

Communications

Process-Integrated Microbial Mercury Removal from Wastewater of Chlor-Alkali Electrolysis Plants

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Dedicated to Prof. Dr.-Ing. Jörg Schwedes on the occasion of his 65th birthday

The enzymatic reduction of Hg(II) to water-insoluble Hg(0) by mercury-resistant bacteria has been used for removal of mercury from wastewater of a chlor-alkali electrolysis plant. The demercurization process essentially consists of a pre-treatment step for pH adjustment, a fixed-bed bioreactor (1 m³) with pumice granules as carrier for the immobilized mercury-resistant bacteria followed by an activated carbon filter (1 m³). The reactor could be operated at volumetric loadings up to 4 m³/h at Hg concentrations ≤ 10 mg/L and high salt loads (up to 80 g/L), the Hg outflow concentration being below the industrial discharge limit (50 µg/L). The wastewater treatment plant was on stream for 8 months at ECI Ibbenbueren (Germany) and is presently in operation at the chlor-alkali electrolysis factory of Spolchemie in the Czech Republic. The technology developed for microbial mercury removal is a low-cost and environmentally friendly process. The plant has been proven to be reliable and robust against operational fluctuations.

1 Mercury Toxicity

In spite of their toxicity mercury and its compounds have found widespread industrial and medical uses. Examples include fungicides, protection colors, catalysts, ammunition igniters, dental products, disinfectants, etc. Special applications result from the property of mercury to form alloys called amalgams. These are used in gold mining and the chlor-alkali electrolysis. The toxic effect is based on the binding of mercury to thiol groups of enzymes and membrane proteins. Low-soluble mercury compounds (HgO, HgS) may be mobilized in the environment by microorganism to generate methyl mercury preferentially under anaerob conditions. Furthermore, mercury compounds accumulate in the food chain and can result in chronic diseases, especially neurological disorders. According to US EPA [1] power plants are obviously

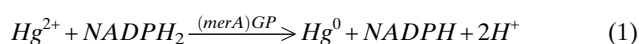
responsible for major mercury emissions which, via their accumulation in the food chain, result in neurological and cardiovascular problems for children.

2 Amalgam Process

The amalgam process of the chlor-alkali electrolysis is used worldwide by about 40 % for chlorine production (in 2000 approx. 26 mil. t). For every electrolysis cell producing in the range of 2000 to 4000 t/a chlorine 1 t of mercury (Hg) is required annually. In spite of many process improvements and recycle fluxes it is even in modern plants not possible to strictly avoid mercury emissions and contaminated wastewater. This water contains chlorine, chloride and some ppm mercury. The industrial discharge limit is 50 µg/L and is reached by the use of ion exchangers, but these are relatively expensive. On the basis of the Hg consumption of chlor-alkali electrolysis plants in Western Europe one can estimate a total loss of about 42 t of mercury in 2000 [2].

3 Microbial Mercury Resistance

Mercury is widespread in our environment. This is not only a result of anthropogenic activity but rather due to various geochemical and biological processes. Hence, a mercury resistance mechanism could develop during the evolution. This resistance mechanism is based on the reduction of Hg(II) compounds to metallic mercury being less toxic for microbial life (see Fig. 1). The transformation inside the microbial cell is a stoichiometric reaction that needs (biochemical reduction equivalents) NADPH₂:



The reaction is catalyzed by the product of the merA gene which is the enzyme mercuric reductase. Fig. 1 shows that the formation of proteins transporting Hg(II) through the inner

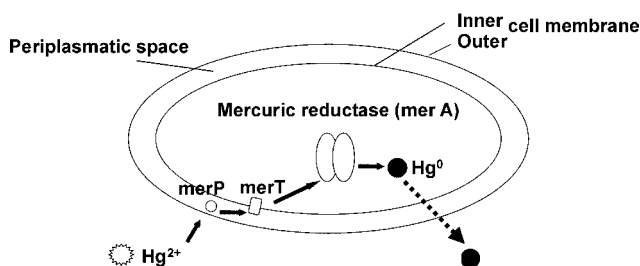


Figure 1. Principle of mercury resistance. Hg²⁺ ions are transferred with the help of transport proteins into the cell interior and reduced to metallic Hg⁰ by the biocatalyst mercuric reductase (the merA gene product, Eq. (1)).

