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ALKALINE RECYCLING WITH BOUNDARY LAYER SEPARATION METHOD (BLSM)

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ABSTRACT. A new method for the treatment of industrial waste water, called Boundary Layer Separation Method (BLSM) has been developed. The phenomena of ion enrichment in the boundary layer of the electrically charged electrode surface compared to the bulk liquid phase have been applied. The essence of the method is that the boundary layer, at a correctly chosen movement velocity, can be taken out of the waste water without damage, and the ion enriched boundary layer can be recycled. For the experiments a batch and a continuous device were built. Graphite was used as working electrode. The extent of ion transport has been compared in the two devices.

Keywords: *boundary layer, electrosorption, cyclic mass transport, graphite electrode*

INTRODUCTION

The hazards of industrial waste materials are widely known. This is reflected by the increasingly strict environmental laws which regulate the amount of contaminants released by chemical plants (e.g. metals, salts, other organic and inorganic components). In order to comply with regulations, environmental-friendly production methods are needed which either do not emit contaminants into the environment at all, or are capable of handling the incidental waste materials in an up-to-date manner.

One of the problems during the olefin production is the high level of Na^+ in the wastewater. The pyrolysis gases that evolve during the pyrolysis process are absorbed in alkaline washing towers. Sodium hydroxide is fed constantly into the system and the sludge is constantly removed. The “traditional”

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wastewater treatment is capable of removing the organic, but not the alkaline contents. The alkaline contents can be neutralized, but then salt is formed, the release of which is very strictly regulated by environmental laws. Knowing the composition of the wastewater, the aim was to devise a technology which is capable of reducing the Na^+-ion concentration and enriching it in another system, thus enabling its recirculation in the technology. The release of harmful materials can thus be significantly reduced.

A new method for the treatment of industrial wastewaters, called Boundary Layer Separation Method (BLSM) has been develeped. The method is based on the electrosorption phenomenon. 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 favored 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 [5-8]. 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 which is rich in ions can be removed from the wastewater, and can be recycled.

The advantage of the procedure is that it does not use dangerous chemicals, only inert electrodes, which do not produce pollutants. The electrochemical parameters can easily be measured and adjusted. The drawback is that it is not ion selective to ions and the hydrogen that emerges during the electrolysis might be dangerous.

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 [9-11]. Electrodes of high surface area can also be made of metals. With the reduction of NiO, Co_3O_4 and Fe_2O_3 with hydrogen, macroporous Ni, Co and Fe can be produced [12]. Porous Ni, Cu, Ag, Pt and Au can be produced by precipitating the metal onto colloidal silicic acid [13]. 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 [14,15]. 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.

Nickel electrodes were manufactured for the boundary layer separation method [16]. The electrochemically effective surface area of the electrodes was estimated in our earlier works. The presence of the diffuse part of the double layer has been experimentally proven. The capacitance of the electrolytic double layer has been determined [17].

With the use of electrosorption, inorganic [18] and organic ions, such as thiocyanate [1], pyridine [2], aniline and bipyridines [3] can be removed from aqueous solutions. Among the practical applications is wastewater cleaning [19].

In this manuscript ion transport by boundary layer separation is presented, which was realized as a cyclic procedure. For the experiments a batch automatic electrosorption device and a continuous cascade appliance were built. A graphite electrode was used as working electrode instead of nickel electrodes. The extent of the ion transport in the two systems have been compared.

RESULTS AND DISCUSSION

The aim of the experiments was to determine the extent of ion transport. The amount of ions transferred from one cell into another can be given relative to area (mg Na^+ m^{-2} $cycle^{-1}$) or mass unit (mg Na^+ kg^{-2} $cycle^{-1}$) per one cycle.

The optimal operational parameters were determined in our earlier works for nickel electrodes manufactured by our research group. The best mass transport can be achieved with the use of 1200 mV polarization potentials in the examined system. The necessary operation intervals were determined with the examination of the velocity of the electrochemical processes. When using 1200 mV polarization potential, the necessary adsorption interval is at least 25 seconds and the desorption interval at least 300 s with the use of the nickel electrode [22]. The measurements were conducted with ~2 m/m% NaOH solution.

