

THE EXAMINATION OF THE BOUNDARY LAYER FORMED ON THE NICKEL ELECTRODE/SOLUTION INTERFACE IN THE BOUNDARY LAYER SEPARATION METHOD IN PLASTIC INDUSTRIAL WASTEWATERS

D. PETHŐ-RIPPEL[✉], G. HORVÁTH

Institute of Chemical and Process Engineering, University of Pannonia, H-8201 Veszprém, HUNGARY

[✉]E-mail: pethod@almos.vein.hu

Strict environmental laws limit the emission of wastewaters formed in the manufacturing of plastics. We have developed a new method for the treatment of alkaline wastewaters, which we have given the name Boundary Layer Separation Method (BLSM). We have utilized the phenomenon that on the surface of an electrically charged electrode, ions can be enriched in the boundary layer, as compared to the liquid phase. The essence of the method is that – with an appropriately chosen velocity – the boundary layer can be removed from the wastewater, and the boundary layer, which is rich in ions, can be recycled. Electrosorption is a surface phenomenon, thus the formation of the boundary layer requires appropriate electrodes. Nickel pastille electrodes prepared with powder metallurgical methods and nickelized nickel electrodes prepared with electrolysis were used for the experiments. The phenomena on the electrode/solution interface were examined in flowing systems. The discharge of the diffuse part of the boundary layer was examined as the function of the flow rate. It is concluded that it is pointless to exceed the relative velocity of 25 cm/s in the case of nickel pastille electrodes and 10 cm/s in the case of nickelized nickel electrodes. Lastly, the ion transport with BLSM and the experimental device is presented. Electrochemical methods, such as BLSM have the advantage of not utilizing dangerous chemicals, only inert electrodes. An additional advantage is that they do not generate further pollutants.

Keywords: electrosorption, electrochemical double layer, diffuse layer, ion transport

Introduction

The plastic industry is inevitable for the automobile industry. However, during the manufacturing of plastics various gaseous and liquid waste materials are formed, which are regulated by strict environmental laws. The gases are usually cleaned with absorption methods which produce additional industrial wastewaters.

Alkaline industrial wastewater is formed during the absorption in alkaline absorber towers of pyrolysis gases which emerge in the production of olefins. Sodium hydroxide is constantly added to the system and the sludge is constantly being removed. The “traditional” wastewater treatment is only capable of removing the organic contents, not the alkaline compounds. The latter poses a considerable threat to the environment. The alkali can be neutralized only to form salt, the emission of which is also strictly regulated by laws of environmental protection.

Recycling is the most effective technological solution for the treatment of the emerging waste. Our aim is to devise a technology that is not only capable of reducing the Na⁺ ion concentration but also of enriching the waste material in another system and reintroducing it into the technology. The pollutants emitted to the environment can be significantly reduced by this method. We have developed a new method for the treatment of industrial

wastewaters and given it the name Boundary Layer Separation Method (BLSM).

The method is based on the phenomenon of electrosorption. Electrosorption is the absorption process that takes place on the surface of charged electrodes [1]. The electric polarization can be carried out galvanostatically or potentiostatically [2]. Generally, the galvanostatic method is favoured in practice [3, 4]. The electrosorption of cations takes place on a cathodically polarized (negative) electrode. This electrosorption is superposed onto the physical adsorption which takes place without charge. If the polarity is reversed, the cations undergo desorption [5, 6, 7, 8]. This phenomenon can be used to produce ion transport with a cyclic method.

During electrosorption, an electrical double-layer forms on the electrode-solution interface. The electrical double-layer has two main parts: the Helmholtz-layer and the diffuse layer. If the electrode is moved, the diffuse layer might be torn apart, producing a zeta-potential between the stationary and the moving parts.

The essence of BLSM is that – with an appropriately chosen velocity – the boundary layer can be removed from the wastewater, and the boundary layer, which is rich in ions, can be recycled.

Electrochemical methods such as BLSM have the obvious advantage of not utilizing additional hazardous chemicals, only inert electrodes. They also do not

generate pollutants. The electrochemical parameters can be measured and adjusted readily.

