

Versatile Bioelectrochemical system for heavy metals removal

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Abstract. Industrial activity has resulted in heavy metals anthropogenic contamination of groundwater, especially in industrial or mining areas. Bioelectrochemical systems (BES) can be used for metals removal and recovery from aqueous solutions. In the framework of GREENER project, double-chamber BES have been adopted to treat groundwater from industrial sites containing copper, nickel and zinc (Cu, Ni and Zn), among other contaminants. Two operation modes, (i) short-circuited microbial fuel cell (MFC), and (ii) power supply driven microbial electrolysis cell (MEC, poisoning the cathode at -0.4 V vs. Ag/AgCl), were studied for metals removal at lab-scale. Two control reactors were run to evaluate metals adsorption on cathodes and membranes, and the effect of anolyte composition. Synthetic water containing different concentrations of Cu, Ni and Zn were treated, and metals removal pathways were studied. MEC and MFC performed similarly and the highest removal efficiencies were $97.1 \pm 3.6\%$, $50.7 \pm 6\%$ and 74.5% for Cu, Ni and Zn respectively, from initial concentrations in the range of 1.1-1.5 mM.

1 Introduction

Heavy metals contamination in groundwaters, especially in industrial or mining areas, is a global concern for environment and human health. It is mandatory to answer this situation by stopping the anthropogenic contamination but also developing new cost-effective and low energy-demand techniques to treat already contaminated aquifers. Bioelectrochemical systems (BES) are within the promising technologies to tackle the challenge. BES technologies are capable to remove (and recover) metals from aqueous streams, reducing the energy and reagents consumption compared to traditional remediation processes [1].

Different bioelectrochemical reactor architectures have been described in literature, to this purpose. Double-chamber reactors with abiotic cathodes have been used to remove and recovery a wide range of different target metals ([2], [3] [4]).

Abiotic cathode removal strategies are mainly based on three pathways: (i) direct electrochemical reduction (DR) of ionic metals such as Cu(II), Pb(II), Hg(II) or Cd (II), which is the most widely reported removal pathway in BES; (ii) indirect by-product precipitation (IBP) where the cathodic reduction by-products such as OH⁻, H₂O₂, and sulphide are the responsible of metal precipitation as in [5] and [6]; (iii) metal ion migration, where the electrons are the driving force for metallic ions movement through the ion exchange membrane. Thus, metallic ions can be separated from the polluted stream and later recovered by direct reduction or precipitation like in [2]. One important limitation of DR, from the water treatment point of view, is the low reduction potential of some metallic ions what could result in a higher energetic cost of the treatment. For this reason, to

design an approach capable to efficiently combine the explained removal pathways could led to a sustainable integrated solution.

In BES, the cathode architecture and operation (together with the catholyte composition) defines the reduction reactions. An air-cathode reduces atmospheric oxygen to water, consuming protons from the solution, i.e., basifying the catholyte. Thus, the use of an air-cathode under specific operational conditions could lead to the removal of metals by both DR and IBP.

This work aims to study the removal of copper, nickel and zinc from groundwaters by using a double-chamber, air-cathode BES reactor that pretend to take benefit of DR and IBP simultaneously to find an efficient and low-energy method for groundwater treatment.

2 Materials & Methods

2.1 Experimental Setup

Six double chamber reactors were designed and constructed. Anionic exchange membranes (AMI-7001, Membrane International) were placed between anodic and cathodic chambers. Planar anodes were made of 25 cm² of battery grade carbon felt (Sigracell® KFD2.5, SGL Carbon GmbH, Meitingen, Germany). The cathodes material was unidirectional carbon fiber non-crimp fabric (Sigratex® C U200, SGL Technologies GmbH, Meitingen, Germany) with 2 mg/cm² of PMF-011904 catalyst from Pajarito Powder with 25cm² of surface. Tyvek® textile (Dupont) was placed on the external side of cathodes acting as water impermeable layer and air diffusion membrane. Stainless-steel current collectors

