Materials Science and Engineering, Volume 44, No. 2 (2019), pp. 79–84.
DOI: 10.32974.mse.2019.008

STUDY OF ELECTRODIALYTIC MATERIAL TRANSPORT AT THE ELECTROLYSIS OF AQUEOUS NaCl SOLUTIONS CONTAMINATED BY EPTC

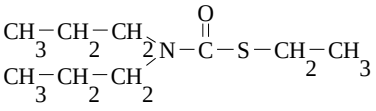
FERENC MOGYORÓDY[1]

The electrolytic degradation of inorganic pollutants in pesticide wastewaters was studied in different electrodialysis systems. The experiments show us that nearby organic pollutant (EPTC) inorganic contamination (NaCl) is also degradable. The endproducts including SO_4^{2-} and NO_3^- are produced from the EPTC, and NaOH is produced from NaCl, in the known manner.

Keywords: electrodialysis, wastewater, degradation, thiocarbamate, inorganic pollutants

INTRODUCTION

Earlier it was reported on attempts to decompose thiolcarbamate type pesticides, including EPTC (1) in electrolysis of wastewater [1],



(1)

in a single undivided electrolysis cell *(Figure 1)* and partly in a two-cell electrolysis cell *(Figure 2)* where electrodialysis processes can also play a role.

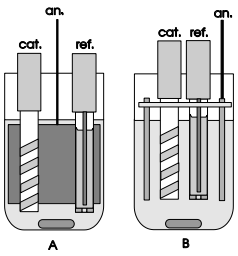


Figure 1
Single-cell electrolysis equipment

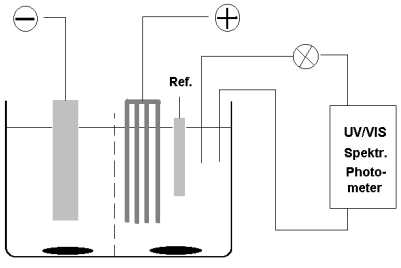


Figure 2
Two-cell electrolysis equipment

[1] Institute of Chemistry, University of Miskolc
H-3515 Miskolc-Egyetemváros, Hungary
fkmmf@uni-miskolc.hu

1. MATERIALS AND METHODS

Different structure electrodialysators were used in the laboratory experiments: the anode was DSA®, the cathode was a perforated sheet made of acid-resistant iron alloy, Ag/AgCl electrode was used as reference electrode. The constant potential was maintained by an EF 427 type potentiostate and a TR-9158 direct current source. The potentiostate was used in potentiometric mode in all our experiments and the current was registered.

The organic endproducts produced were analyzed by a Hewlett-Packard 1084B HPLC or a Chrompack Gas Chromatograph. Chlorine concentration and UV absorbance were measured with a Hewlett-Packard 8452A diode-array spectrophotometer. During the electrodialysis experiments pH was not measured, the produced NaOH was measured titrimetrically with HCl solution. The Cl^- concentration was determined titrimetrically with $AgNO_3$ solution. The SO_4^{2-} was determined gravimetrically by $BaCl_2$ precipitation and NO_3^- concentrations were determined photometrically by Na-salycilate method. COD measurements were made by standard bichromate measuring method.

Industrial filter fabric was used as diaphragm and also membranes (ion selective and bipolar membranes) i.e. NAFION (Du Pont products) with different codes were used.

Reagents

The initial concentration of the EPTC made by Sagrochem Ltd. was 100 ppm. The conducting electrolyte was 0.5 $kmol.m^{-3}$ NaCl (Reanal). The pH was set by HCl in the acid or by NaOH in the basic range. Distilled water was used as the solvent.

2. RESULTS AND DISCUSSION

Electrodialysis of NaCl and NaOH-containing EPTC solutions was first studied in a classical three-cell electrodialysis device known in the art *(Figure 3)*.

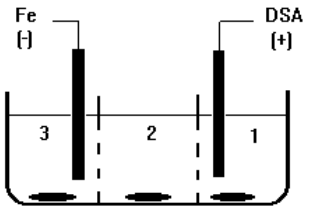


Figure 3
The classic three-cell electrodialysator

The device is made of polypropylene. The semi-permeable wall (diaphragm) was an industrial filter fabric through which clean water could not flow (without overpressure). Of the electrodes, the anode was DSA®, the cathode was stainless steel. In the cells, strong mixing was provided by magnetic stirrers. Each cells volume were about 15–20 ml. The surface of the electrodes was not determined exactly, the aim was the constant potential electrolysis. It worked visible. Due to the distance between the

electrodes and the diaphragms, the potential of 6.14 V, which is provided by the type of TR-9158 direct current source, the current was 0.6–0.7 A, and the change (decrease) shown in the figure 4 could be achieved by the initial solution (2) (Na^+) at the concentration of Cl^- and NaOH, while the anolyte concentration of the anion in the anode space increased, the catholyte concentration of catholyte increased in the cathode space.