Electrosorption is a surface phenomenon. It can only be utilized with good efficiency if the surface area of the electrode is high. Mostly, porous carbon electrodes with high specific surface areas are used [9, 10, 11, 12, 13, 14, 15]. Electrodes of high surface area can also be made of metals. With the reduction of NiO, Co₃O₄ and Fe₂O₃ with hydrogen, macroporous Ni, Co and Fe can be produced [16].

Porous Ni, Cu, Ag, Pt and Au can be produced by precipitating the metal onto colloidal silicic acid [17]. Silicon-dioxide is removed with HF after calcination. Among electrochemical methods, the production of platinized platinum is well-known. High specific surface area "black" or "gray" nickel electrodes can be made by the same method [18, 19]. The high surface area is not always an advantage because if the pore size distribution is not adequate, parts of the surface might become electrochemically inaccessible.

With the use of electrosorption, inorganic [20] and organic ions, such as thiocyanate [1], pyridine [2], aniline and bipyridines [3] can be removed from aqueous solutions. Among the practical applications wastewater cleaning [22] and water desalination [23, 24, 25] are remarkable.

Experimental

Porous nickel working electrodes, which were produced by powder metallurgical methods, and nickelized nickel electrodes, which were produced electrochemically, were used for the experiments [26]. The experiments were carried out with 0.2% (m/m) NaOH model solutions. The phenomena were also proven with 2% (m/m) NaOH solutions and actual industrial wastewater.

The Na⁺ ion concentration was determined with an AA-6601F type Atomic Absorption Flame Emission Spectrophotometer (Shimadzu Corporation, Analytical Instrument Division, Kyoto, Japan) in emission mode. The samples for analysis were prepared with the mixture of nitric acid:distilled water (1:5).

The examination of the diffuse part of the electrochemical double layer

If the electrode and the solution move relative to each other, the diffuse part of the double layer is torn and a Zeta-potential emerges. The value of the zeta-potential is a function of the velocity of the shift in space, i.e. how fast the electrode is taken out of the solution, or how fast the liquid flows around the electrode. We examined, how the Zeta-potential (and thus the place where the double layer is torn) changes as the function of the flow rate of the liquid. The experiments were conducted with nickelized nickel and then also with nickille pastille electrodes.

For the measurement of the zeta-potential, we constructed the device illustrated in Fig. 1.

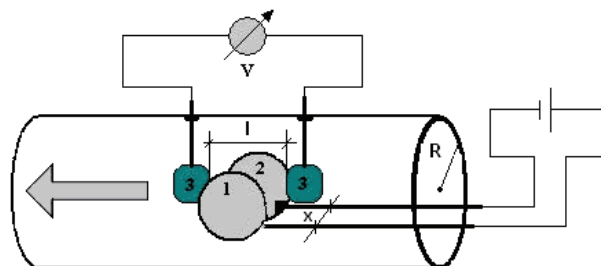


Figure 1: Measurement of the zeta-potential, where: $R = 15$ mm, $x = 15$ mm, $l = 40$ mm, 1. cathode, 2. anode, 3. auxiliary electrode

The nickel electrodes were mounted in a plastic (PVC) pipe ($R = 15$ mm) equidistant from the centerline, so that the distance between them is $x = 15$ mm.

A continuous potential difference was introduced between the cathode (1) and the anode (2). The cations are in excess in the diffuse layer of the cathode, whereas the anions are in excess in the diffuse layer of the anode. 0.05 M NaOH solution was being flowed in the system at all measurements in the direction given by the arrow. The flow rate was constantly being increased.

The stripping of the diffusion layer was followed by putting (plane platinum) auxiliary electrodes before and behind the examined electrodes. The potential difference, the so-called space potential was measured between the auxiliary electrodes (3) as the function of the liquid's laminar flow rate at different polarization potentials. Since a potential difference can be measured between the auxiliary electrodes, the diffusion layer must be able to be gradually swept off with the flowing liquid. The measured space potential is in proportion with the amount of ions that were swept off.

Fig. 2 illustrates the experiments conducted with the nickel pastille electrodes.