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were used in both anodes and cathodes, to ensure a uniform electron harvesting and distribution. The anodes' inoculation was done in single chamber reactors with three electrodes configuration, applying different potential steps in several cycles from -0.050 to -0.350 V vs Ag/AgCl. The biomass used for the inoculation was a mixed culture coming from the outflow of an operating MFC. During the inoculation reactors were fed with acetate based mineral media (ABMM) containing 2.5g /L of NaCH₃COO, 8.3g/L of NaHCO₃, 128mg/L of K₂HPO₄, 49.5mg/L of NH₄Cl, 15.3mg/L of Mg₂SO₄, 13.6 mg/L of CaCl₂, trace elements and Wolfe vitamins.

2.2 Experimental design and operation

Reactors were operated in batch recirculating the electrolytes to external buffer tanks. Thus, 0.5L ABMM were used as anolyte in metals removal experiments. The catholyte was 1L of 1.1 mM CuSO₄(H₂O)₅ solution in the first bench of experiments, 1L of 1.1 mM of NiSO₄(H₂O)₆ solution in the second and 1L of 1.6 mM of ZnSO₄(H₂O)₇ solution in the third bench of experiments.

In metals removal experiments, the reactors were operated in replicate: two control reactors, two MFCs operated under short-circuit condition ($E_{cell}=0V$) and two MECs, poisoning the cathode at -0.4V vs Ag/AgCl. The control reactors were abiotic and fed with two different anolytes: ABMM (OCV_{Ac}) and NaCl solution at the same conductivity of ABMM. The electric data were collected by means of a VMP3 potentiostat (BioLogic).

2.3 Analysis and Calculations

For the anolytes, liquid samples were taken at the beginning and the end of the experiment. The pH and electric conductivity were measured with HQ40D multi-meter (Hach Lange) with probes intelicall® PHC101 and intelicall® CDC401 respectively. Chemical Oxygen Demand (COD) was analysed using Hach Lange LCK kits. For the catholytes, liquid samples were taken at each sampling time and metals concentration determination was done by ICP-MS analysis (ICPMS Agilent 7500). Also, electric conductivity and pH were monitored every 24h.

The removal efficiency of metals and was calculated with the following equation, where C_0 represents the initial and C_F the final metal concentration.

$$R_{EF} = \frac{C_0 - C_F}{C_0}$$

Removal rate (RR) represent the removal per time and catholyte volume unit, and is calculated as follows:

$$R_R = \frac{\Delta C_M \times V}{Q \cdot t}$$

Where ΔC_M is the change of metal concentration in the catholytes ($g \cdot m^{-3}$); V , the catholyte volume in m^3 ; representing, the product $\Delta C_M \times V$, the mass of metals removed; Q operating in batch mode is equivalent to the catholyte volume in m^3 ; and t , the experiment time in days.

Current density (j) represents the electron flowrate, i.e., averaged current (I in Amperes), per electrode surface unit (A in m^2) and is calculated with the following equation:

$$j = \frac{I}{A_m}$$

The Cathode coulombic efficiency (CE_{cat}) represents the fraction of electrons, i.e., the circulated charge, eventually involved in the metal removal and is calculated as follows:

$$CE_{cat} = \frac{F \times n \times V_{cat} \times \Delta C_M}{M_M \times \int Idt}$$

Where F is Faraday constant, n is the molar number of electrons required for metal reduction ($mol \cdot mol^{-1}$), V_{CAT} is the catholyte volume (L), ΔC_M is the change of metal concentration in the catholytes ($g \cdot L^{-1}$), M_M is the molar mass of the removed metal ion ($g \cdot mol^{-1}$).