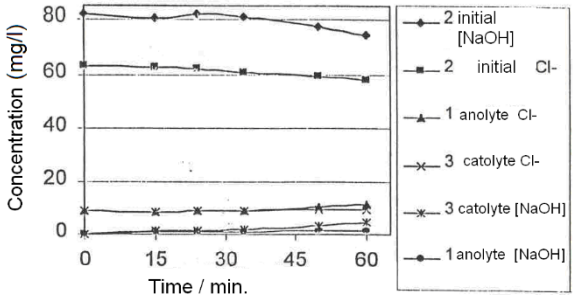


Figure 4
The electrolysis of 100 μl EPTC 10% NaCl, 10% NaOH in classic three-cell electrodialysator

According to our UV spectrophotometric measurements, the EPTC concentration of the starting mixture, and more specifically the magnitude of the UV absorbance, did not change significantly. 100 ml of the starting mixture was extracted with 4 ml of CCl_4 and the UV absorbance was measured at 262 nm with a diode array spectrophotometer. Not in the catholyte, a barely detectable UV absorbance at 262 nm appeared in the anolyte, which means that EPTC transport in such an electrical dialysis is negligible but occurs as well as NaCl transport to the negligible cathode space and NaOH transport to the anode space.

Thus, in addition to electrodialysis, signs (effects) of diffusion in the traditional sense can be seen in the *Figure 4*.

In a two-cell device constructed from the same elements, but with a different design, at smaller cell voltages *(Figure 2)* we were able to achieve much greater changes in the composition of the starting NaCl and NaOH-containing EPTC solutions by the combination of electrodialysis and electrolysis. The electrolysis cell was the same volume as the three-cell electrodialysator but without the middle part. (Anode was DSA®, cathode Fe, membrane: NAFION 324.) In these experiments, the EPTC concentration was measured by gas chromatography (Chrompack), NaOH, Cl^-, SO_4^{2-}, and NO_3^- concentrations were determined as discribed earlier, chlorine concentration and UV absorbance were measured with a diode-array spectrophotometer.

Figure 5 shows that the rate of increase in NaOH concentration in the catholyte is significantly higher than in the 3-cell classical electrodialysis, so the transport of the Na^+-ion through the diaphragm is significant and the rate of increase in chlorine

UV absorbance is very fast in the anolyte until the saturation concentration is reached, chlorine is released from the system in gas form.

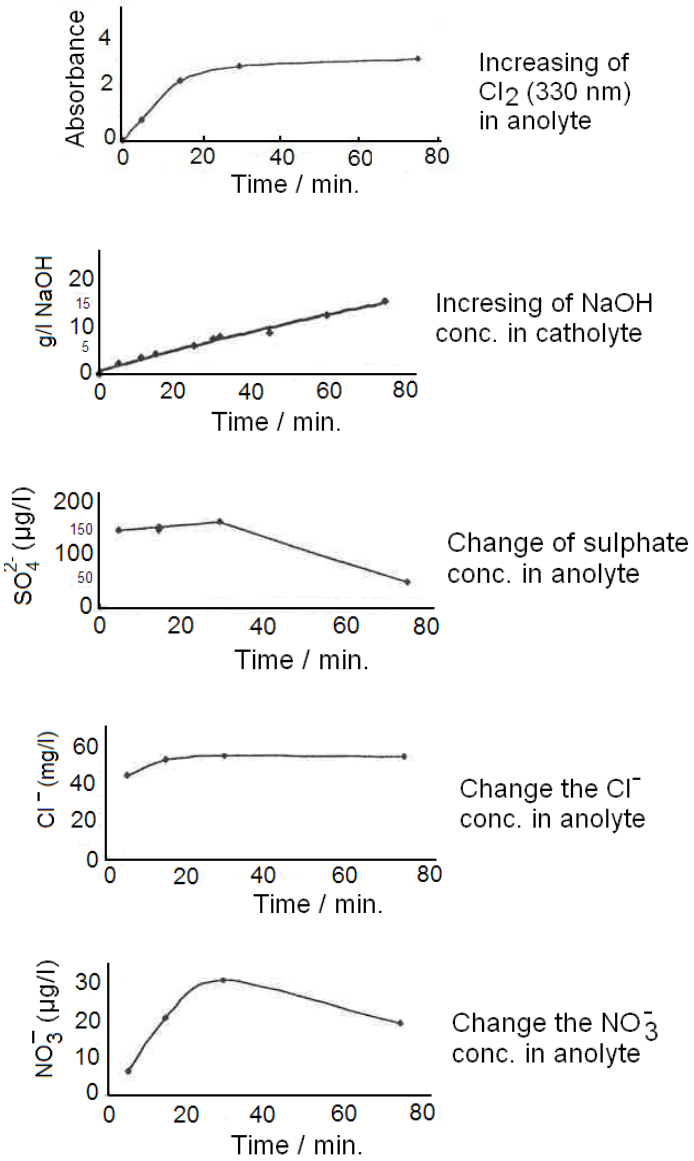


Figure 5

Diaphragm electrolysis – electrodialysis (200 µl EPTC/L 10% NaCl solution) Pot.: 1.7 V, I = 4 A. Cl_2 – UV absorbance, the change of concentration of NaOH, SO_4^{2-}, C^-, and NO_3^- in time

The strong Na^+-ion transport can also be deduced from the fact that the fluid level in the cathode space is always higher than in the anode space (due to the solvation of Na^+-ion, water also passes through the membrane and thus a significant osmotic pressure is generated). In the anolyte, the increase in Cl^--ion concentration – up to saturation concentration – provides the Cl^--ion supply for Cl_2 generation.