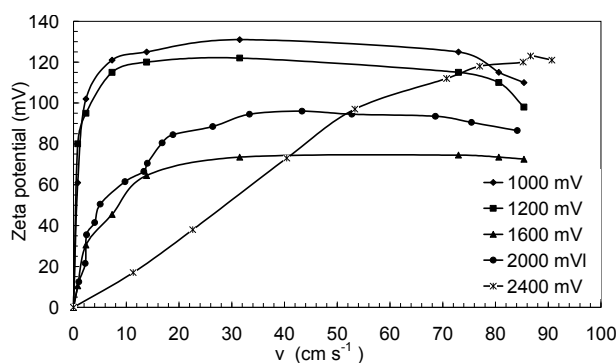


Figure 2: Zeta-potential as the function of the flow rate of the liquid, with porous nickel pastille electrodes

The results show that at low flow rates and polarization potentials between 1000 and 2000 mV, the measured Zeta-potential values increased rapidly. This leads to the conclusion that most of the ions are swept off. The Zeta-potential is however, a linear function of the flow rate at 2400 mV polarization potential. A firmly adhering diffusion layer is formed which is harder to be swept off. The Zeta-potential does not change significantly below 2400 mV above 25 cm/s linear velocity. It is pointless to use a higher relative velocity in the given system.

Fig. 3 illustrates the experiments conducted with the nickelized nickel electrodes.

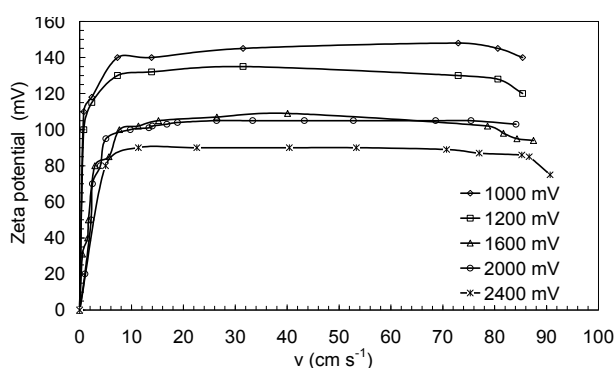


Figure 3: Zeta-potential as the function of the liquid's flow rate with nickelized nickel electrodes

Compared to the nickel pastille electrodes it can be concluded, that most of the ions tear off even at low flow rates, irrespective of the polarization potential. It is thus unadvantageous to have a relative velocity of higher than 10 cm/s in systems using nickelized nickel electrodes. By examining Fig. 2 and 3, it can be observed that the steepness of all the diagrams turn to negative at 70–80 cm/s flow rates, that is to say the end of the diagram breaks. Before examining this phenomenon, one has to make sure that it is really the because of the behavior of the diagram and not because of a systematic error.

For proving the formers, the device was modified as follows: first the anode then the cathode in the pipe (Fig. 1) were changed to nickel plate electrodes that have minimal surfaces. This way the discharge velocity of both the anions and the cations could be measured separately at a given potential (1200 mV). No other parameters of the measurement were changed.

Fig. 4 illustrates the anodic and cathodic polarization diagrams gained in the measurement with nickel pastille and nickelized nickel electrodes. The experimental results show well the difference between the discharge of the cations and the anions. The tendencies are the same for both electrodes. According to the cathodic polarization diagram, the cations can be swept off of the surface easily even at low flow rates. By increasing the flow rate, the curve becomes constant, indicative of the total discharge of the diffusion layer.

By examining the anodic polarization diagram, we experienced that a bigger force is needed to sweep off the anions. The discharge process also commences rapidly, but its extent is significantly lower. The potential difference as the function of the flow rate does not become steady between the measuring limits. In the interval, where the cathodic diagram becomes constant, the anodic diagram is linear. This is because the anions do not have hydration shells, which would make a tighter fit possible in the diffusion layer. Also, the anions can get closer to the surface of the adsorbent because they lack the hydration shell. This experiment proves the phenomenon of specific adsorption: the anions bond to the surface not only by electric attraction, but also by specific adsorption (e.g. van der Waals-bonding).

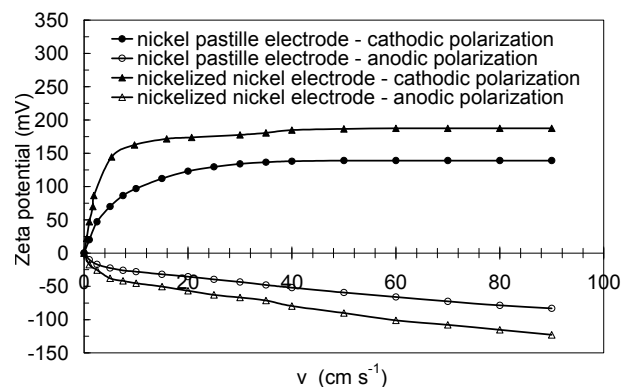


Figure 4: The anodic and cathodic polarization potentials as the function of the flow rate

Since the experimental setup was the same for the measurement of the anion and cation discharge potentials, the points in the curves were added. The expected tendency can be seen on Fig. 5.