The batch and the continuous devices were compared by these experiments. Since graphite electrodes were used in the continuous device, results under similar conditions (i.e. with graphite electrodes) had to be collected with the batch device as well. The experiments were also conducted with graphite electrodes in the batch device. The experiments proved, that the optimal parameters determined with the nickel electrodes gave equally the best mass transfer with graphite electrodes. The extent of mass transfer is given in mg Na^+/m^2 per cycle (Figure 1). The mass transfer is lower compared to the nickel electrodes but in the continuous device these graphite electrodes were used.

The experiments were also conducted with the continuous device at optimal operation parameters (adsorption interval: 25 s, desorption interval: 300 s, polarization potential: 1200 mV) with graphite working electrodes. The amount of transferred ions from the anode to the cathode compartment was calculated for the mass unit of the electrode per cycle (mg Na^+ ion/ kg cycle) in order to have comparable results.

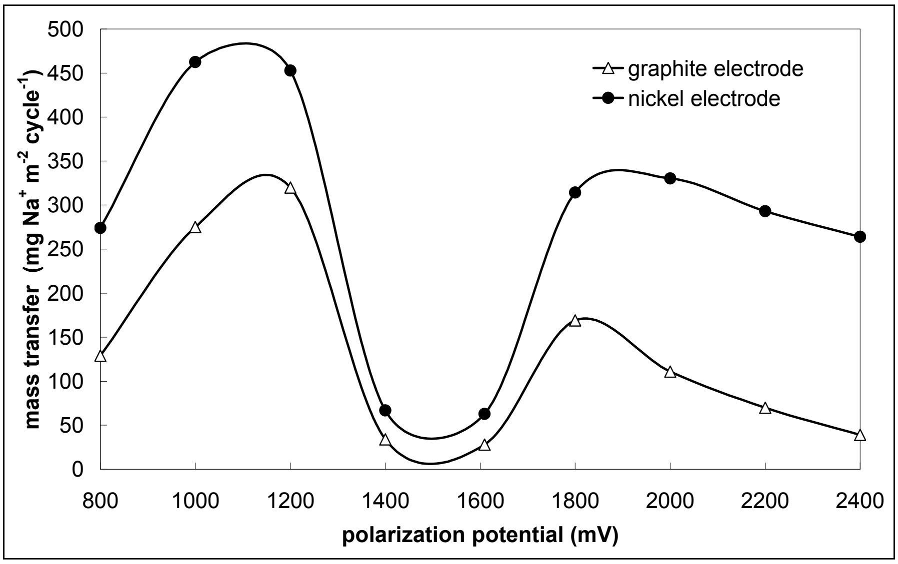

Figure 1. Mass transfer measurements with graphite and nickel electrodes on the batch device (adsorption interval: 25 s, desorption interval: 300 s)

Figure 2 illustrates that mass transfer is greater in the continuous device at the same parameter.

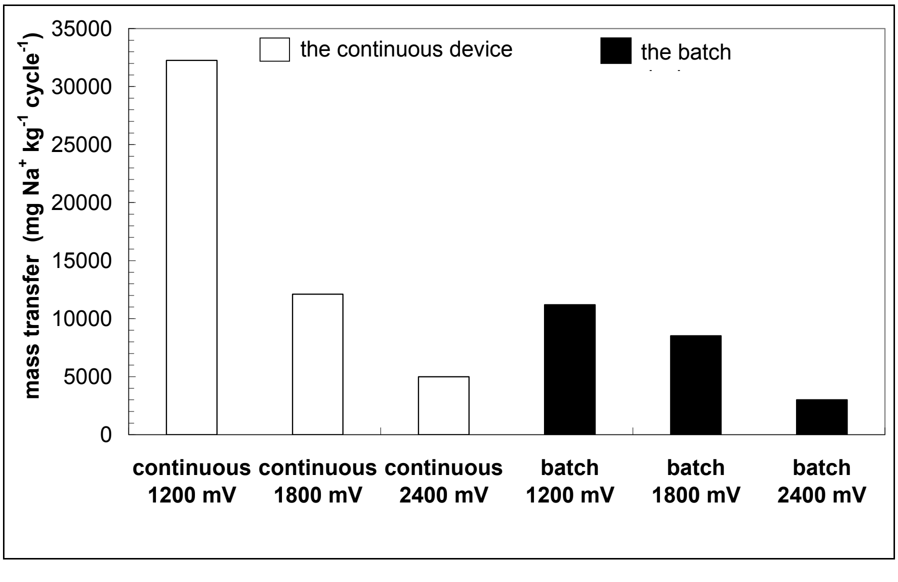

Figure 2. Mass transfer measurements relative to mass unit on the batch and the continuous devices (adsorption interval: 25 s, desorption interval: 300 s)