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and outer cell membrane is also necessary (merP and merT products) and constitutes an essential part of the mercury resistance mechanism. The resistance is normally coded on a plasmid and hence easily transferable between microorganisms. This is the reason for its spreading in the microbial world. Accordingly, isolates can be obtained from many environments as, for instance, river sediments. Isolates usually exhibit metabolic activity and growth up to mercury concentration of 5 to 50 mg/L depending on other physiological conditions.

4 Kinetics of the Biotransformation

Measurements with intact and permeabilized cells under variation of the NADPH₂ concentration [3] indicated that the mercury biotransformation according to Eq. (1) is reaction-controlled. It is an ordered bireactant mechanism with substrate inhibition, while Hg(II) is an uncompetitive inhibitor and the reducing cofactor NADPH₂ a competitive inhibitor. The complete description of the enzyme kinetics in the cell interior can be done appropriately by the King-Altman method. The expression obtained can be simplified by anticipating that the NADPH₂ concentration is constant (either in surplus or in steady state). Thus, the following relation is generated:

$$v = \frac{v'_{\max} [Hg^{2+}]}{K_m + [Hg^{2+}] + [Hg^{2+}]^2 / K_i} \quad (2)$$

$$\text{with } K_{CF} = 1 + K_{m,CF} / [CF] \quad (3)$$

$$v'_{\max} = v_{\max} / K_{CF} \quad (4)$$

$$K_m = K_{m,Hg} (1 + [CF] / K_{i,CF}) / K_{CF} \quad (5)$$

$$K_i = K_{i,Hg} K_{CF} \quad (6)$$

whereas CF refers to the cofactor NADPH₂.

Fig. 2 shows experimental rate data of a genetically engineered microorganism as function of the external Hg(II) concentration by applying a stabilized assay [3–5]. As can be seen from Fig. 2, the data can be well described by Eq. (2). Particularly, a maximum is passed as expected from the rate law (Eq. (2)). One can assume that natural isolates having the mer resistance genes as well as the microorganisms used in the detoxification process described below exhibit the same general kinetic behavior as shown in Fig. 2. However, it is understood that the kinetic parameters involved in the rate law can hardly be predicted when using microbial consortia and wastewaters from the chlor-alkali electrolysis, both being subjected to large fluctuations under process conditions.

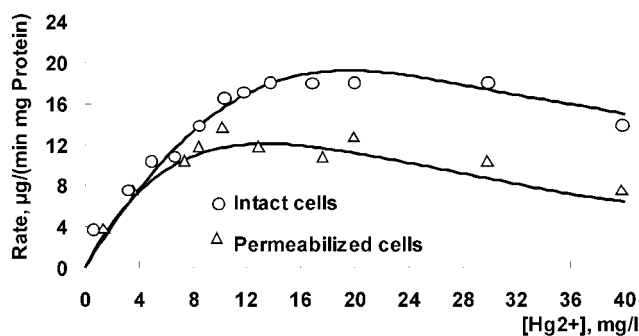


Figure 2. Reaction rate of the Hg biotransformation (Eq.(1)) with *Pseudomonas putida* KT 2442::mer73 in a stabilized assay (30 °C, pH 7, 1 mM BME, 1 mM NADPH₂) with permeabilized cells. The passing of a maximum rate as function of the substrate is characteristic of substrate inhibition.

For the technical development of a process for demercurization of wastewater the choice of a suitable bioreactor for carrying out the microbial Hg transformation plays an important role. Usually, the rate law supplies the appropriate information in this regard. In the present case of a substrate inhibition as to Eq. (2) a stirred tank followed by a plug flow reactor will be the optimal choice. However, for operating conditions with Hg(II) concentrations below the maximum value a continuous flow system without any back-mixing (i.e. plug flow) is the optimal reactor.