Thus, Cl^--ion transport from the cathode space continuously provides equilibrium Cl^- concentration around the anode. The change in the concentration of organic pollutant (EPTC) and the rate of decrease are not shown in the figure, this has already reported in detail [4].

Now it was only checked by the fact of rapid, complete decomposition by gas chromatography. EPTC, the organic pollution, disappeared completely from the anolyte.

From the EPTC in the anode space, as a result of degradation, nitrate and sulphate are also produced (this also indicates that not only the EPTC but also its degradation intermediates are degraded) and nitrate and sulphate are likely to be involved in further reactions – based on the nature of the curves (maximum curve).

Thus, our experiments with electrodialysis and electrolysis (diaphragm electrolysis), in addition to organic contamination, also highlighted the degradation of inorganic contaminants.

In the following experiments, it was investigated how to accelerate the degradation of inorganic contaminants, especially NaCl, with a similar arrangement.

Without changing the dimensions of the diaphragm and the electrode, we changed the geometry of the cells.

The volume of the cells was reduced by half, then further, or the surface of the electrodes was increased at a given volume.

Thus, the EPTC and NaCl content of the starting solutions (EPTC and NaCl) could be broken down faster.

This was reflected in the decrease in COD of the treated solutions in the reduction of the anolyte concentration of the anolyte and in the increase of the catholyte NaOH concentration.

According to the data in *Table 1*, this is also true for real industrial wastewater. In such a device, we investigated the degradation of the organic and inorganic impurities of the diluted end lye produced by neutralizing a phosgene operating end gas, and of the effluent discharged through a centralized wastewater treatment plant.

Table 1

Real industrial wastewater electrodialysis and electrolysis

Wastewater	**COD (mg/l)**				**Na^+ (g/l)**			
	initial		**after electrolysis**		**initial**		**after electrolysis**	
Phosgene end lye	anolyte	catholyte	anolyte	catholyte	anolyte	catholyte	anolyte	catholyte
					5.55	5.55	2.3	8.8
Wastewater treatment plant effluent	123	123	88	46				

In addition to the undiluted 8.6% NaOH, concentrated diaphragm (NAFION 324 perfluoro-sulphonic acid/carboxylic acid cation selective membrane) was used to convert NaCl and Na_2CO_3 impurities in NaOH and Na_2CO_3 containing concentrated phosgene which exhibits more advantageous properties for more concentrated NaOH solutions than the NAFION 417 membrane tested. But it is also very susceptible to contamination like most membranes and diaphragms.

CONCLUSION

By the electrodialysis of aqueous solutions containing NaCl and thiolcarbamate (EPTC) contaminates both organic contamination (EPTC) and inorganic contamination (NaCl) are degradable, where end products, including SO_4^{2-} and NO_3^-, are produced from the EPTC and NaOH is produced from NaCl in the known manner.

Electrodialysis plays a role in transport processes depending on cell geometry, diaphragm and membrane and reaction parameters and affects the transport and concentration of Cl^-, Cl_2 and (Na^+OH^-) in the anolyte and catholyte.

ACKNOWLEDGEMENT

This research was supported by the European Regional Development Fund in the framework of the GINOP-2.2.1-15-2016-00005 project. The author would like to thank Béla Viskolcz, Head of Institute of Chemistry, for his helpful contribution.

REFERENCES

[1] Mogyoródy, F. (2016). Study of the electrolytic degradation of organic pollutants in waste water. *Material Science and Engineering,* vol. 41 no. 1. pp. 89–95.

[2] Seignez, S., Pulgarin, C., Péringer, P., Comninellis, C., Plattner, E. (1992). Degradation of industrial organic pollutants. Electrochemical and biological treatment and combined treatment. *Swiss Chem.*, vol. 14, no. 1, pp. 25–30.

[3] Vidal, A., Dinya, Z., Mogyoródy, F., Mogyoródi, F. (1999). Photocatalytic Degradation of Thiocarbamate Herbicide Active Ingredients in Water. *Applied Catalysis B: Environmental,* vol. 21, no. 4, pp. 259–267.

[4] Mogyoródy, F. (2006). Influence of Chlorine-Water Equilibria on the Electrochemical Destruction of Thiocarbamate Herbicides in NaCl Solutions. *Journal of Applied Electrochemistry*, vol. 36, no. 7. pp. 765–771.

[5] Boxal, C., Kelsall, G. H. (1992). Hypochlorite electrogeneration. II. Thermodynamics and kinetic model of the anode reaction layer. *Icheme Symposium,* no. 127, p. 59.