MEMBRANE PROCESSES FOR INDUSTRIAL WASTEWATER TREATMENT – DEMINERALIZATION STATION

MEMBRÁNOVÉ PROCESY V TECHNOLOGII ÚPRAVY PRŮMYSLOVÝCH ODPADNÍCH VOD – DEMINERALIZAČNÍ STANICE

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Abstract

The paper deals with treatment of wastewater produced by the energy industry using a membrane processes (electrodialysis). Prior to application of this technology, the influence of wastewater on the chosen type of membranes is solved. Specifically, it means eliminating the influence of formation soluble (insoluble) salts which could negatively affect water treatment by the chosen technology. The paper also summarizes the results of laboratory tests of electrodialysis with the aim to acquire treated wastewater of such quality meeting legislative limits for discharges to surface water (i.e. total dissolved solids below $1 g.l^{-1}$).

Abstrakt

Příspěvek se zabývá problematikou úpravy odpadních vod z energetiky s využitím membránových procesů (elektrodialýzy). Před samotnou aplikací této technologie je řešen vliv chemismu upravované vody na použitý typ membrán. Konkrétně jde o eliminaci vlivu tvorby málo rozpustných (nerozpustných) solí, které by úpravu vody zvolenou technologií negativně ovlivnily. Příspěvek dále shrnuje získané výsledky doposud provedených testů elektrodialýzy se zaměřením na získání upravené odpadní vody vyhovující legislativním limitům pro vypouštění do vod povrchových (tj. rozpuštěné látky pod $1 g.l^{-1}$)

Key words: wastewater, treatment, chemical precipitation, clarification

1 INTRODUCTION

Membrane technologies are the ones of the ways of wastewater treatment. In comparison with conventional technologies, they have considerable advantages. These are high quality of treated water and reduction of the amount of chemical agents. Other advantages are high selectivity and low energy consumption. The development of the membrane technology affects current increased demands for the quality of discharged wastewater and current needs of high-quality process water.

The scale of desalinated water usage is largely dependent on the cost effectiveness of the desalination process. When membrane methods are used, the basic costs for desalination include those of water pre-treatment, membranes and production equipment, electrical power consumption for desalination and auxiliary operations [1].

The application of membrane technologies is limited by the quality of feed water. The performance of membrane process may be limited by the concentration changes in the vicinity of the membrane or the deposition of dirt on the surface of the membrane material. Therefore, the first indispensable step in the design of water treatment using membrane technology is a suitable pre-treatment method.

This paper summarizes the results of laboratory experiments of wastewater treatment using the laboratory units EDR-Z10/0.8. Electrodialysis (ED) was developed first for the desalination of saline solutions, particularly brackish water. The production of potable water is still currently the most important industrial application of electrodialysis. Other applications, such as the treatment of industrial effluents, the production of boiler feed water are gaining increasing importance in large-scale industrial installations [2,3]. Another industrial application is the production of table salt in Japan and Kuwait. In this application, ED is used for the concentration of NaCl from seawater prior to evaporation [3]. For water with a relatively low degree of salinity (below 5 $g.l^{-1}$), ED is an economically advantageous process compared to reverse osmosis [4]. Also water with high salinity (30 $g.l^{-1}$) may be successfully treated by ED. Thanks to the high selectivity and low demands for chemical agents, ED may be a reliable and effective method in wastewater demineralization.

2 MATERIALS AND METHODS

2.1 Wastewater characteristics

The research is focused on the treatment of wastewater from a demineralization station generated during chemical water treatment for boilers, turbines and piping. The chemical treatment of a water demineralization station with a mixed bed (MB) assures consistent water quality of treated water required for each device. MB consists of a homogenous mixture of strongly acid and strongly basic anion-exchange resins. The chemical agents for water treatment are: HCl, $Fe_2(SO_4)_3$ and hydrate $Ca(OH)_2$.

Wastewater produced by cleaning ion-exchange resins. Wastewater discharged together with other wastewater from the drainage system on a physico-chemical treatment plant. The treated water is discharged to surface water; part of this water is recycled as operating water.

The aim of the research is to design and verify the effectiveness of water treatment technology using electrodialysis. The criterion for successful application is to obtain the treated water meeting legislative limits for its discharge into surface waters.