5 Process Requirements

The range of mercury concentrations in wastewater of chlor-alkali electrolysis plants varies from 1 to 10 mg Hg/L. In view of the kinetics and the reactor systems discussed above it is assumable that the mercury concentration of real wastewaters is in the first lower region of the kinetic law, e.g., below the maximum value of the rate. Hence, the plug flow reactor is the best choice. This requires that the microorganism performing the desired biotransformation must be stably and stationary fixed in the reactor. This can be obtained by immobilization or growth on a suitable support matrix. Therefore, the development of a microbial demercurization process for wastewater from a chlor-alkali electrolysis using the amalgam route requires a biomass which has to fulfill the following tasks:

- Provision of all enzymes and proteins of the mercury resistance mechanism (transport proteins plus mercury reductase) => action as biocatalyst
- Production of the cofactor NADPH₂ by metabolizing an available carbon source for the stoichiometric reaction according to Eq. (1)
- Microbial growth on a porous support of low cost (self-immobilization) and replacement of dead cells

The mentioned tasks and requirements must be performed by the biomass in real wastewater with varying salt loadings, temperatures, pH values and other stress conditions. Therefore, the biomass has to be supplied with oxygen and energy-

delivering substrates. Microbial consortia of high diversity, e.g., with the coexistence of many species, provide for an adaptation potential and high flexibility to successfully cope with the severe stress effects under industrial conditions. Additionally, it is necessary that the fixed-bed reactor is colonized uniformly with the biocatalyst. Thus, short-circuiting and dead zones clogging of the bed can be avoided and a uniform flow over the entire cross-sectional area of the bed is guaranteed. Additionally, the flow in the catalytic fixed bed has to remove excess biomass. However, the secreted metallic mercury which accumulates in the form of small droplets ($d \leq 12 \mu\text{m}$) must be retained in the fixed-bed reactor. Fig. 3 shows a REM micrograph with mercury droplets in the fixed bed, demonstrating the unique transformation capacity of the microorganism.

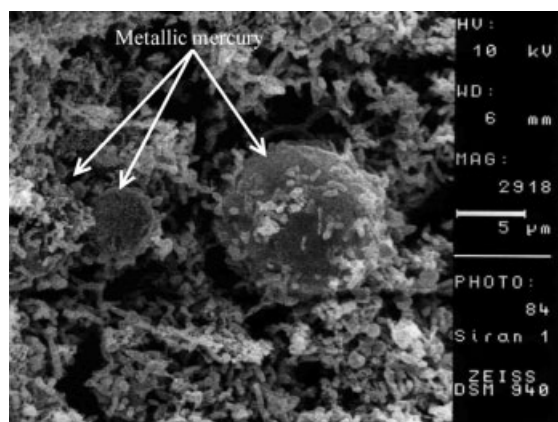


Figure 3. REM micrograph showing the deposition of metallic mercury in form of droplets within the biocatalytic fixed-bed reactor.

Of most importance for a process development for wastewater decontamination is to meet the legislative requirements, of course. This implies that the industrial discharge limit for mercury-contaminated wastewater is not exceeded. This value is $50 \mu\text{g Hg/L}$. Even if the fixed bed is long enough and a sufficient catalytic activity is provided and, therefore, a complete transformation as to Eq. (1) is achieved, a mercury concentration below the industrial discharge limit is still a critical point. This is due to the relatively high solubility of metallic mercury in water, as can be seen from the data given in Tab. 1 [5]. The solubility of elemental Hg strongly depends on temperature (solution enthalpy: 36.8 kJ/mol) and at 40°C – a normal operation temperature – there are $55 \mu\text{g Hg/L}$ dissolved. By adsorption of dissolved metallic Hg on biomass as well as complex formation (with proteins) the mercury load can be increased and, therefore, a subsequent activated carbon filter is necessary.

Table 1. Solubility of metallic Hg in water.

