °BRIX	>50
MEG, g/L	1.47
DEG, g/L	785

With respect to chloride titration by Mohr method of the diluted and pretreated DEG the initial NaCl concentration in the raw DEG solution was 68 g/L. The tested pretreatment process consists of the following steps: dilution, coagulation, precipitation, active carbon treatment and MF and ED.

The dilution of DEG solution was carried out in order to:

- destabilize oligomers micelles;
- increase the speed of the coagulation and
- decrease the sample viscosity.

Dilution of the DEG sample was carried out with demineralized water continuously added to the mixed vessel to reach the DEG to water volume ratio 1:1. The surface layer of DEG/water solution was covered by the lighter oil phase. The oil content was approximately 1% of whole volume estimated from graduated cylinder. The oil removal was performed by syringe and residuals were sucked into the filter paper. The dilution process is shown in Fig. 1. The coagulation of the solid phase (glycol rubber) together with solution color change was observed. The spontaneous coagulation started after the addition of approximately 1 L of the demineralized water into 2.0 L of the DEG solution.

Multivalent metals were precipitated by the addition of organic coagulant Superfloc C-577 with a dosage of 0.7–1.0 mL/L of raw DEG solution. The initial solution pH 3.2 was then adjusted with use of 1 M solution of NaOH to reach pH in the range of 8–10 to ensure that the presented iron will be precipitated (Pourbaix diagram in Fig. 2). The mixture was left still for 24 h. The created flocks and sediments (Fig. 3) were separated in the funnel. To maximize the subsequent filtration, the 1 g of the active carbon powder (S 835) was added to the 1 L of the diluted DEG solution, which was heated to 60°C and mixed for 2 h. After settling period the freely floating solid residues were removed during the filtration with 0.5 μm filter. The filtration apparatus can be then cleaned with H_2SO_4. The solution after filtration has obtained a light yellow color.

ED was used for the final desalination of the filtered solution. The ED module was assembled by combination of 11 cation-exchange and 10 anion-exchange heterogeneous

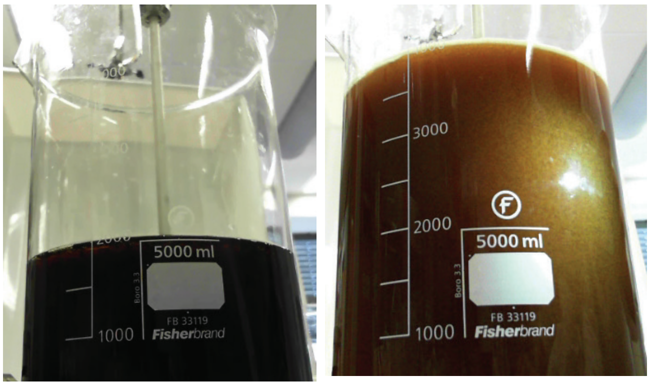


Fig. 1. Coagulation of 2.2 L of DEG with 2.2 L of demineralized water by organic agent before (left) and after (right) addition of water and chemicals.