The extent to which the mass transfer is increasing is not proportionate to the extent of which the area was increased. The reason for this is that the effect of physical adsorption is superposed onto the electrosorption and that the hydrodynamic adhesive layer also takes part in the ion transport. Let factor f stand for the proportion of the mass of the hydrodynamic adhesive layer that is formed on the surface of the electrodes compared to the mass of the original solution. The hydrodynamic layer formed on the surface of the planar electrodes of the batch device is significantly smaller (f_{batch}=0.025) than that formed on the granular packing in the continuous device ($f_{continuous}$=0.14). Because of this, the efficiency of the separation is deteriorated by the greater back-mixing in the two cells.

This is also proved by giving the experimental results of the continuous and the batch device with graphite electrodes relative to unit of surface (Figure 3). Because of back-mixing the ion transport is lower in the continuous device. However, almost the same ion transport can be reached with the continuous device as well if the pore size is chosen appropriately and the value of the f factor is minimized.

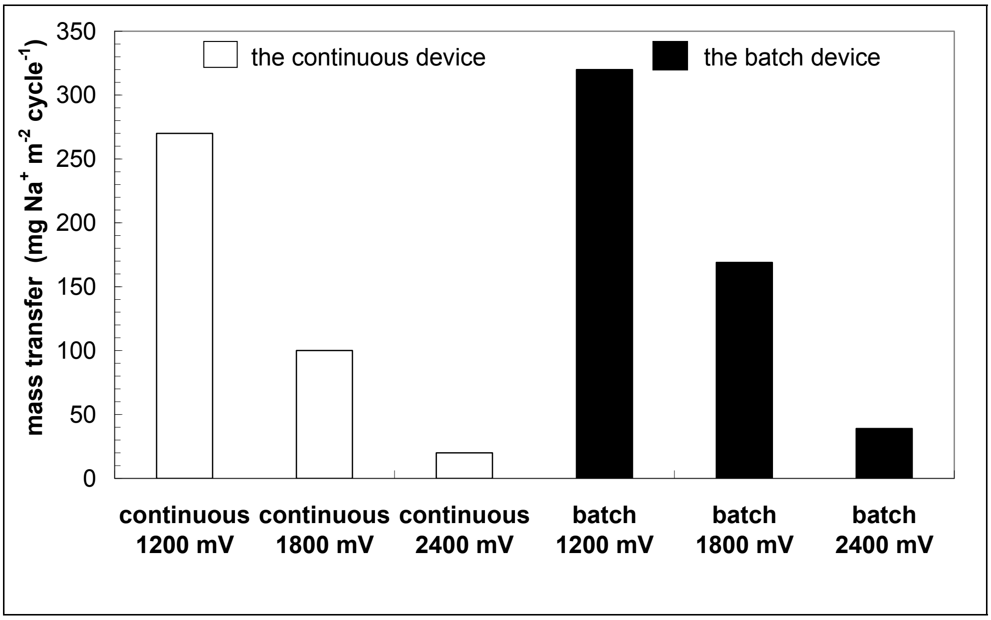

Figure 3. Mass transfer measurements relative to surface unit on the batch and the continuous devices (adsorption interval: 25 s, desorption interval: 300 s)

EXPERIMENTAL SECTION

Experimental setup – Batch device

The laboratory scale experimental equipment and peripheral instruments are presented in Figure 4 [20, 22].

The basic control is done by the process control computer, with which the polarization potentials can be set. This also controls sample-taking. A power supply unit, which provides the necessary voltage, is attached to the computer. Adsorption and desorption intervals can be set by the control unit's interval-switch. The desired number of cycles can be set on the programmable cycle-counter.