T, °C	10	26	40	46
Hg ⁰ , μg/L	13	26	55	67

6 Investigation in the Fixed-Bed Bioreactor

For the determination of appropriate design criteria of a technical plant studies were carried out in small-scale fixed bed bioreactors with $20, 80$ and 1000 cm^3 bed volume using different supports. Among others Siran ($1, 3$ and 5 mm), wood and cellulose compounds (Lignocell, Arbocell), lava slag and pumice granules were used as materials for the immobilization of microbial isolates from river sediments. In addition to a model wastewater, effluent streams from three European chlor-alkali plants being different in pH (2.4 to 13), Hg concentration (1.5 to $7.6 \text{ mg Hg}^{2+}/\text{L}$) and chloride content (up to 25 g/L) were applied [6]. By adjusting the pH to 7 and O_2 to above 5 to 8 mg/L at the inlet it was possible to reach in a 20 cm^3 reactor with space velocities of approx. 1 h^{-1} a mercury retention efficiency of $90\text{--}98 \%$ [6]. Similar results were also obtained in the 80 cm^3 and the 1 L fixed-bed reactors by using microbial communities under nonsterile conditions and increasing space loadings during long-term operation of several months.

7 Technical Plant

Within the frame of a 1997 EU R&D program (LIFE) demonstration projects including industrial partners were sponsored. This offered the possibility to design a larger plant together with an industrial partner (Preussag Wassertechnik) and to test the microbial potential for mercury decontamination in larger scale and under industrial conditions at the company ECI–Elektrochemie Ibbenbueren. Fig. 4 is a principal scheme of the plant. Before the wastewater from the chlor-alkali electrolysis enters the bioreactor, a pH adjustment to 7 of the chlorine-free wastewater in a three-

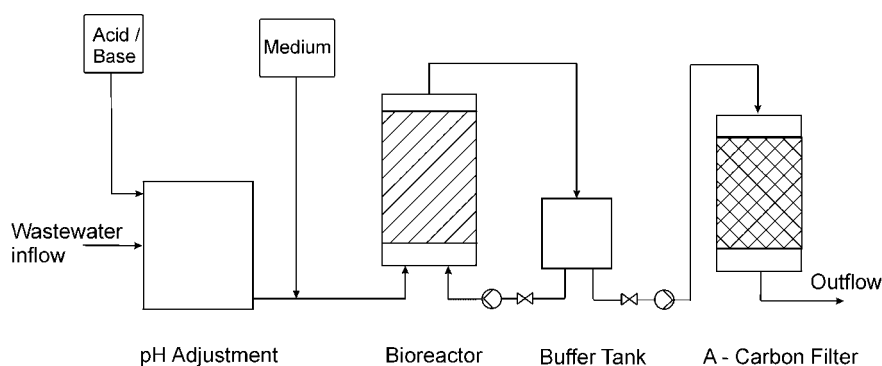


Figure 4. Schematic diagram of demercurization of wastewater from a chlor-alkali electrolysis plant.

chamber vessel (approx. 1.5 m³) is required. After the nutrient medium (approx. 50 mg/L saccharose and 10 mg/L yeast extract) was added, the bioreactor of 1 m in diameter was filled with 1 m³ pumice granules (4 to 6 mm, bed height 1.27 m). Here, the growth of immobilized microorganism and the decontamination reaction (Eq. (1)) takes place. The reactor exit flow enters a buffer tank which is followed by a downflow activated carbon filter (1 m³ with particles from 1 to 3 mm) to achieve the wastewater discharge limit of 50 µg Hg/L by adsorbing dissolved Hg⁰ and retaining suspended particles (biomass, mercury particles, etc.). The inoculation of the reactor was done with 7 subspecies of *Pseudomonas putida*, *stutzeri* and *fulva*. These are isolates from river sediments that were cultivated separately in 15 L stirred bioreactors and were mixed just before their use as inoculum of the fixed bed [7].

8 Operation Results

The plant at ECI was operated continuously over a time period of 8 months. Fig. 5 shows as an example the pH and Hg concentration over a time period of 2 weeks. The average temperature was 42 °C and the pH was adjusted to 7. The inflow volume was 0.7 m³/h at the beginning of the time slot in Fig. 5 and was increased 60 hours later to 2 m³/h. The Hg²⁺ concentration in the inflow fluctuated between 3 and some-

times more than 10 mg/L. If the concentration was higher than 10 mg/L, it was possible to run the plant in bypass mode. Aside from two mercury peaks between day 196 and 198 in Fig. 5 the maximum reactor outflow concentration was about 500 µg/L. In the average the mercury retention efficiency was roughly at 95 % [7]. The wastewater leaving the plant after the activated carbon filter has an average Hg concentration slightly below 50 µg/L. Hence, it is below the required discharge limit.