3 Results

3.1 Copper removal experiments

Bioelectrochemical reactors successfully treated synthetic water containing 1.1mM Cu, as can be observed in Figure 1. At 24h, MEC removed $97.1 \pm 3.6\%$ of Cu and MFC, a $88.1 \pm 5.5\%$, with Cu removal rates of $64.1 \pm 2.1 g \cdot d^{-1} \cdot m^{-3}$ and $53.3 \pm 0.35 g \cdot d^{-1} \cdot m^{-3}$, respectively. These Cu removal rates are below the average values of previous studies, as $218 g \cdot d^{-1} \cdot m^{-3}$, $504 g \cdot d^{-1} \cdot m^{-3}$ and $7.92 g \cdot d^{-1} \cdot m^{-3}$ were achieved in [7], [8] and [2], respectively. Regarding the current densities, MEC reactors reached $0.109 \pm 0.038 A/m^2$ while MFC ones $0.078 \pm 0.027 A/m^2$, with CE_{cat} of $45 \pm 16\%$ and $58 \pm 24\%$ respectively. Therefore, from an efficiency and sustainability point of view MFC operation would be more appropriate for copper removal. At 24 h, the control OCV-Ac removed 45% of copper with a removal rate of $12 g \cdot Cu \cdot m^{-3} \cdot d^{-1}$, while the control OCV-Na had no quantifiable removal. After 48 h of treatment, the control OCV-Ac removed almost the same copper than BES reactors (95% OCV-Na vs $98 - >99\%$ BES). OCV-Na removal was still unquantifiable. This demonstrates that the composition of the anolyte is playing a role in the copper removal, in the absence of electrical field. Anions present in the ABMM anolyte could cross the anionic exchange membrane, by concentration gradient, having as a result the copper removal by precipitate formation. In bioelectroactive reactors, both MEC and MFC, the electrical field generated between the electrodes led to an ion migration force opposed to the concentration gradient. Thus, the effect of the anolyte is expected to be lower in the bioelectrochemical reactors, but it was not quantified.

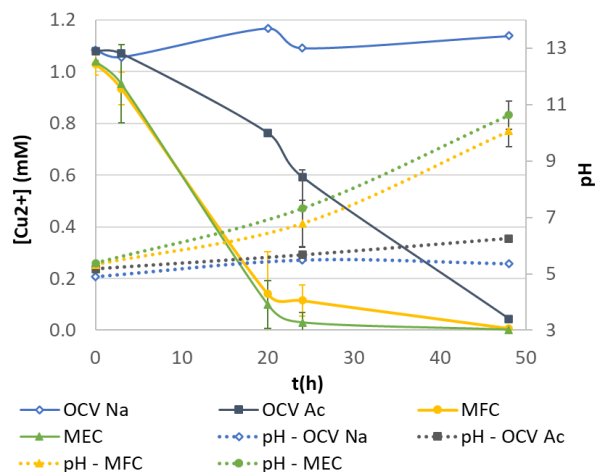


Fig. 1. Copper concentration and pH evolution of catholyte, under different operation modes

Figure 1 also shows that pH increased during the whole experiment, in all cases except in OCV-NaCl. Moreover, in MEC and MFC reactors, after the removal of most of copper, the pH curve slope increased, indicating higher hydroxide ions production in the catholyte. This can be attributed to the lack of electrons consumption in the direct reduction of copper resulting in a higher rate of catholyte basifying reactions, and, to the lack of OH⁻ ions consumption to form metallic hydroxide precipitates. During the experiments, precipitate formation was observed in the buffer tanks of MEC, MFC and in lower measure in OCV-Na. After the experiments the reactors were opened, and precipitates were observed also in the cathode chamber and in the AEM surface. Cu⁰ colored deposits were observed in the cathode surface of MEC and MFC reactors, suggesting that the copper removal was carried out by both DR and IBP, as it was expected given the high standard reduction potential of copper (0.06V vs Ag/AgCl).

3.2 Nickel removal experiments

Figure 2 shows similar trend between MEC and MFC in terms of nickel removal. MFC had higher averaged value of removal efficiency but there is no statistical significance due to the variations among replicates. After 48h of operation, facing an initial nickel concentration of 1.1mM, bioelectrochemical reactors achieved a removal efficiency of $41.0 \pm 12.3\%$ in MEC and $50.7 \pm 6.23\%$ in MFC removing $13.1 \pm 3.5 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-3}$ and $17.4 \pm 1.6 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-3}$ of Ni, respectively. The nickel concentration curves of OCV-Ac and OCV-Na reactors had more similar behaviour in this case. After 48h the removal efficiencies accounted for 4.6% and 7.9%, respectively, indicating that the effect of the anolyte in Ni removal was significantly lower compared to Cu removal experiments.

