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Electrochemical Removal of *Microcystis Aeruginosa* in a Fixed Bed Reactor

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The removal of *M. aeruginosa* from natural waters has been investigated by using a fixed bed cell with 3-dimensional electrodes in continuous mode. Steady state values of chlorophyll-a pigment, contained in the microalgae, were obtained, as well as concentrations of oxidizing species in the outlet stream of the system.

In particular, attention was paid to two key parameters, flow rate and current density, to determine their influence on the removal of microalgae and on the concentration.

Experiments were performed in a plastic cylindrical single pass cell, filled with glass spheres, connected to a hydraulic circuit. Grids of Titanium, arranged in stacks in-series, were employed as electrodes packing. The grids of the cathode packing were coated with platinum, while the grids of the anode packing were coated with Ir/Ru mixed oxides.

The effect of the operative parameters on the possible mechanism of removal, namely electric field and electro-generated oxidants was investigated.

The results show that the removal of *M. aeruguinosa* may be related to the synergistic effect of electro-generated oxidants produced from the chloride ions and electric field, although the main mechanism is the killing by long life oxidants electro-generated at the anode surface.

1. Introduction

M. aeruginosa is a photoautotrophic gram-negative bacteria that has been found in surface waters worldwide as lakes, reservoirs, shores of ponds and slow-moving rivers (Corbel et al., 2014). The presence of cyanobacteria in water may constitute a serious risk for health and environment, because of the possible release of cyanotoxins. If contained in high concentrations, these substances can be toxic and dangerous to humans, but also under the lethal dose, cyanotoxins in drinking water are implicated as one of the key risk factors for the high occurrence of primary liver cancer (Codd, 2000). Moreover, the water contaminated with toxic cyanobacteria also might cause the death of domestic and wild animals (Zakaria, 2001). Cyanotoxins are released into water following cyanobacterial cell lysis, which often happens during their passage through a conventional water treatment plant (Tran and Drogui, 2012).

The removal of algae from wastewater has then gained importance in recent years; however, due to their small size and low specific gravity, it is difficult to remove algae effectively with conventional processes of water treatment such as sedimentation or filtration (Ma and Liu, 2002).

The interest on electrochemical oxidation procedures has increased for the treatment of wastewater (Ghernaout and Ghernaout, 2010) because it is relatively economical, has higher treatment efficiency, and does not require storage of chemicals. Additionally, the construction of the reactors and managements are simples, which makes it suitable for automation (Vacca et al., 2011). The inactivation of bacteria and viruses has been documented (Feng et al., 2004).

In the water disinfection by direct electrolysis algae may behave as colloidal particles, and can be separated from water solution by the electric field. Moreover, disinfecting agents, such as reactive oxygen species and chlorinated compounds may be generated, and can inactivate the bacteria. The effectiveness of the process, regarding the high bactericidal effect, is based mostly on the anode material, flow conditions, pH gradients in

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the reactor, electro-generated oxidants and on the applied electric field on the cell membrane (Vacca et al., 2011).

Fixed bed reactors with 3-D electrodes for electrochemical treatment of waters for disinfection have been recently investigated (Mascia et al., 2012), while the use of dimensionally stable anodes (DSA) has been proposed for the study of *M. aeruginosa* inhibition by electrochemical method (Xu et al., 2007).

Three dimensional electrodes have attracted much attention for electrochemical treatment of water and wastewater when high specific areas and high mass transfer rates are requested, and to obtain high space time yields in reactors for processing dilute solutions (Nath et al., 2011).

Depending on the operative conditions, different amounts of free chlorine are produced from the electrochemical oxidation of chloride ions present in the solution. The free chlorine may react with water to give hypochlorous acid and hypochlorite ions, depending on the pH. The active chlorine may act as powerful disinfecting agent in the process, however, the cathodic reduction of active chlorine occurs along with the hydrogen evolution, thus reducing the effectiveness of the process (Mascia et al., 2012).

The system used in this work is constituted by a flow through tubular reactor operating in continuous mode with three dimensional electrodes. The anode packing is constituted by stacks in-series of expanded meshes of commercial Ir/Ru mixed oxides (DSA).