Characteristics of the quality of the wastewater are given in Tasb.1 below. The analyses were carried out in the laboratory of VŠB-TU Ostrava, at the Institute of Clean Technology. The wastewater contains significant quantities of ions that can decrease the performance and life-span of the membrane technology. The problematic ions are: Ca^{2+} and Mg^{2+} (formation of low soluble salts). Heavy metals and humic substances could also pose a risk for the electrodialysis process as they foul the active centres on the surface of the ion-exchange membrane and prevent entrance of salts to be converted into the membrane. Increase levels of COD and BOD may cause problems for the membrane technology (formation of gel layer) as well.

Tab 1: Industrial wastewater characteristics

INDICATOR	UNIT	SAMPLE 1	SAMPLE 2	SAMPLE 3
pH		7.81	6.66	6.97
K	[$mS.cm^{-1}$]	10.2	11.63	13.35
Turbidity	[ZF]	31.97	>40	>40
HCO_3^-	[$mg.l^{-1}$]	220.82	68.32	208.01
CO_2	[$mg.l^{-1}$]	25.52	47.96	70.84
Hardness	[$mmo.l^{-1}$]	16.46	17.35	29.15
Ca^{2+}	[$mg.l^{-1}$]	526.65	535.07	983.16
Mg^{2+}	[$mg.l^{-1}$]	80.69	91.77	112.56
Cl^-	[$mg.l^{-1}$]	2 907.15	3 261.68	4 148.00
SO_4^{2-}	[$mg.l^{-1}$]	720.00	820.00	1238.00
COD	[$mg.l^{-1}$]	33.60	47.84	52.20
TOC	[$mg.l^{-1}$]	41.56	-	-
BOD	[$mg.l^{-1}$]	4.97	5.29	-
Mn	[$mg.l^{-1}$]	<0.30	<0.30	<0.30
Fe	[$mg.l^{-1}$]	0.15	0.25	0.52
Al	[$mg.l^{-1}$]	<0.10	<0.10	<0.10
NO_3^-	[$mg.l^{-1}$]	193.00	115.00	150.00
TDS	[$mg.l^{-1}$]	7 640.00	8 036.00	10 778.00

In order to apply the membrane technology (electrodialysis), it is necessary to eliminate the influence of undesirable constituents. It is necessary to achieve such quality of feed water which corresponds to the ED standard (critical) limit for the type of used membranes and equipment.

2.2 Water treatment for applying membrane technology

Based on the observed chemical composition of wastewater, the need occurred to adapt the technology of water treatment by focusing on pre-treatment – elimination of the influence of problematic quality indicators on the membrane technology (see Tab. 2). In particular, it is the case of removal of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions.

Tab. 2: Standard and critical indicators for ED [5]

INDICATOR	UNIT	STANDARD	CRITICAL
pH		2-8	>10
Turbidity	[NTU]	0.5	5
Mn	[mg.l^{-1}]	0.1	1.0
Fe	[mg.l^{-1}]	0.30	3.00
Al	[mg.l^{-1}]	0.10	1.00

In order to choose a suitable pre-treatment method prior to the application of membrane technology, several methods were tested:

- reducing the concentration of Ca^{2+} and Mg^{2+} ions
  - alkalization (NaOH), sedimentation, filtration, acidification;
  - precipitation (Na_2CO_3), sedimentation, filtration;
  - precipitation ($Na_3PO_4.12H_2O$), sedimentation, filtration;
- reducing the concentration of SO_4^{2-} ions
  - alkalization, sedimentation, filtration, acidification;
  - precipitation (metal salts of Al^{3+}), sedimentation, filtration, acidification;
  - precipitation according to Patent No. 290953 [6];
- reducing the overall pollution
  - clarification, sedimentation, filtration;
- antiscalant.

2.3 Electrodialysis equipment

The tests were carried out on the lab-scale units EDR-Z/10-0.8; the electrodialysis module is fitted with 10 pairs of ion-selective membranes AM(H)-PES and CM(H)-PES. The tests were conducted in a form of batch cycles (batch process). The time duration was chosen based on the desired quality of the treated water (diluate).

The first part of the research was focused on the determination of specifications and operating parameters for the maximum of desalination rate. Another part of the research was focused on the relevant performance parameters and the time required for reaching the total dissolved solids concentration in the treated water below 1 g.l^{-1} [7].

The procedure of the batch test is as follows:

- dosage relevant volume of wastewater;
- 250 ml electrode solution for electrode circuit;
- set desired voltage;
- switch on equipment;
- pH, conductivity, temperature, voltage and current measured at interval of 5 minutes;
- analysis of products.