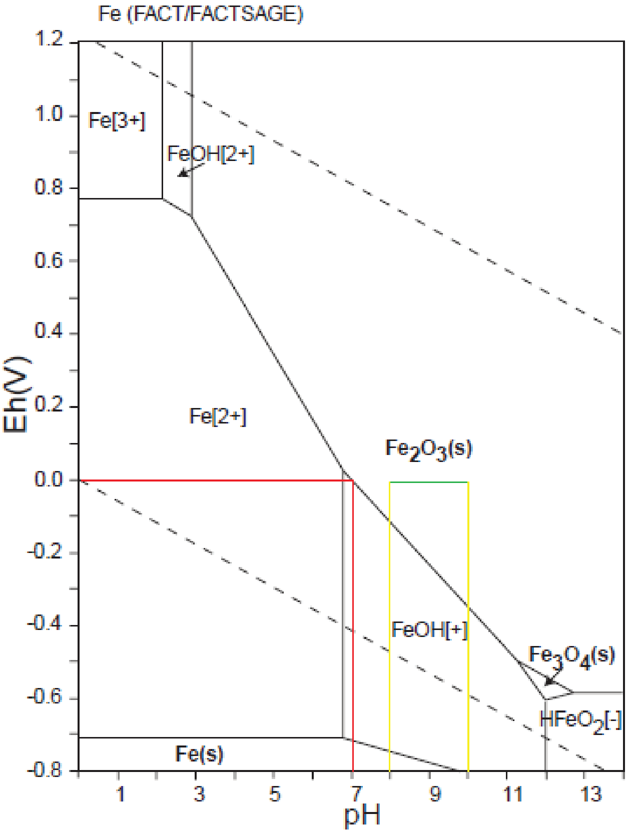


Fig. 2. Pourbaix diagram for iron. Optimum pH for precipitation is between 8 and 10.

membranes RALEX®. The experimental setup was performed with non-alternating polarity setup. Voltage applied on the assembled module was 1.5 V per membrane pair. Flow rate in the diluate and concentrate circuit was 58 L/h. As the electrode solution we used 10–20 g/L of $NaNO_3$ at flow rate 50 L/h. The apparatus worked in the batch mode, where all circuits were cycled until the demanded diluate solution conductivity (0.5 mS/cm) was reached, and/or electric current decreased below 0.15 A and/or the desalination exceeds 200 min.

The apparatus was installed in the laboratory at MemBrain. All pH and conductivity cells were calibrated by standard solutions. ED module was controlled by standard tests for the external and the internal leakage after assembly and salt tests, which characterize module ability of desalination.

Three experiments were carried with DEG solution. The first one utilizes pH 8 for heavy metals precipitation. The second one utilizes pH 10. The third one utilizes pH 10 during precipitation and in difference with two previous experiments in the final desalination with ED unit the diluate circuit pH was maintained as low as 3.5. Cleaning in place was carried between each experiment.

3. Results

We focused in our experiments on the effect of the lowering demands for pretreatment chemicals. According to Pourbaix diagram for the iron (Fig. 2), it is possible to carry out the precipitation in a pH scale from 8 to 10. In the first experiment, we tried to keep pH as low as possible to still enable heavy metals precipitation (pH 8). The pretreatment procedure passed as expected according to procedure described in the previous section. The degree of desalination in the first experiment reaches 50% after 200 min of ED.