The purpose of this study was therefore to determine the feasibility of *M. aeruginosa* removal through the electrochemical process. Particularly, attention was paid on the effect of operating conditions such as current density and flow rate. The possible presence of chloride ions was also investigated, measuring the effect of chloride concentration on the electrochemical generation of active chlorine and on the removal of *M. aeruginosa*.

2. Materials and methods

2.1 Microalgae and culture conditions

M. aeruginosa was obtained from SAG (Culture Collection of Algae) of the University of Göttingen (Germany). This specie is an unicellular planktonic freshwater cyanobacterium with a spherical shape 3-7 μm in diameter. BG-11 was adopted as microorganism growth substrate including distilled water and chemical components (g dm^{-3}) as follows: $NaNO_3$ 150; $K_2HPO_4 \cdot 3H_2O$ 4; $MgSO_4 \cdot 7H_2O$ 7.5; $CaCl_2 \cdot 2H_2O$ 3.6; citric acid 0.6; ferric ammonium citrate 0.6; EDTA (dinatrium-salt) 0.1; Na_2CO_3 2; and 1 mL per dm^{-3} of a solution containing (mg dm^{-3}): H_3BO_3 61; $MnSO_4 \cdot H_2O$ 169; $ZnSO_4 \cdot 7H_2O$ 287; $CuSO_4 \cdot 5H_2O$ 2.5; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ 12,5. *M. aeruginosa* was cultivated under continuous fluorescent light in three flasks containing each one a liter of BG-11. Electrolysis experiments were tried out when microalgae was in the log growth phase, which corresponded to an algae concentration between $1 \cdot 10^9$ and $3 \cdot 10^9$ cells dm^{-3}.

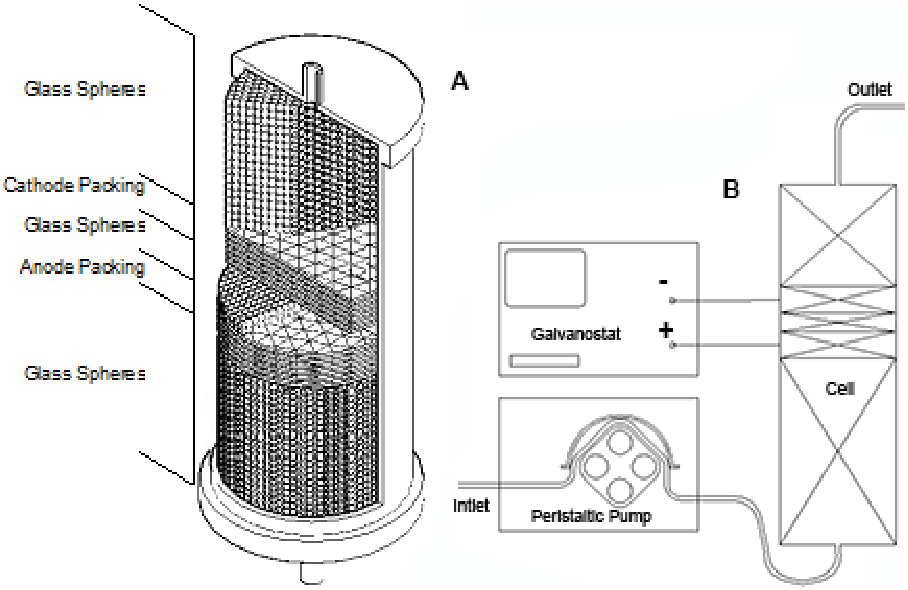

Figure 1: details of the cell (A), and scheme of the experimental apparatus used for the electrolysis (B)

2.2 Electrochemical cell

Electrolysis experiments were performed in a fixed bed electrochemical cell constituted by a plexiglass cylindrical single compartment reactor with a dimension of 15 cm (height) x 5 cm (inner diameter). Details of the reactor (A) and of the experimental apparatus used for the electrolysis (B) are shown in Figure 1.

The cell is equipped with three-dimensional electrodes, six discs of titanium grids coated with Ir/Ru mixed oxides (DSA) constituted the anode packing, while six discs of titanium grids coated with platinum constituted the cathode packing. Both anode and cathode packings have a surfaces of 100 cm^2, and the inter-electrode gap was 0.5 cm. The cell was filled with glass spheres (d_p = 2 mm).