3 RESULTS AND DISCUSION

3.1 Water treatment for applying membrane technology

Alkalization and acidification are effective methods for reducing the concentration of Mg^{2+} ions (Fig. 1). To reduce the concentration of Ca^{2+} ions is ineffective. After alkalization, it is necessary to introduce the stage of neutralization which ensures an optimum pH value for the course of membrane processes. This type of pre-treatment brings along high costs of both the equipment and the own operation. It is necessary to deal with the formed sludge.

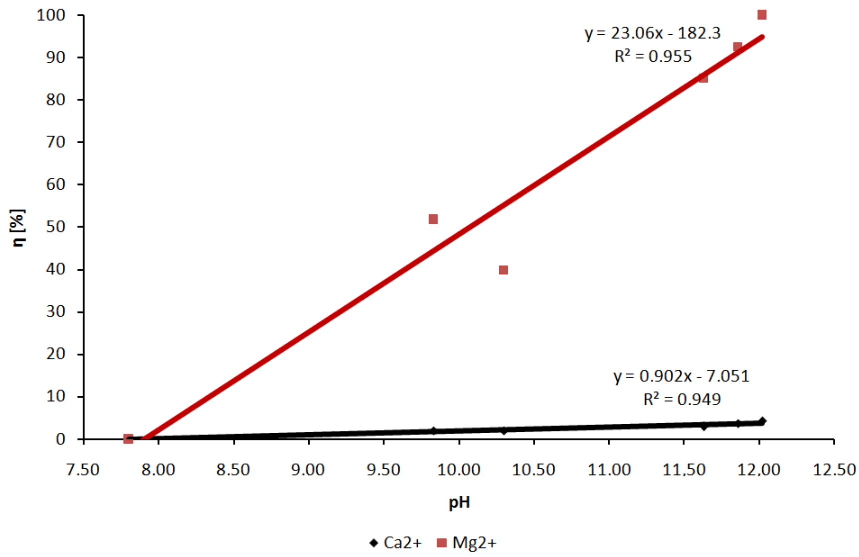

Fig. 1: Reduction of Ca^{2+} and Mg^{2+} ions – alkalization NaOH

Better results were obtained when using the precipitants Na_2CO_3 and $Na_3PO_4.12H_2O$. The main conditions for the tests were the optimum pH of treated water, i.e. less than 10 (the critical value of pH for the operation of ED). The tests results are shown in Fig. 2.

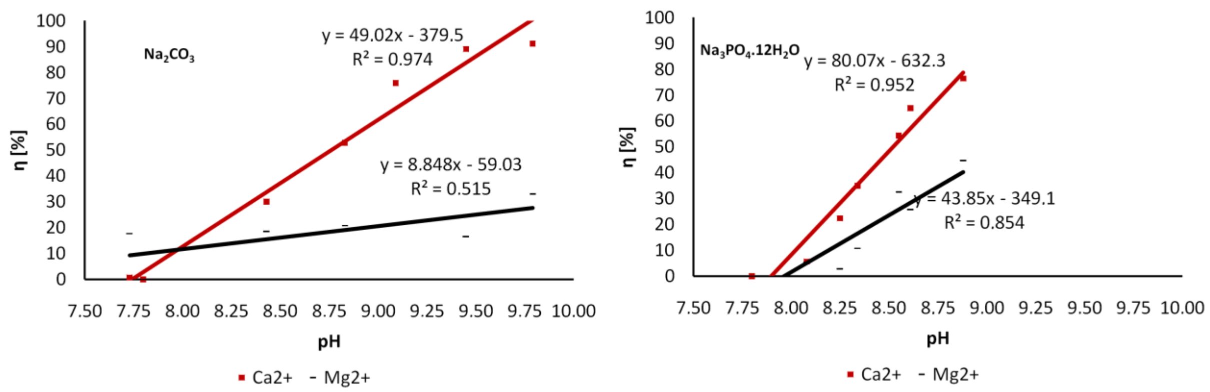

Fig. 2: Reducing the concentration of Ca^{2+} and Mg^{2+} ions – precipitation Na_2CO_3 and $Na_3PO_4.12H_2O$

The best results were achieved during clarification through the use of aluminium coagulants. Satisfactory results were obtained for both turbidity and total water pollution (COD). The indicator COD decreased by 53 %, turbidity reducing efficiency was around 98 %. During the tests, the emphasis was placed on keeping the residual coagulant Al^{3+} concentration below $0.1 g.l^{-1}$ and a minimal change of pH. The advantage of this method is the simultaneous reduction of sulphate ions.