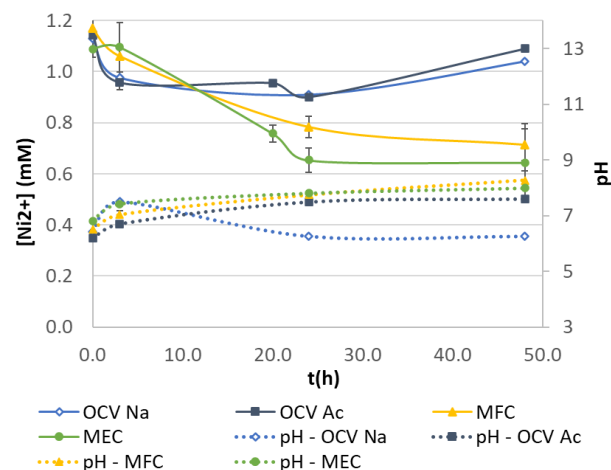


Fig. 2. Nickel concentration and pH evolution of catholyte, under different operation modes

The current density was $0.08 \pm 0.03 \text{ A}/\text{m}^2$ in MEC and $0.04 \pm 0.01 \text{ A}/\text{m}^2$ in MFC and the CE_{cat} was $30.7 \pm 20.82\%$ and $73.87 \pm 19.5\%$ respectively. With less than 1/3 of electric conductivity compared with copper experiments, current density decreased 26% in MEC and 48% in MFC. However, MEC CE_{cat} was 15% lower in nickel experiments, but MFC CE_{cat} was 15% higher. The lower current density, in this case, could have an effect in the Ni removal efficiency and Ni removal rate, as the current density is the main driving force for the metal's removal in all expected pathways. Hence, it also had an effect in the pH evolution, compared with copper experiments. The final pH was 7.99 ± 0.17 , 8.27 ± 0.34 , 7.61 and 6.26 in MEC, MFC, OCV-Ac and OCV-Na, respectively. In this case, the BES (MEC and MFC) and the OCV-Ac control pH curves had a behaviour more similar between them than in the copper case, pointing that most of the hydroxide molecules produced in the reduction reactions were consumed in the nickel precipitation, still after 48h of operation.

Previous studies have reported the bioelectrochemical removal of nickel by direct reduction in MEC with similar initial concentration achieving a removal efficiency around 99% with a Ni removal rate of $118.8 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-3}$ [4]. Also, higher Ni concentration in acid mine drainage synthetic solution have been reported using BES in MEC and achieving an 87% of removal efficiency with a Ni removal rate of $282 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-3}$ [9]. Even though no previous works have been found for nickel removal by precipitation in the catholyte using BES, the bioelectrochemical induced precipitation has been described before as a potential mechanism for Nickel separation in BES [10]. Ni(OH)₂ or NiCO₃ precipitation needs a high pH to take place [10] and this could be more challenging for BES compared to the removal of other metals by precipitation. However, after the experiments the reactors were opened and green and white precipitates were observed in the cathode surface and in the cathode chamber of both MEC and MFC, but not in OCV-Na nor OCV-Ac cases. That fact suggests that the local pH

conditions of the catholyte surroundings were high enough to result in the Ni removal by precipitation.

