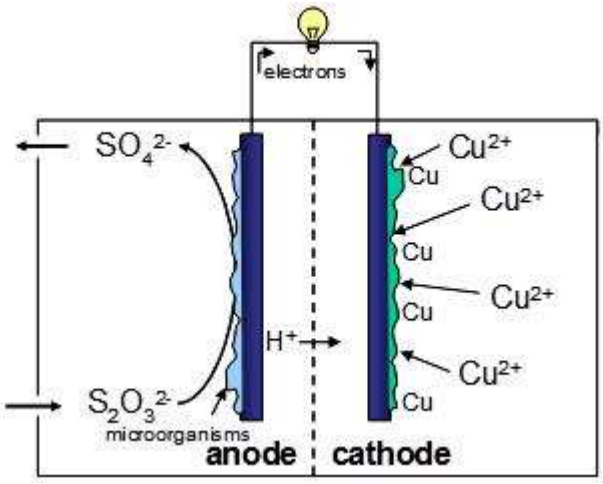
Publishable summary

Project context & objectives

BioElectroMET is a collaborative research project between Magneto special anodes (NL), MAST Carbon International ltd (UK), Centre de Recherche Public Henri Tudor (Lux), Universitat Jaume I (ES), Linnaeus University (SE), Tampere University of Technology (FI) and Wetsus, centre of excellence for sustainable water technology (NL). The project is funded by Europe's 7th Framework Programme and is coordinated by Wetsus. BioElectroMET will investigate, develop and demonstrate a bioelectrochemical system capable of recovering metals from metallurgical waste and process streams with no or limited energy input.

Concept

In BioElectroMET the oxidation of a biodegradable electron donor at the bioanode is coupled to the reduction of dissolved metals, present in waste or process streams, at the cathode. Subsequently the electrodeposited metal can recovered in pure elemental form from the cathode, similar to electroplating. Thiosulfate might be a suitable substrate for the bioanode, is it can donate 8 electrons, is biodegradable and occurs in leachates produced during hydrometallurgical mineral processes.



Objectives

BioElectroMET aims to achieve sustainable production, recovery, and removal of metals from metallurgical waste and process streams using bioelectrochemical systems. Four objectives of BioElectroMET are:

- To design a device that can efficiently recover copper (>99% of recovery) and other metals from both high (>1g/L) and low (<100mg/L) concentrated process and waste streams.

- To build a bioelectrochemical device which can selectively produce, recover, and remediate metals from mixed metal streams (>90% selectivity).
- To demonstrate bioelectrochemical metal recovery on-site at mining or metallurgical plants.
- To show that this device is economically and environmentally attractive compared to current technologies.

Work performed and main results achieved

During the BioElectroMET project the consortium has focussed on the different tasks described in the work plan. The main results are summarized here.

Search for alternative electron donors

In the original concept acetate has been used as electron donor. If the BioElectroMET concept will be applied in practice, which is the main goal of the proposal, an alternative electron donor has to be found. Together with end users, an inventory has been made of possible interesting streams. Looking at the composition of these streams an analysis was made of possible substrates but also to possible inhibitors. From these possibilities tetrathionate was selected as an interesting electron donor. In WP 1 and 2 it was shown that indeed tetrathionate can be used to supply electrons to a solid electrode. Despite several strategies that have been tested to increase the current density, the removal rate is still low and the energy level is so far insufficient to be able to recover copper at the cathode.

Another electron donor that has been investigated is hydrogen gas, which is in some cases a waste product of the metallurgical industry. We have shown that hydrogen can be used directly by microorganisms to produce energy and recover copper simultaneously.

Testing of electrode materials

For the anode a cheap, electrical conductive and biocompatible material is required as an electron acceptor. To increase the electron transfer, the hydrophobicity of the electrode material can be changed, but also several catalysts can help to accelerate the reaction at the anode.