The possibility of using antiscalant for wastewater treatment has not been confirmed. The problem is associated with the short functionality of antiscalant and its circulation in the concentrate circuit. It creates the membrane gel deposition. For the application of antiscalant, the optimization depending on the proper selection of a type and dosage of antiscalant is very important. When selecting a wrong type or non-optimal dosage, the effect of pre-treatment is rather the opposite.

3.2 Electrodialysis equipment

Fig. 3 and Fig. 4 show the course of the batch tests without pre-treatment and with pre-treatment of wastewater clarification. The desire degree of desalination is reached in the course of about 45 minutes and 14V (an input capacity of wastewater – 3 litters). The voltage regulating flow rates of the circuits are in a range of 60-70 l.h^{-1}.

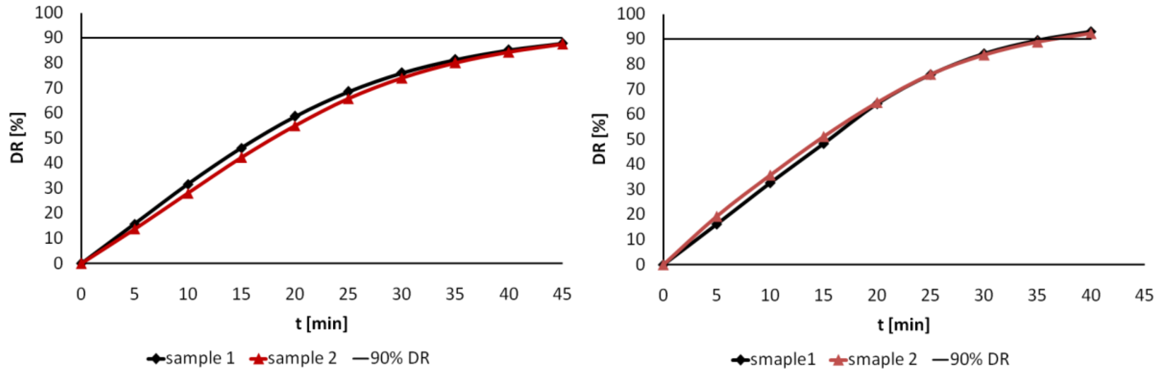

Fig. 3: Desalination rate of wastewater without pre-treatment (left) and with pre-treatment clarifier (right)

Without pre-treatment of wastewater, the process of desalination slows down, a precipitate is formed and the gradual introduction of input and output concentrate current happens. The desalination rate of 90 % without pre-treatment was achieved after 45 minutes of the test. The same effect with pre-treatment was achieved after 35 minutes of testing.

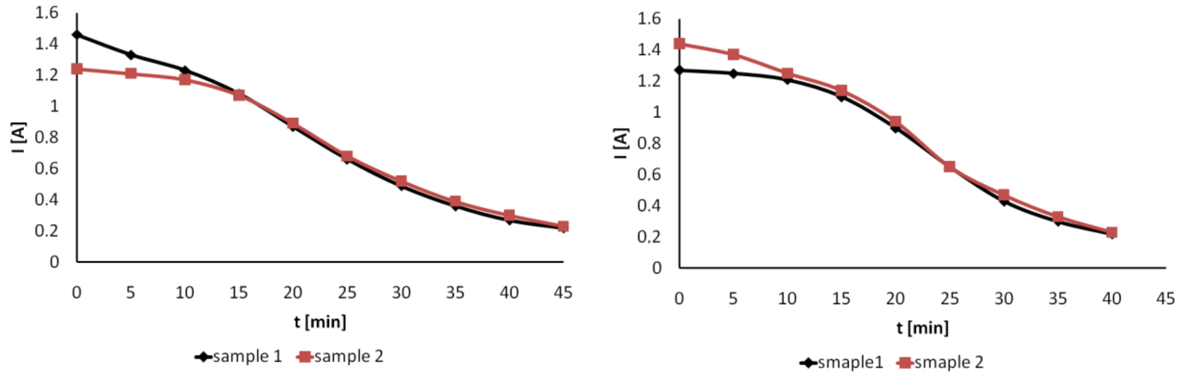

Fig. 4: Course of ED tests without pre-treatment (left) and with pre-treatment clarifier (right)