3.3 Zinc removal experiments

Figure 3 shows that Zn can be removed using BES. After 48h, MEC achieved a removal efficiency of 73.17% and MFC 74.49% with Zn removal rates of $40.25 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-3}$ and $39.03 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-3}$, respectively. The current density achieved was $0.032 \text{ A}/\text{m}^2$ in MEC and $0.031 \text{ A}/\text{m}^2$ in MFC with CE_{cat} of 169.7% and 174.2%. This indicates that at least 31.1% (MEC) and 30.6% (MFC) of Zn removal efficiency was not driven by electrochemical processes. These results match with the removal efficiency achieved by the control OCV-Ac which accounted for 28.7% with a Zn removal rate of $15 \text{ g}\cdot\text{d}^{-1}\cdot\text{m}^{-3}$ suggesting that the effect of the anolyte in the zinc removal efficiency could be the same under the effect of the electrical field. The control OCV-Na positioned the zinc removal efficiency baseline due to the reactor design and materials at 10.24%.

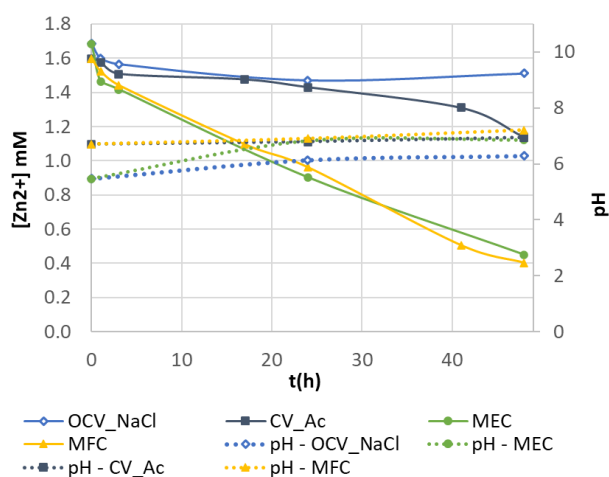


Fig. 3. Zinc concentration and pH evolution of catholyte, under different operation modes.

At the end of the experiments, when the reactors were opened, white precipitate was observed in the cathode surface and settled in the cathodic chamber. Also, a small amount of precipitate was observed in the bottom of the buffer tanks and in the AEM surface, like in copper removal experiments, where OCV-Ac had a role too in the metal's removal. Hence, IBP is a functional removal pathway for Zn with the adopted integrated metals removal approach, at least, when the initial pH is higher than 5.5.

BES for DR of Zn has been reported before in MEC as in [3] were 71.9% of removal efficiency was reached treating synthetic water with an initial concentration of 285 mg/L of Zn. Few works have reported before the bioelectrochemical zinc removal with O_2 reduction as the main cathodic reaction. In [11] 96% of removal

efficiency was reached in MFC reactors treating synthetic water with a removal rate of $135.5 \text{ g}\cdot\text{Zn}\cdot\text{d}^{-1}\cdot\text{m}^{-3}$. In this case the removal of controls was 52%. Other studies like [12] reported also relevant Zn removal in control reactors (52.1%). It is worth mentioning that the membranes used as chambers separator, in both cases, were anionic exchange membranes and the anolytes were mineral mediums containing acetate, like in the present study. These high removal in controls results would coincide with the anolyte effect demonstrated in the present work.

4 Conclusions

The experiments carried out demonstrated that the tested reactor design is capable to remove Cu, Ni and Zn under different electrochemical operation modes. Depending on the operational conditions, different removal rates could be achieved. DR evidence was found only in Cu removal experiments, while IBP evidences were found in all experiments (Cu, Ni and Zn) confirming the versatility of the bioelectrochemical reactor. It is worth to mention that in most of the experiments there was no significant differences in terms of removal efficiency between MEC and MFC. As MFC is spontaneous and produces electricity, instead of consuming it like MEC, it becomes an interesting low-energy operation mode for metals removal under the studied operational conditions. Moreover, MFC, which in most of cases reached lower current density, usually led to higher CE_{cat} . Thus, a higher current density does not necessarily imply a greater removal efficiency. This suggests that other limitations would be acting as the concentration gradient between the electrode surface and the bulk solution (e.g. mass transport limitations). The effect of the composition of the anolyte has been demonstrated to be relevant in terms of metals removal performance when an anionic exchange membrane is separating electrolytes in BES reactors.

