

Bioelectrochemical Treatment of Contaminated Groundwater

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Water contamination is a worldwide environmental challenge. Consumption of water containing high nitrate, sulphate or Chlorinated Aliphatic Hydrocarbons (CAHs) levels as drinking water can cause many diseases (i.e. cancer, skin irritation, an increased risk of respiratory tract infections and goiter development in children). Both the Water Framework Directive (2000/60/EC) and the Groundwater Directive (2006/118/EC) consider these pollutants the main threats to water quality, requiring urgent and intensive monitoring and strong policies.

To remove these pollutants from groundwater, different technologies can be used. Currently, the Environmental Protection Agency (EPA) considers ion exchange, reverse osmosis and reverse electrodialysis to be effective methods for the decrease of their concentrations, below their limit in drinking water. These technologies have some drawbacks, such as low selectivity towards the target pollutant, high energy or chemicals requirements, and the generation of waste brine (pollutants are separated from water, not treated), which require an additional treatment.

Bio Electro Chemical Systems (BES) could fill this niche. BES use microorganisms to catalyse different electrochemical reactions, as well as generating electrical power from wastes [1-3], the generation of many different chemical products or biofuels [4,5], and the removal of organic, and/or inorganic compounds from water flows. Groundwater, as the main resource of drinking water, is usually characterized by low conductivity (less than 1 mS·cm⁻¹). Low ionic strength influences oxidation and reduction processes (in terms of removal efficiencies and loads), and the energy and current productions [6]. Cathode over potential represents almost 80% of the total energy losses, as cathode microbial community consumes energy to catalyse reduction reactions.

Intensive agriculture and livestock production and other non point sources have led to nitrate pollution in aquifers around the world [7]. Groundwater contaminated with nitrate contains almost no organic matter. As a result, using biological denitrification in activated heterotrophic sludge systems requires the addition of an external carbon source, producing considerable amount of sludge, which should be treated before disposal. Autotrophic denitrification is a more sustainable solution because carbon is not necessary, and thus, no carbon dioxide is released, leading to better bio stability. The cathode of BES can perform autotrophic nitrogen oxidised compounds (nitrate, nitrite and even nitrous oxide) removals [8-10]. BES are capable to treat nitrates at a maximum removal of 226 gNO₃⁻·m⁻³·d⁻¹, without no nitrous oxide emission (a greenhouse gas), neither affecting other parameters of quality [11]. Not only BES removes nitrogen oxidised compounds, they also produce electrical power (0.013 kWh·m⁻³), if an organic waste is fed in the anode compartment.

Sulphate, one of the most abundant anions in the environment, is generated and discharged from many industrial processes. Despite its relatively low direct environmental risk compared to other pollutants, in situ sulphate reduction to sulphide (toxic, corrosive and odorous compound) may occur under anaerobic conditions. Therefore, drinking water directives fixed a control concentration of 250 mg SO₄²⁻·L⁻¹. Removal of sulphate from liquid is restricted to anaerobic

bioreactors coupled to oxidation of organic matter. However, sulphate-rich water, as in the case of nitrate contaminated groundwater, is usually deficient in electron donors [12]. BES can provide the electrons required for sulphate reduction in a biologically activated cathode, by coupling the oxidation of organic substrates in a separated anode, or by direct power supply. Despite a minimum power supply is required to overcome activation energy, thermodynamic potential losses and cathode over potentials, sulphate can be reduced *via* direct electron transfer, when poisoning the electrode too high (-0.26 V vs. SHE) for appreciable hydrogen production [13,14]. Sulphate groundwater-like streams can be treated with a minimum energy requirement of 0.7 V, while maximum removal of 60 g SO₄²⁻·m⁻³·d⁻¹ occurs at 1.4 V applied. The reduction of sulphate leads mainly to sulphide production, which is entrapped in the ionic form, thanks to high bio cathode pH obtained during the process [13].

Chlorinated Aliphatic Hydrocarbons (CAHs), a family of compounds that are commonly used as chlorinated organic solvents for degreasing in the dry cleaning, electronics, industrial manufacturing and machine maintenance industries, are increasingly being detected in groundwater. The most prevalent of these CAHs are perchlorethylene (PCE), trichloroethylene (TCE), cis-dichloroethene (cis-DCE) and trichloroethane (TCA). Aulenta et al. [15] developed an electrochemically assisted reductive dechlorination, which a polarized glassy carbon electrode (i.e. cathode), is used as an electron donor for the microbial reductive dechlorination of TCE to harmless ethane. Not only TCE could be removed using BES, carbon-based electrode polarized at -0.55 V vs. SHE can serve as direct electron donor for the microbial reductive dechlorination of chloroethenes (TCE and cis-DCE) to harmless non-chlorinated end-products [16].

Finally, it is important to highlight that conventional technologies for groundwater treatment have high operational costs, and that the BES-based technology potentially allows decreasing these costs considerably to meet groundwater standards, and the selective and sustainable removal of its pollutants. The effluent of BES is biologically stable, minimizing the potential health risks and other possible problems with the infrastructure of the water supply, such as clogging of point-of-use filters, biofouling of distribution pipes and bio corrosion [8]. Therefore, it exist a clear niche and demand on the groundwater treatment market.

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