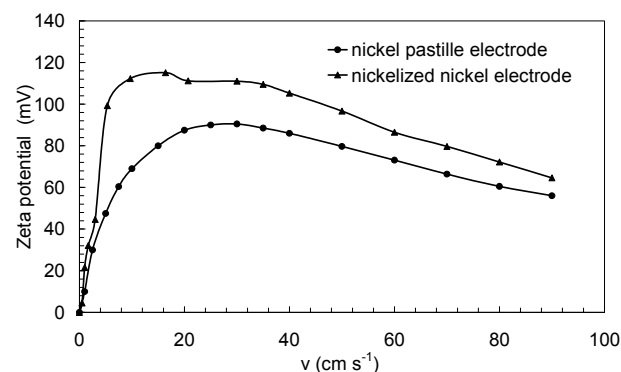


Figure 5: The sum diagram of the anodic and cathodic polarization potentials

The difference in potentials decreases at higher flow rates in the sum diagrams. The steepness of the diagrams however, becomes negative at lower flow rates than in the previous measurements, the diagrams of which are in Fig. 2 and 3. The reason for this is that electrodes were placed differently in the two measurements which caused different flow circumstances.

With experiments we confirmed that the break in the diagrams is not due to measurement error, but to the different nature of anions and cations.

Experiments in flowing systems

The experimental setup is illustrated on Fig. 6 [27], where 1. is anode compartment, 2. is cathode compartment, 3. is graphite counter-electrodes, 4. is mobile working electrodes, 5. is lever, 6. is driven axle, 7. is program dial, 8. is electric motor, 9. is microswitches.

The two compartments form the chemical cell below. The compartment, where the fix counter electrode is switched as the anode is called the anode compartment, whereas the moving working electrode is switched as the cathode. The compartment, where the fix counter electrode is switched as the cathode and the moving

working electrode is the anode, is called the anode compartment.

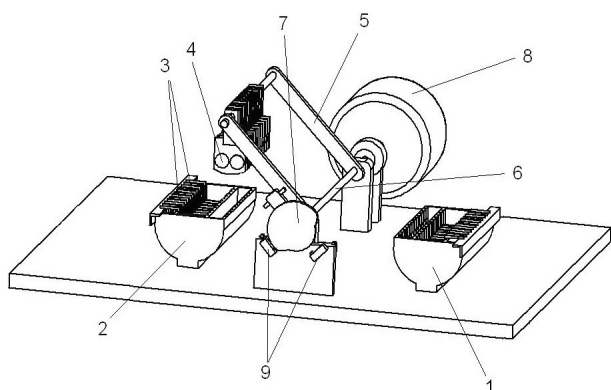


Figure 6: The automatic electrosorption device

The operation is cyclic, one cycle is composed of the following sub-operations. The high area nickel electrodes are immersed into the solution of the anode compartment, between the graphite counter electrodes. The cell which is thus formed, is given a polarization potential so that the working electrode is the negative (cathode) and the counter electrode is the positive (anode). The positively charged ions then move to the working electrode and absorb on its surface. This is the electroadsorption phase. The saturation of the working electrode can be followed by measuring the current that flows through the cell. When the electroadsorption process concludes, the working electrode is taken out of the anode compartment together with the boundary layer rich in ions, and the polarization potential is switched off. The electrode is then immersed into the other solution (the cathode compartment), where the polarity is reversed. The working electrode becomes the positive, the counter electrodes in the other cell the positive ones. The ions are desorbed from the surface of the working electrode because of the electrical repulsion and get into the solution. This process can also be monitored by measuring the current that flows through the cell. The working electrode is taken out of the solution, the potential switched off, and the electrode immersed into the anode compartment once again.

By using the appropriate cycle, a concentration difference can be achieved between the anode and the cathode compartments. By mass transfer, the amount of ions transferred from the anode to the cathode compartment at the given parameters is understood. At the cyclic procedure, the values can be given in units of $\text{mg}/(\text{m}^2 \times \text{cycle})$.