These first trials proved the feasibility of the reactors to remove metals from polluted waters and paved the way for the next step, treating polluted groundwaters from industrial sites.

5 References

- [1] Dominguez-Benetton, X., Varia, J.C., Pozo, G., Modin, O., Ter Heijne, A., Fransaeer, J., Rabaey, K., 2018. Metal recovery by microbial electro-metallurgy. *Progress in Materials Science* **94**, 435–461. <https://doi.org/10.1016/j.pmatsci.2018.01.007>
- [2] Jiang, Q., Song, X., Liu, J., Shao, Y., He, W., Feng, Y., 2020. In-situ enrichment and removal of Cu(II) and Cd(II) from low-strength wastewater by a novel microbial metals enrichment and recovery cell (MMERC). *Journal of Power Sources* **451**, 227627. <https://doi.org/10.1016/j.jpowsour.2019.227627>
- [3] Modin, O., Fuad, N., Rauch, S., 2017. Microbial electrochemical recovery of zinc. *Electrochimica Acta*

- 248**, 58–63.
<https://doi.org/10.1016/j.electacta.2017.07.120>
- [4] Qin, B., Luo, H., Liu, G., Zhang, R., Chen, S., Hou, Y., Luo, Y., 2012. Nickel ion removal from wastewater using the microbial electrolysis cell. *Bioresource Technology* **121**, 458–461.
<https://doi.org/10.1016/j.biortech.2012.06.068>
- [5] Song, X., Yang, W., Lin, Z., Huang, L., Quan, X., 2019. A loop of catholyte effluent feeding to bioanodes for complete recovery of Sn, Fe, and Cu with simultaneous treatment of the co-present organics in microbial fuel cells. *Science of The Total Environment* **651**, 1698–1708.
- [6] Wang, Q., Huang, L., Quan, X., Zhao, Q., 2017. Preferable utilization of in-situ produced H₂O₂ rather than externally added for efficient deposition of tungsten and molybdenum in microbial fuel cells. *Electrochimica Acta* **247**, 880–890.
<https://doi.org/10.1016/j.electacta.2017.07.079>
- [7] Heijne, A.T., Liu, F., Weijden, R. van der, Weijma, J., Buisman, C.J.N., Hamelers, H.V.M., 2010. Copper Recovery Combined with Electricity Production in a Microbial Fuel Cell. *Environ. Sci. Technol.* **44**, 4376–4381. <https://doi.org/10.1021/es100526g>
- [8] Luo, H., Qin, B., Liu, G., Zhang, R., Tang, Y., Hou, Y., 2015. Selective recovery of Cu²⁺ and Ni²⁺ from wastewater using bioelectrochemical system. *Front. Environ. Sci. Eng.* **9**, 522–527.
<https://doi.org/10.1007/s11783-014-0633-5>
- [9] Luo, H., Liu, G., Zhang, R., Bai, Y., Fu, S., Hou, Y., 2014. Heavy metal recovery combined with H₂ production from artificial acid mine drainage using the microbial electrolysis cell. *Journal of Hazardous Materials* **270**, 153–159.
- [10] Hui Guo, Y.K., 2019. Mechanisms of Heavy Metal Separation in Bioelectrochemical Systems and Relative Significance of Precipitation, in: *Microbial Electrochemical Technologies*. pp. 128–144.
- [11] Lim, S.S., Fontmorin, J.-M., Pham, H.T., Milner, E., Abdul, P.M., Scott, K., Head, I., Yu, E.H., 2021. Zinc removal and recovery from industrial wastewater with a microbial fuel cell: Experimental investigation and theoretical prediction. *Science of The Total Environment* **776**, 145934.
<https://doi.org/10.1016/j.scitotenv.2021.145934>
- [12] Wang, X., Li, J., Wang, Z., Tursun, H., Liu, R., Gao, Y., Li, Y., 2016. Increasing the recovery of heavy metal ions using two microbial fuel cells operating in parallel with no power output. *Environ Sci Pollut Res* **23**, 20368–20377. <https://doi.org/10.1007/s11356-016-7045-y>