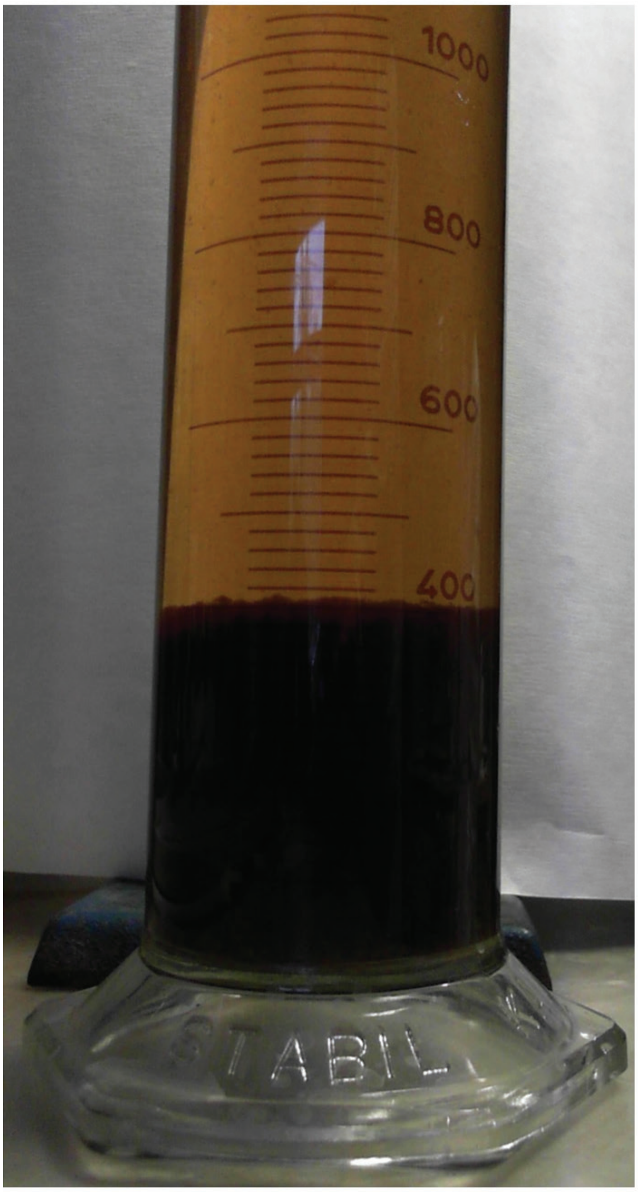


Fig. 3. Glycol after 24 h sedimentation. The glycol rubber was 20 vol% of cylinder after sedimentation.

The second experiment carried after precipitation at pH 10 evinced a slight decrease of desalination capability. The ED module was disassembled after the end of the second experiment to check the membrane clogging (Fig. 4). The presented thin gel-like film was taken for analysis on Fourier transform infrared (spectroscopy) (FTIR) Nicolet iS50.

The clogging film can be mechanically removed; however, such treatment cannot be applicable from the industrial point of view. Also, the lifetime of membranes decreases after mechanical cleaning. To ensure proper continuous function of the ED unit, it is necessary to suppress the formation of clogs.

With respect to the obtained spectrum (Fig. 5) the clogging film is composed mostly from calcium carbonate and magnesium hydroxide (detail analysis is shown in Table 2). The presence of the detected 2-hydroxy ether (here taken as organic residues) is assigned to the polymer chain residues, which can be stabilized by present magnesium and/or calcium ions and so they can precipitate on the membrane surface. To suppress the formation of these clogs it was suggested to carry the third ED experiment with maintained diluate pH value of 3.5.

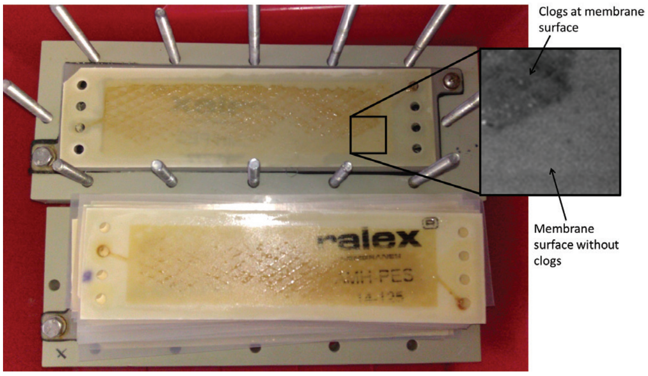


Fig. 4. Disassembled ED module. Clogs at membrane surface are highlighted by grayscale image.

Before the third experiment, the module was assembled and cleaned. The desalination during third experiment results in degree of 55% after 200 min. This experiment evinced better performance than both previous experiments. Module disassembly confirms that no clogs occurred on the membranes, which is desired. Fig. 6 summarizes all carried out desalination experiments.

Average composition of the diluate taken during all experiments is summarized in Table 3. It is observable that the ED produces partially desalinated solution of the DEG with water content about 40–60 wt%, and NaCl desalination degree between 35% and 55%.

The efficiency of the pretreatment could be also demonstrated on the absorbance spectrum of the raw DEG with ED feed, diluate and concentrate. The set point wavelength was 430 nm. At this value if absorbance is higher than 3.00 A.U., then the initial raw material is dark brown or black. The pretreated ED feed is yellow if the absorbance at the set point wavelength is as low as 0.50 A.U. for 1 cm optical cuvette length (Fig. 7). The standard reference method (SRM) can be used for the comparison of the solution color. The DEG solution color changes similarly to the beer color scale. The color comparison with similar color system (European brewing convention (EBC)) is shown in Fig. 8.