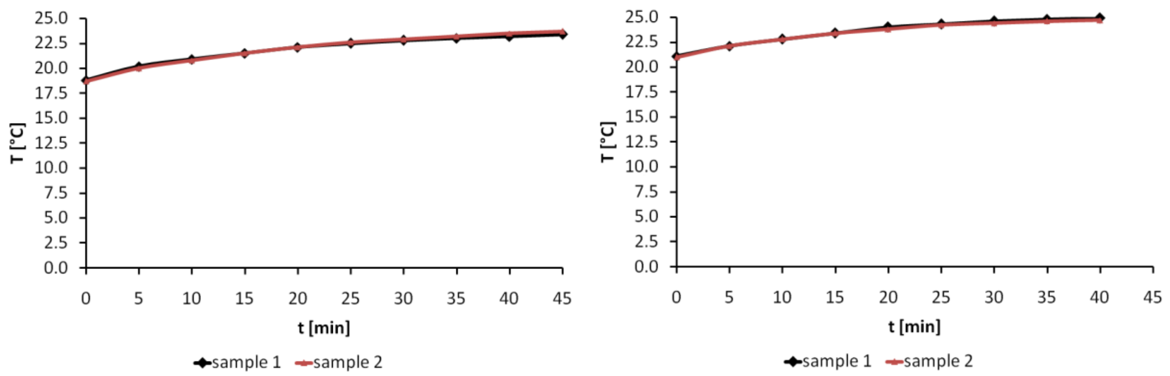

Fig. 5: Temperature of wastewater without pre-treatment (left) and with pre-treatment clarifier (right)

The quality of treated water with the application of electrodialysis corresponds to legislative limits for surface water in all indicators. Another product of desalination is a concentrated solution which is an area of our future research.

3 CONCLUSIONS

The results of previous research confirmed the possibility of using membrane technology, specifically electrodialysis, for treatment of wastewater from a demineralisation station. The successful application of the technology is dependent on many factors, especially on the choice of a suitable membrane type, associated with the pre-treatment of feed water for the application of membrane technology. The choice of an appropriate pre-treatment method is a complex process that requires the thorough comparison of the requirements for the quality of treated water, the requirements for operating conditions, and the associated economic cost of the process water treatment. The areas for further research are to verify the results obtained during feed-and-bleed tests and dealing with the treatment and further treatment of ED waste product.

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[7] Nařízení vlády č. 61/2003 Sb. o ukazatelích a hodnotách přípustného znečištění povrchových vod a odpadních vod, náležitostech povolení k vypouštění odpadních vod do vod povrchových a do kanalizací a o citlivých oblastech, ve znění nařízení vlády č. 229/2007 Sb. a nařízení vlády č. 23/2011 Sb.

RESUMÉ

Předložený příspěvek shrnuje dosavadní výsledky testů úpravy odpadních vod z demineralizační stanice s využitím laboratorní jednotky EDR-Z10/1.0. Tyto odpadní vody vznikají zpětným vymýváním směsného lože. Z pohledu možné aplikace membránové technologie odpadní voda obsahuje významné množství iontů, které by bez předúpravy mohly snižovat výkon a životnost membránové technologie. Jde zejména o kombinaci iontů Ca^{2+} a Mg^{2+} (tvorba málo rozpustných solí). Problematické by pro proces elektrodialýzy mohly být i těžké kovy a huminové látky (zanáší aktivní centra na povrchu iontovýměnné membrány a znemožňují vstup do membrány převáděným solím).

První část výzkumu se zabývá návrhem vhodného typu předúpravy před samotnou membránovou technologií. Další část výzkumu se zaměřuje již na testy elektorodialýzy ve vsádkovém režimu (batch test). Cílem těchto testů je ověřit účinnost zvolené předúpravy a samotné membránové technologie. Při laboratorních testech je kladen důraz na zjištění maximálního stupně odsolení testovaných vod a zjištění provozních parametrů potřebných pro dosažení požadované kvality upravené vody. Kritériem pro úpravu odpadních vod je dosažení koncentrace RL_{105} pod 1 $g.l^{-1}$.

Provedené testy potvrdily, že bez předúpravy odpadní vody dochází ke zpomalení procesu odsolení, k tvorbě sraženin a k postupnému zanesení vstupu a výstupu koncentrátového proudu. 90% účinnosti odsolení bylo u odpadní vody bez předúpravy dosaženo po 45 minutách testu. U předupravené odpadní vody čířením bylo stejné účinnosti dosaženo po 35 minutách testu. Upravená odpadní voda vyhovuje legislativním limitům pro vypouštění do vod povrchových ve všech námi sledovaných ukazatelích. Dalším produktem odsolení je zakoncentrovaný roztok (koncentrát), který je oblastí našeho dalšího výzkumu.