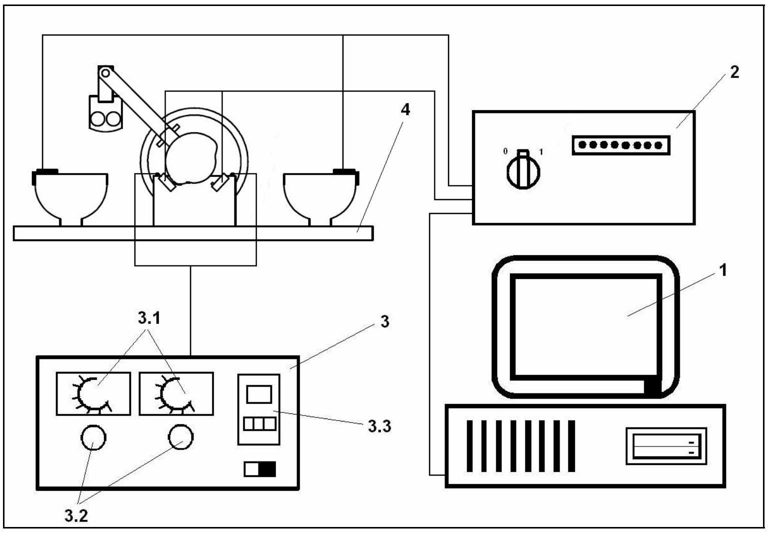

Figure 4. Experimental equipment and peripheral instruments, where 1. Process control computer, 2. Power supply, 3. Regulator unit, 3.1. Adjustable interval-switches, 3.2. Control lamps, 3.3. Programmable cycle-counter, 4. Automatic electrosorption device

The main part of the system is the automatic electrosorption equipment. Structure and units of equipment are presented by Figure 5.

The mobile counter-electrodes are fixed to a driven axle, which is leveled by a lever from the anode compartment into the cathode compartment. The lever is moved by the driven axle, at one end of which there is a program dial and four joint micro-switches. These micro-switches are responsible for stopping the lever in a given position, turning the polarization potential on and off, and changing polarity. To the other end of the driven axle is attached a transmission electric motor by transmission, which drives the axle. Graphite counter-electrodes are fixed inside the compartments. The mobile working electrodes were placed between these. The experimental device is stable, reliable, and easy-to-handle. The electrochemical parameters can be set quickly and on a broad spectrum. A 0.05 M aqueous solution of NaOH (Fluka) was used as a model solution.

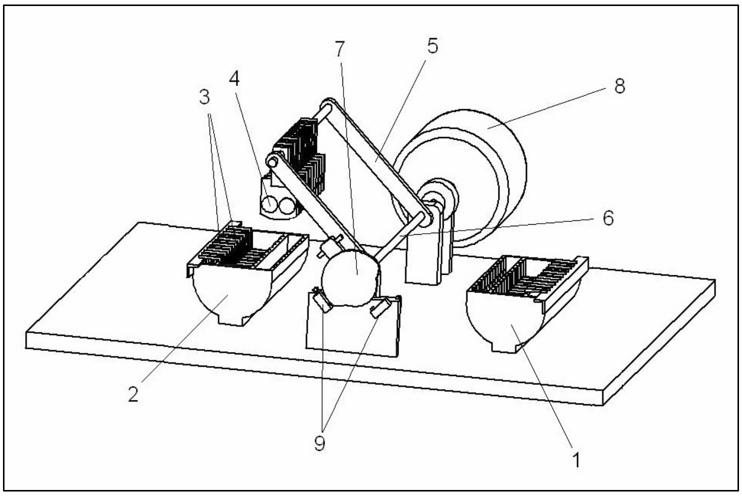

Figure 5. The automatic batch electrosorption device, where
1. Anode compartment 2. Cathode compartment 3. Graphite counter-electrodes
4. Mobile working electrodes 5. Lever 6. Driven axle
7. Program dial 8. Electric motor 9. Microswitches

In the Boundary Layer Separation Method (BLSM) the electrosorption process that undergoes on the surface of the charged electrode is used in a cyclic procedure. Two separate fluid compartments (anode and cathode compartments) were formed.

50-50 cm^3 of fluid are poured into the anode and cathode compartments. 6 graphite counter-electrodes are fixed inside the compartments. The high surface area nickel working electrodes are dipped into the solution inside the anode compartment, between the graphite counter-electrodes. The appropriate polarization potential is switched onto the cell so that the working electrode becomes the negative (cathode) and the counter-electrode becomes the positive (anode). Then the positively charged ions move to the working electrodes and bond to their surfaces. This is the electroadsorption phase. The saturation of the working electrode can be monitored by measuring the current that passes trough the cell. After electrosorption took place, the working electrode, with the boundary layer that is saturated with ions, is pulled out of the solution (from the anode compartment) and the polarization potential is switched off. The working electrode is then put into the other solution (cathode compartment) where the polarity is reversed. Now the working electrode is the positive, and the counter-electrodes in the other cell are the negative. The ions desorbe from the surface of the working electrode due to the electrostatic repulsion, and enter the solution. This process can also be monitored by measuring the current passing through the cell. The working electrode is once again taken out of solution and the potential is switched off. The procedure described above is one cycle. By using appropriate cycles, the ion concentration is reduced in the anode compartment while it is risen in the cathode compartment.