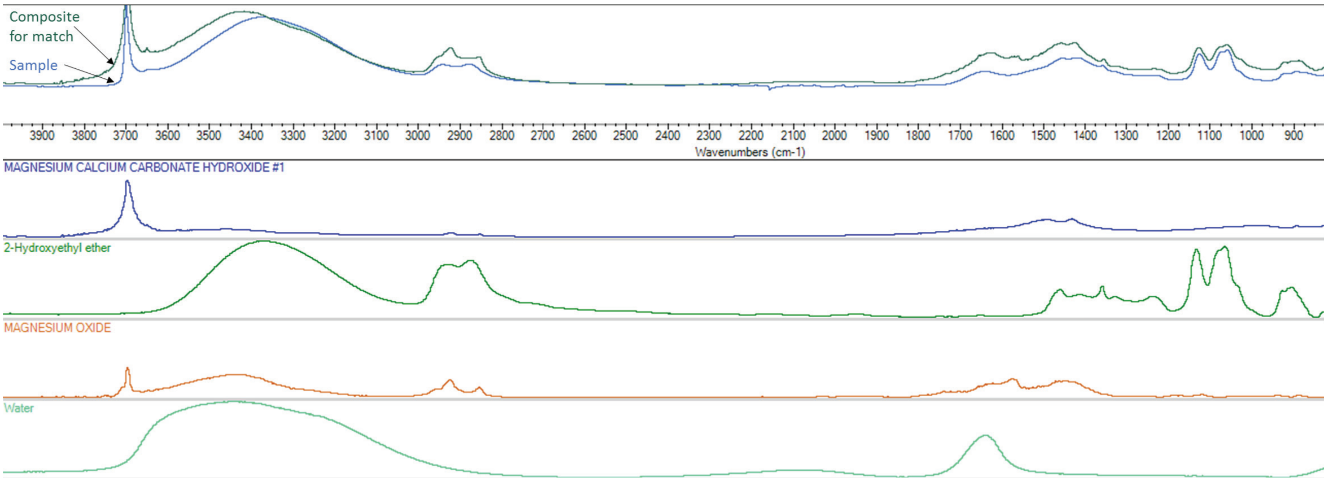


Fig. 5. FTIR spectrum of the clogging film.

Table 2
Fourier transform infrared (spectroscopy) (FTIR) peak analysis of the clogging film

Title	Cumulative	Composite %	Index in database	Database used for spectra match
Magnesium calcium, carbonate, hydroxide	62.67	52.92	1,245	High-resolution (HR) polymer additives and plasticizers
2-Hydroxyethyl ether	72.25	14.12	67	HR Aldrich solvents
Magnesium oxide	75.98	21.29	695	HR polymer additives and plasticizers
Water	76.79	11.67	123	HR Aldrich solvents

Note: The cumulative value indicates how well a spectrum describes the component and shows its contribution to the overall match (75%), including the known component.

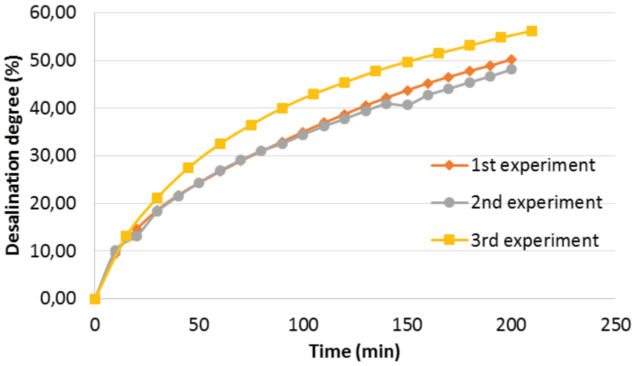


Fig. 6. Desalination degree evolution during three experiments (percentage expression of the amount of salts that can be removed by one passage during the electrodialysis process at given linear flow rate and inlet salt concentration).

Table 3
Electrodialysis average results

Species	Feed	Diluate	Concentrate
NO_3^-, mg/L	13	4.07	24
NO_2^-, mg/L	<0.01	<0.01	<0.01
NH_4^+, mg/L	0.75	<0.25	<0.2
SO_4^{2-}, mg/L	<5	<5	15.6
S^{2-}, mg/L	<0.2	<0.2	<0.2
Cl^-, mg/L	17,000	7,170	21,900
Mn^{2+}, mg/L	0.6	0.3	0.75
Fe^{3+}, mg/L	6.1	5.1	6.6
Ca^{2+}, mg/L	414	212	515
Mg^{2+}, mg/L	48.4	37.2	46.5
Na^+, mg/L	6,930	3,680	11,600
K^+, mg/L	605	265	1,350
MEG, mg/L	813	718	176
Total solids (TS), °Brix	35.3	31.6	10.2
DEG, mg/L	460,000	417,000	68,900