The experimental device is capable of measuring flowing systems. In the experiments the liquids in both the anode and the cathode compartments were recycled with the help of peristaltic pumps. During this, the working electrodes were being displaced from one compartment into the other in the given operational time. The extent of the ion transport was examined as the function of the flow rate. Fig. 7 illustrates the

experimental results. The mass transfer significantly decreases with both electrodes by increasing the flow rate.

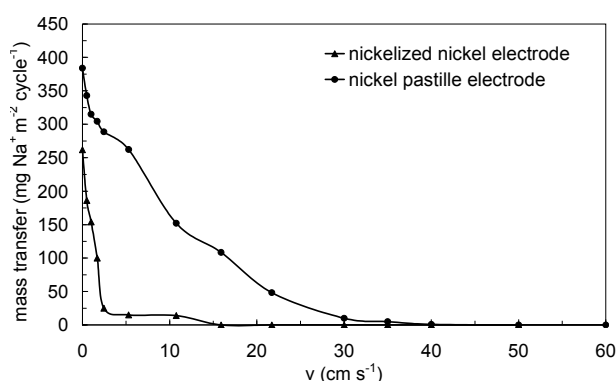


Figure 7: The extent of mass transfer as the function of flow rate in the case of nickelized nickel and nickel pastille electrodes

In the case of nickelized nickel electrodes, linear speeds of some centimeters per second were enough to sweep off all the excess ions of the surface of the electrode. A similar phenomenon can be observed in the case of pastille electrodes, but, as previously observed, its extent is smaller.

We got a similar diagram when the decrease in the reduced transfer was plotted as the function of the flow rate (Fig. 8). For this we defined the mass transport at the flow rate $v = 0$, and the deviation from this was calculated as percentage giving the decrease in the reduced transfer at the measured velocities.

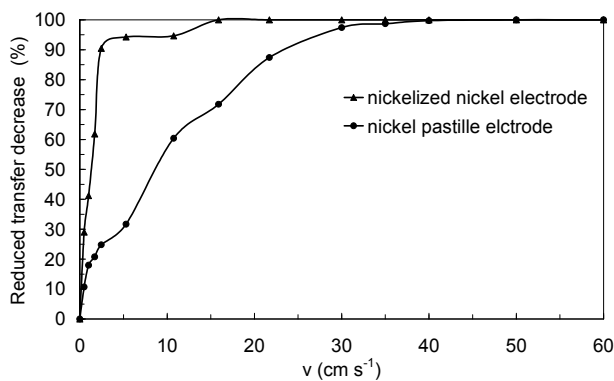


Figure 8: Reduced transfer decrease with nickelized nickel and nickel pastille electrodes

The experiments prove that the decrease in reduced transfer increases with the increasing flow rates, its extent reaching 100% with nickelized nickel electrodes at 10 cm/s ; and at 30 cm/s with nickel pastille electrodes. After this, the ion transfer is zero, the flowing liquid sweeps all the excess ions off of the surface of the electrode.

It was concluded that for the sake of higher mass transfer, the lowest possible flow rate should be used for the liquid.

Summary

A new method has been devised for the treatment of industrial wastewaters which we have given the name Boundary Layer Separation Method (BLSM). We have utilized the phenomenon that on the surface of an electrically charged electrode, ions can be enriched in the boundary layer, as compared to the liquid phase. The electrodes are removed from the wastewater with an appropriately chosen velocity in a way that the ion-rich boundary layer remains on its surface. By placing this boundary layer into another phase, separation is realized. Nickel pastille electrodes prepared with powder metallurgical methods and nickelized nickel electrodes prepared with electrolysis were used for the experiments.

By measuring the Zeta-potential, we proved that if the electrode and the solution move relative to each other, the diffuse part of the double layer is torn, affecting the efficiency of the separation. We concluded that it is pointless to exceed the relative velocity (between the solution and the electrode) of 25 cm/s in the case of nickel pastille electrodes and 10 cm/s in the case of nickelized nickel electrodes. Ion transport can be realized with the Boundary Layer Separation Method, for which we constructed a device. The device is capable of measuring flowing systems as well. The ion transport changed as the function of the flow rate in accord with the results gained in the measurements of the Zeta-potential. The ion transfer is approximately zero beyond the limit velocities given.