Experimental setup – Continuous device

The advantage of this device is that instead of moving the electrode, the liquid is flowing. The device is different from those that can be found in the literature [21] in the followings: the electrodes are not separated by a separator (ion-exchange membrane), and the work done in the cell and the surface area of the counter-electrode are orders of magnitude different. The absence of membrane was solved with the different surfaces of the electrodes and the selection of operation intervals. The structure of the columnar device is illustrated in Figure 6.

The counter electrode in the chemical cell is the acid-proof steel cylinder that functions as the column's lateral surface. Appropriate electric connections are mounted to the packing and the lateral surface. The inlet and outlet of the electrolyte solution from the anode and cathode compartments is carried out through the connections at the bottom of the column. The working electrode in the column is build from graphite particles of 1-1.5 mm diameter filled in a packing net. The counter electrode in the chemical cell is the acid-proof steel cylinder that functions as the column's lateral surface. Appropriate electrical connections are mounted to the packing and the lateral surface. The inlet and outlet of the electrolyte solution from the anode and cathode compartments is carried out through the connections at the bottom of the column.

During the measurement, a cycle consists of the following steps takes place: filling of the column from the anode compartment; switching the appropriate polarity onto the column (packing: negative, lateral surface: positive); electrosorption for a given interval while the liquid is stationary; draining down the liquid into the anode compartment; ceasing the column's polarity (possibly by discharge); filling the column with liquid from the cathode compartment; switching the appropriate polarity onto the column (packing: positive, lateral surface: negative); desorption for a given interval while the liquid is stationary; draining down the liquid into the cathode compartment.

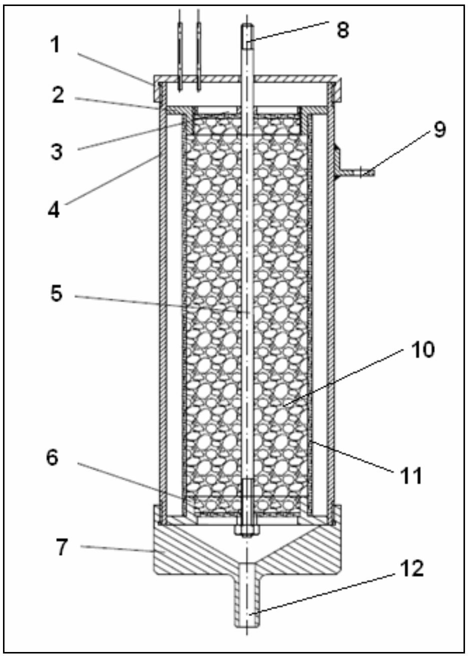

Figure 6. Continuous electrosorption device

1. Cover, 2. Top packing closure 3. Fluid splitter, 4. Lateral surface, 5. Metallic rod, 6. Bottom packing closure, 7. Bottom closure, 8-9. Electrical connection, 10. Graphite packing, 11. Packing holder, 12. Fluid inlet and outlet

CONCLUSIONS

We have developed a new method for the treatment of industrial wastewaters and given it the name Boundary Layer Separation Method (BLSM). The phenomenon, that ions can be enriched in the boundary layer, as compared to the liquid phase on the surface of an electrically charged electrode has been utilized. If this boundary layer is then immersed into another liquid phase, separation is realized. A batch and a continuous device were built for the experiments. Graphite was used as the working electrode. It has been concluded, that the optimal parameters determined with the nickel electrodes gave equally the best mass transfer with graphite working electrodes. The extents of the ion transport in the two devices were compared. Under similar conditions, the extent of the mass transfer is greater in the continuous device. The increase of the mass transfer is not proportionate to the increase of surface area because the formation of the hydrodynamic adhesive layer causes back-mixing between the two cells.

The procedure might be successfully improved with the use of electrodes produced with nanotechnology, or with placing the device into a cascade system.

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