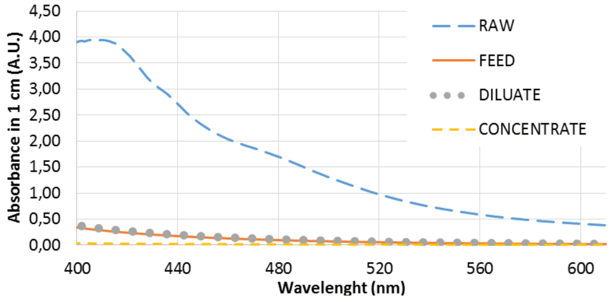
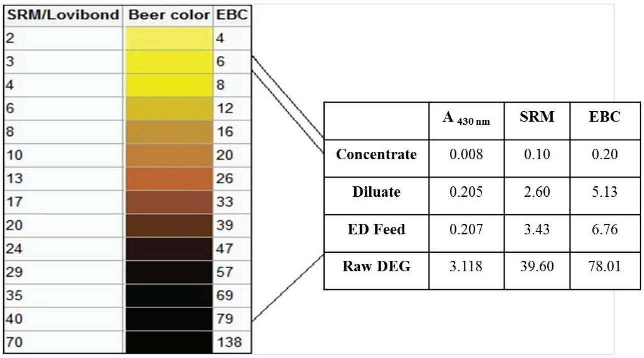


Fig. 7. Absorbance spectra of DEG solutions.



SRM/Lovibond	Beer color	EBC
2	🟨	4
3	🟨	6
4	🟨	8
6	🟨	12
8	🟧	16
10	🟧	20
13	🟧	26
17	🟫	33
20	🟫	39
24	⬛	47
29	⬛	57
35	⬛	69
40	⬛	79
70	⬛	138

	$A_{430\ nm}$	SRM	EBC
Concentrate	0.008	0.10	0.20
Diluate	0.205	2.60	5.13
ED Feed	0.207	3.43	6.76
Raw DEG	3.118	39.60	78.01

Fig. 8. SRM demonstration to DEG discoloration process.

The conceptual design of our suggested DEG purification technology is summarized in the process flow diagram (PFD) diagram (Fig. 9). The final pretreatment and purification should consist of the gravitational oil removal, sufficient dilution for better coagulation and sedimentation, hydroxides precipitation with pH adjustment to value 10, active carbon treatment, press filtration and MF followed by ED. The solution after pretreatment is desalinated from 25% to 50% desalination degree. The diluate from the ED should be further concentrated by the flash distillation.

Process economics will strongly depend on degree of produced impurities in DEG. The main items of operating expenditure will be ED spare parts, chemicals for pretreatment, electrical power and water.

Expected consumptions are listed per ton of raw DEG solution. Consumptions are water 1 ton, organic coagulant (Superfloc C-577) consumption 0.8 kg, caustic soda (50 wt%) 1 kg, HCl (31 wt%) 1 kg and electricity consumption 55 kWh. An expected lifetime of membranes was set to 4 years, 10 years for working spacers and 2 years for electrodes. In case of proper coagulation the addition of active carbon is not necessary and could be omitted.

The model capacity example of treating 1 ton diluted purified DEG solution per day resulted in 600 €/ton specific cost related to concentrated DEG solution. The following process economics are indicating the simple payback time to be in <3 years.

4. Conclusion

The formerly suggested spent DEG pretreatment is suitable procedure for its purification. Here, the presented experiments focusing on the minimization of chemical demand were less successful. The unsuccessful trial occurred due to low pH (8.0) which was insufficient for complete coagulation and removal of “glycol rubber”. The organic residues together with magnesium and calcium ions caused clogging of the membranes which led to a decrease of ED desalination capability.

The minimized pretreatment was able to remove:

- hydrocarbons of petroleum origin;
- partial removal of “glycol rubber” (detergents and dispersants) by the coagulation;
- removal of multivalent ions by the precipitation and
- effective removal of the color from black to yellow solution.