Both methods have been tested for their suitability in the concept. Depending on the electron donor and the nature of the oxidation reaction at the electrode options have been identified to use as anode material.

For the cathode also a cheap material is required, preferably with a high specific surface. Because a product is formed at the cathode, the removal of the cathode and reuse or replacement of the electrode is important. Stainless steel, carbon and copper have been tested as suitable substrate for copper deposition. Stainless steel has been identified as the most

suitable substrate while copper still has the advantage that the entire electrode can be processed as a product.

Mathematical modelling

To fully understand the process and its limitations a mathematical model has been constructed. The model is based on Electrochemical Impedance Spectroscopy (EIS). EIS is a powerful tool to identify limitations in an electrochemical process. To do this analysis, measurements were performed of every part of the process separately, expending the range of the measurements stepwise to more complex parts of the system. Measurements include anode, cathode and membrane measurements. Surprisingly, mass transfer was identified as the most important limiting parameter in every part of the process. In the design of the up scaled device this is valuable information, which led for example to integrate gas sparing in both compartments to enhance the mass transfer.

System integration and up scaled design

The first step for upscaling of the process was to show that it was possible to produce high current densities. Through improvements of the system known form previous research on MFCs the current generation was increased from 5 to 21 A/m^2. Consequently also the power production increased, here to almost 8 W/m^2.

All the generated knowledge was used to construct an up-scaled device of 1 m^2 electrode material. After an inventory of electrochemical devices and a thorough look at the design criteria of the BioElectroMET process a tank cell was chosen as the most suitable design for upscaling.

All equipment for this up-scaled design has been bought, installed and is now being tested. First a hydrodynamic characterisation was made after which the system was inoculated. The system should be able to produce 6 A/m^2 as stable current. The up-scaled device will first be tested with artificial streams (electron donor and acceptor) after which more complex and realistic streams will be used.

Environment and economic analysis

The net benefit of replacing the current cementation process to remove Cu^{2+} from raw zinc sulphate liquor of a copper refinery, with the BioElectroMET process was estimated. The Capex were calculated from the actual costs to build the 1m^2 up-scaled prototype, these were 48 000€. At a current density of 15 A/m^2 and a Coulombic efficiency of 90%, the copper recovery rate will be 384 g Cu° per day. Per kg Cu° the Capex are therefore 78 €/kg. The technology would cost around 27.6 €/day (loss instead of benefit). Other scenarios have been studied for the developed technology to be applied; application could still be economical in the

recovery of rare earth metals which have a higher specific value. Overall, the main benefit of the technology is the positive environmental impact it has.

Dissemination of the project

The project was widely disseminated through different initiatives of the partners covering a broad audience from the scientific specialists to the public at large. This was achieved through communications in peer reviewed journals but also conferences and workshops with end users. A highlight was the workshop at the end of the project which attracted numerous participants from different backgrounds. An overview of the dissemination activities can be found on the project website: www.bioelectromet.eu.

Expected final results and their potential impact and use

The expected final results of BioElectroMET include a model, cell design, operational protocols and working prototypes of bioelectrochemical systems for the removal and selective recovery of metals from process and waste streams.

Model

To fully understand the process and its limitations a mathematical model has been constructed. The model is based on Electrochemical Impedance Spectroscopy (EIS). EIS is a powerful tool to identify limitations in an electrochemical process. To do this analysis, measurements were performed of every part of the process separately, expending the range of the measurements stepwise to more complex parts of the system. Measurements include anode, cathode and membrane measurements. Surprisingly, mass transfer was identified as the most important limiting parameter in every part of the process. In the design of the up scaled device this is valuable information, which led for example to integrate gas sparing in both compartments to enhance the mass transfer.