On the whole, the plant was not only able to deal with fluctuations of the Hg concentration (≤10 mg/L) but also maintained stable and safe operation at high salt loads and temperatures up to 47 °C. Even for interruptions of the water inflow up to 12 hours and the medium supply over several days the biological system was surprisingly robust and able to quickly return to normal operation with high mercury retention efficiency [7]. Indeed, the mercury decontamination process proved to possess a high degree of self-regularity and adjustability. It was operated for 8 months at the chlor-alkali electrolysis plant (ECI, Ibbenbueren) and was capable to demercurize up to 2 m³/h wastewater being approx. 50 % of the total wastewater of this plant. Over the whole time period a retention efficiency of 98 % was reached. The wastewater could be discharged directly into an on-site prefloder. A cost estimation revealed that the biological mercury decontamination plant is less expensive than an ion-exchanger system by around 50 % [7,8].

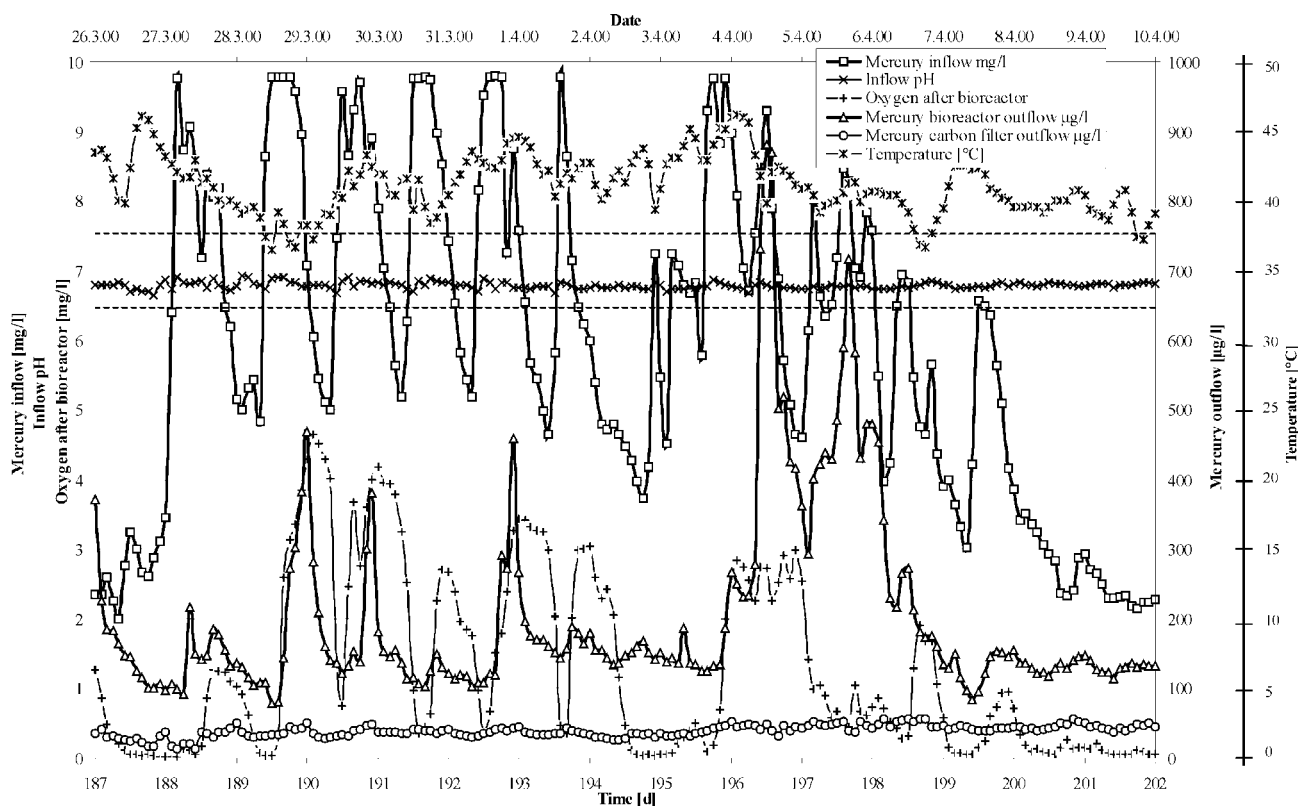


Figure 5. Time course of the mercury inlet and outlet concentrations as well as other operational parameters (time slot from operation days 187 to 202).

9 Perspective

The entire plant is highly automated and placed into a mobile container. Presently, the plant is in operation at a chlor-alkali electrolysis plant in the Czech Republic (Spolchemie, Usti nad Labem). Thus, additional experiences concerning the service time of the biocatalytic reactor as well as especially the regeneration including the separation of the mercury from the fixed bed will be collected. At the present operation the total volume of mercury-contaminated wastewater of this factory is successfully cleaned by the biological process. The results confirm the previous data and conclusions. Therefore, it appears timely and challenging to make use of the microbial mercury decontamination process also for other mercury-contaminated wastewater streams, e.g., from gold mining, soil remediation flue gas washing, the production of vaccines, etc.

Received: July 18, 2002 [K 2943]

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This paper was also published in German in Chem. Ing. Tech. **2002**, 74 (4), 504.

Product Recovery and Reduction of Wastewater Disposal Costs in a Detergent Production Facility

By Markus Forstmeier*, Bernd Goers, and Günter Wozny

In an applied research project in cooperation with industrial partners investigations have been made on the application of ultrafiltration and nanofiltration membrane processes for the separation of surfactants from Cleaning-in-Place (CIP) rinsing waters in a liquid detergent production plant. A membrane screening has been performed as well as pilot plant