The ED after the corresponding pretreatment with higher pH together with diluate pH control appears as a

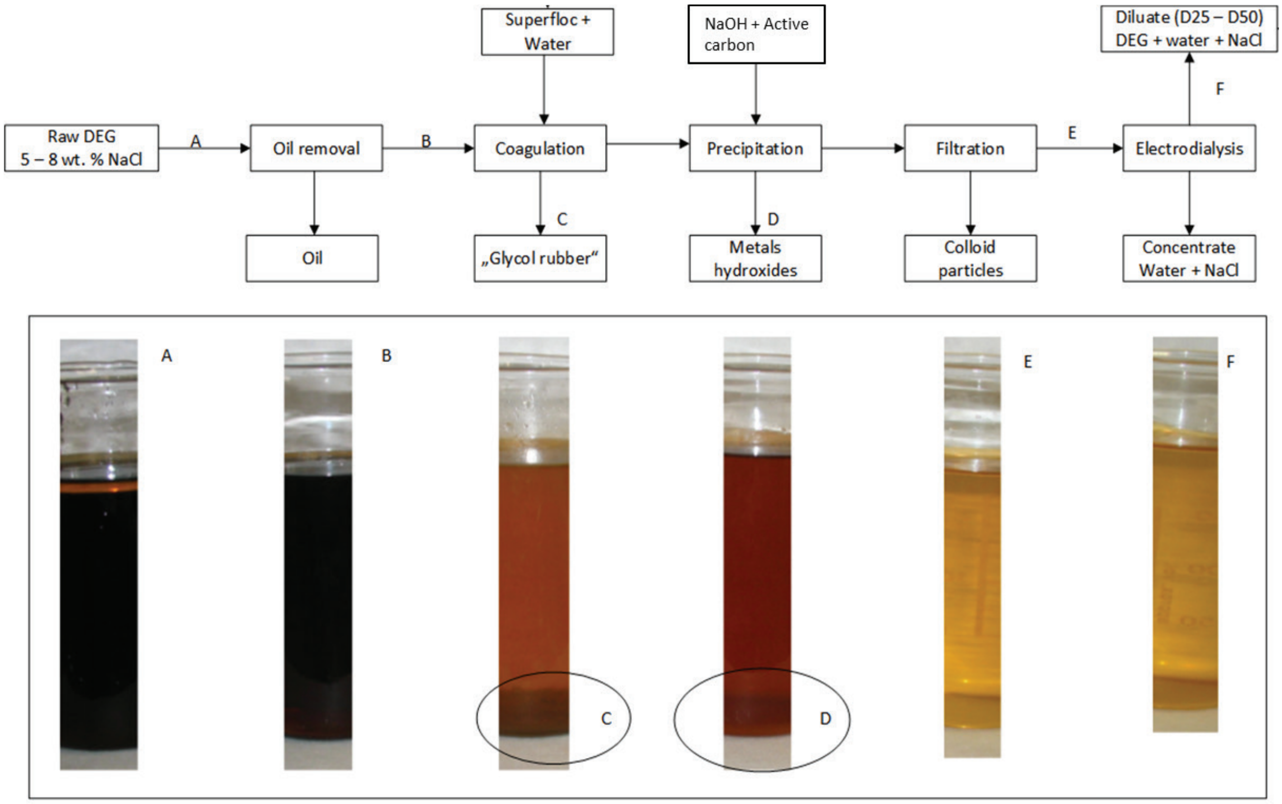


Fig. 9. PFD of the purification technology with products taken in each step.

suitable solution for the spent DEG purification. It enables removal of a large part of the contaminants and the pH control in the diluate ensures that no membrane clogging appears. These confirmed laboratory results could be used as a first step in the construction of a technology suitable for purification of large volumes of the spent glycol drying solution. This technology is demanded for potential reuse of the spent glycol from gas drying. Generally, the ED could produce a partially desalinated solution of DEG with water content about 40–60 wt% and NaCl desalination degree between 35% and 55%, which could be further concentrated by the distillation process with lower costs.

Similar pretreatment process could be also suitable for other glycol solutions like MEG or TEG. These experiments have to be verified to confirm pretreatment versatility across all glycols.

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