The method, called BLSM by us, is novel from a technical point of view. We have already applied for a patent at the Hungarian Patent Office [27].

ACKNOWLEDGEMENT

The authors express their gratitude to the Institute of Chemical Engineering - Cooperative Research Center of the University of Pannonia for the financial support of this research.

REFERENCES

1. C. RONG, H. XIEN: *J. Colloid Interf. Sci.*, 290, 2005, 190–195.
2. J. NIU, B. E. CONWAY: *J. Electroanal. Chem.*, 521, 2002, 16–28.
3. J. NIU, B. E. CONWAY: *J. Electroanal. Chem.*, 536, 2002, 83–92.
4. A. VAŠKELIS, E. NORKUS, J. STALNIONIENE, G. STALNIONIS: *Electrochim. Acta*, 49, 2004, 1613–1621.
5. A. AFKHAUNI, B. E. CONWAY: *J. Colloid Interf. Sci.*, 251, 2002, 248–255.
6. Y. XU, J. W. ZONDLO, H. O. FINKLEA, A. BRENNSTEINER: *Fuel Process. Technol.*, 68, 2000, 189–208.
7. J. C. FARMER, D. V. FIX, G. V. MACK, R. W. PEKALA, J. F. POCO: *J. Electrochem. Soc.*, 143, 1996, 159–169.
8. E. AYRANCI, B. E. CONWAY: *Anal. Chem.*, 73, 2001, 1181–1189.
9. E. BAYRAM, N. HODA, E. AYRANCI: *J. Hazard. Mater.*, 168, 2009, 1459–1466.
10. L. PAN, X. WANG, Y. GAO, Y. ZHANG, Y. CHEN, S. ZHUO: *Desalination*, 244, 2009, 139–143.
11. J. NIU, B. E. CONWAY: *J. Electroanal. Chem.*, 564, 2004, 53–63.
12. A. ALFARRA, E. FRACKOWIAK, F. BÉGUIN: *Electrochim. Acta*, 47, 2002, 1545–1553.
13. T. Y. YING, K. L. YANG, S. YIACOUMI, C. TSOURIS: *J. Colloid Interf. Sci.*, 250, 2002, 18–27.
14. A. BÁN, A. SCHÄFER, H. WENDT: *J. Appl. Electrochem.*, 28, 1998, 227–236.
15. J. KORESH, A. SOFFER: *J. Electrochem. Soc.*, 124, 1977, 1379–1385.
16. H. YAN, C. F. BLANFORD, B. T. HOLLAND, M. PARENT, W. H. SMYRL, A. STEIN: *Adv. Mater.*, 11, 1999, 1003–1006.
17. P. JIANG, J. CIZERON, J. F. BERTONE, V. L. COLVIN: *J. Am. Chem. Soc.*, 121, 1999, 7957–7958.
18. S. J. BEREZINA, G. S. VOZDVISENSZKIJ, G. P. DEZIDEREV: *Dokl. Akad. Nauk SSSR*, 77, 1951, 53–55.
19. G. HORÁNYI, E. M. RIZMAYER: *J. Electroanal. Chem.*, 180, 1984, 97–108.
20. Y. OREN, A. SOFFER: *J. Electrochem. Soc.*, 125, 1978, 869–875.
21. D. HALL, Z. PRIEL, Y. OREN, A. SOFFER: *Separ. Sci. Technol.*, 22, 1987, 1017–1027.
22. V. GANESH, V. LAKSHMINARAYANON: *Electrochim. Acta*, 49, 2004, 3561–3572.
23. Y. OREN, Y. EGOZY: *Desalination*, 86, 1992, 155–172.
24. Y. OREN, A. SOFFER: *J. Appl. Electrochem.*, 13, 1983, 473–487.
25. E. NORKUS, A. VAŠKELIS, J. STALNIONIENE: *J. Solid State Electrochem.*, 4, 2000, 337–341.
26. D. PETHŐ, GY. GÁSPÁR, G. HORVÁTH, J. LISZI, R. SZAKÁLY, I. TÓTH: *Hun. J. Ind. Chem.*, 36, 2008, 101–106.
27. Hungarian Patent Office (2009) Reg. No: P0900569.