Operational conditions

In the original concept acetate has been used as electron donor. If the BioElectroMET concept will be applied in practice, which was the main goal of the proposal, an alternative electron donor needed to be found. Together with end users, an inventory has been made of possible interesting streams. Looking at the composition of these streams an analysis was made of possible substrates but also to possible inhibitors. From these possibilities tetrathionate was selected as an interesting electron donor. It was shown that indeed tetrathionate can be used to supply electrons to a solid electrode. Despite several strategies that have been tested to increase the current density, the removal rate is still low and the energy level is so far insufficient to be able to recover copper at the cathode.

Another electron donor that has been investigated is hydrogen gas, which is in some cases a waste product of the metallurgical industry. We have shown that hydrogen can be used directly by microorganisms to produce energy and recover copper simultaneously.

Working prototype

The first step for upscaling of the process was to show that it was possible to produce high current densities. Through improvements of the system known form previous research on MFCs the current generation was increased from 5 to 21 A/m^2. Consequently also the power production increased, here to almost 8 W/m^2.

All the generated knowledge was used to construct an up-scaled device of 1 m^2 electrode material. After an inventory of electrochemical devices and a thorough look at the design criteria of the BioElectroMET process a tank cell was chosen as the most suitable design for upscaling.

First a hydrodynamic characterisation was made after which the system was inoculated. From these hydrodynamic test a protocol was set-up for operation of the scaled-up device. Unfortunately, construction and start-up of the device took more time than originally planned. Therefore, the up-scaled device will be tested after the project period first with artificial streams (electron donor and acceptor) after which more complex and realistic streams will be used.

Already, extensive new insights were gained on how to construct and operate an up scaled bioelectrochemical device. This knowledge is highly valuable for future application of devices of this type.

Expected impact

Bioelectrochemistry produces a net energy gain as the technology can utilise the chemical energy in wastewaters. Conventional electrowinning of copper at a cathode is completed to water disassociation at the anode (to form O_2) and consumes 2 kWh/kg Cu. Copper electrolysis in an MFC potentially generates approximately 0.5 kWh/k Cu (corresponding to a CO_2 reduction of ≈ 1.2 kg CO_2/kg Cu).

We have shown in this project that this new method to recover copper can be achieved at high rate (~20A/m^2) and power production (~8W/m^2) at lab scale.

An up scaled device was designed and constructed and many valuable lessons were learned during this process. These lessons were shared with an international community of scientists and industry in a final workshop so they can be applied to design of future scaled up bioelectrochemical systems.

New substrates have been tested and shown to be suitable for bioelectrochemical devices to be used as electron donor. Furthermore, the oxidation of these (partly) reduced organic or

inorganic compounds in wastewaters at the anode, like tetratithionate, decreases the requirement to supply oxidising agents (oxygen or peroxide) to treat these wastewaters.

A direct benefit of applying bioelectrochemistry to these waste streams is that metals can be recovered from waste streams as alternative for unselective precipitation. This reduces the production of heavy metal rich solid wastes, and thus eliminate the risk of future contamination that affects vegetation, fish farming, rivers, agriculture and recreation. In addition, metal recovery increases the ore to product ratio.

An environment and economic analysis of the system in an early stage showed that application of a bioelectrochemical system for the removal of metals from a waste stream in the metallurgical industry requires too high investment costs. The net benefit of replacing the current cementation process to remove Cu^{2+} from raw zinc sulphate liquor of a copper refinery, with the BioElectroMET process was estimated. The Capex were calculated from the actual costs to build the $1m^2$ up-scaled prototype, these were 48 000€. At a current density of 15 A/m^2 and a Coulombic efficiency of 90%, the copper recovery rate will be 384 g Cu° per day. Per kg Cu° the Capex are therefore 78 €/kg. The technology would cost around 27.6 €/day (loss instead of benefit).
Nice application were investigated to be able to apply the BioElectroMET technology to. Other scenarios have been studied for the developed technology to be applied; application could still be economical in the recovery of rare earth metals which have a higher specific value. Overall, the main benefit of the technology is the positive environmental impact it has which, unfortunately, cannot be expressed in economic value.