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experiments. Chemical oxygen demand (COD) reductions in the wastewater of up to 96 % have been achieved resulting in less environmental impact and lower wastewater disposal costs. The final membrane plant design has been derived by MINLP optimization in consideration of economical aspects.

1 Problem

Modern multiproduct plants with flexible just-in-time production and batch processes have high demands on the related water management. In order to avoid cross-contamination, multiple product changes require intermediate rinsing of the entire plant accomplished by a two-step cleaning-in-place (CIP) system (hot tap water followed by deionized water). This type of system allows a cleaning process without the necessity for disassembling the plant and allows a central collection of the wastewater, but generates large product losses and highly loaded wastewater.

Case Study: Liquid Detergent Production Plant

In this case study with a liquid detergent manufacturer, the Henkel Genthin GmbH, the load mainly consists of surfactants causing a high COD load of up to 300 g/L. Additional components are dyes, ethyl alcohol, glycerol, silicone-based antifoam agents and perfumes. Together with the corresponding amounts of deionized water utilized in the cleaning process this procedure results in high extra expenses and avoidable environmental impact.

Due to its high COD load the hot water CIP cleaning step causes 70 per cent of the total wastewater disposal costs though it is less than one third of the wastewater volume. Therefore a separate treatment of this stream seems appropriate.

Based on the promising results achieved in former research projects on CIP water management and surfactant separation by means of membrane processes published in [1] now in cooperation with Henkel Genthin GmbH and Enviro-Chemie GmbH the potential application of ultra- and nanofiltration has been investigated. It has been aimed to recover resources and process water as well as to reduce the high COD load of the rinsing waters which is the decisive parameter for the high wastewater fees raised by the disposal enterprise.

2 Analysis of the General Conditions

For the optimization of the Henkel Genthin water network the systematic approach of the Concept for Retrofit Optimization of Water Networks (CROWN) has been applied [4]. Initially the general conditions on the production site have been analyzed including legal, economical, technical and logistic aspects. Furthermore, the water network of the entire plant has been balanced as far as water flow rate and COD load are concerned. Fig. 1 shows a Sankey diagram of the