A complete experimental characterization of the reactor for mass transfer and flow behaviour, as well as a mathematical model of flow and electrolysis of water with low chloride content can be found in a previous work (Mascia et al., 2012).

2.3 Electrolysis

The runs were performed in continuous mode and the electrolyte was fed by a peristaltic pump to the electrochemical cell.

The flow rates ranged from 0.025 to 0.1 dm^3 min^{-1}, and the hydraulic residence time (τ= V/Q) in the electrochemical system was between 1 and 4.2 min.

Experiments were accomplished at constant current density ranging from 1 to 2 mA cm^{-2}. The electrolysis with algae were carried out in the growing medium, to which 400 to 600 mg dm^{-3} of Cl^- were added as NaCl.

2.4 Analyses

The concentration of microalgae were evaluated by using UV spectrum (Spectrophotometer VARIAN—50), which measures the absorbance of the chlorophyll-a at 690 nm. The algae cell density was also analysed through counting under microscope (Olympus) at x40 magnification with a Thoma counting chamber.

The oxidant concentrations, expressed as mg L^{-1} of ClO^-, were determined employing the N,N-diethyl-p-phenylenediamine (DPD) by spectral photometer detection at 515 nm (APHA, 2005). This standard method is a colorimetric technique where DPD is oxidized to form a red-purple product. This procedure is only valid in a range of active chlorine concentrations from 0.05 to 4 mg dm^{-3} of ClO^- (Moberg and Karlberg, 2000), so samples were diluted when necessary, and between pH 6.3 and 6.5.

3. Results and discussion

Figure 2 shows the percentage of chlorophyll-a removed, as a function of the ratio between the electrolysis time and the hydraulic residence time, obtained under different operative conditions.

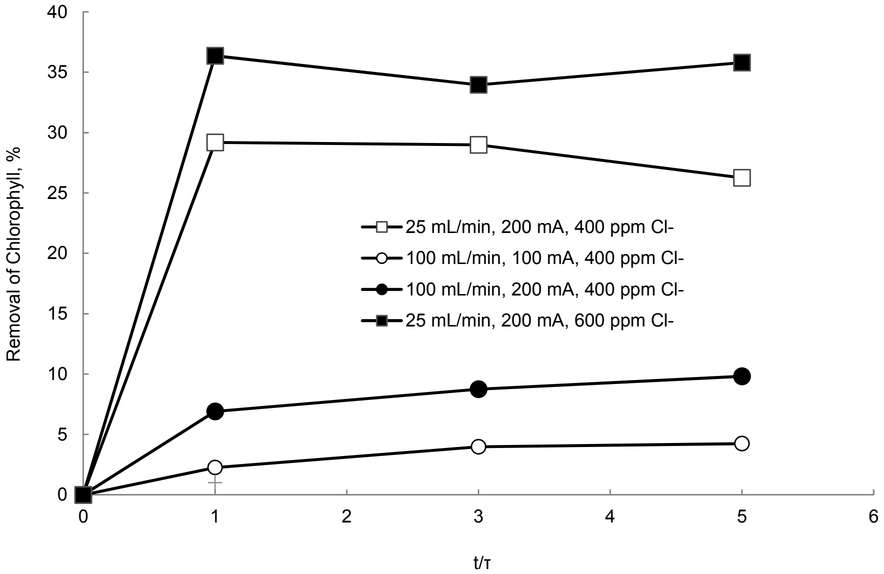

Figure 2: trend of the removal of chlorophyll–a as a function of the ratio between electrolysis time and residence time obtained under different operative conditions

For all the runs, it can be noticed that the removal quantity of chlorophyll-a increases significantly up to 1τ, and at this time the system reaches the steady state.

By operating at a flow rate value of 100 mL min^{-1}, at applied current density of 1 mA cm^{-2} and at initial Cl$^-$ concentration of 400 mg dm^{-3}, the removal efficiency of the chlorophyll-a amounted to 4.24 %.

On the other hand, working at 2 mA cm^{-2} and maintaining constant the other parameters, the algae removal reached the 9.83 %. The highest removal of chlorophyll (33.95 %) was obtained when an initial concentration of 600 mg dm^{-3} of chloride ions were used, operating with the lowest flow rate and at the highest current density. Comparing the experiments performed at 400 mg dm^{-3} with those at 600 mg dm^{-3}, it is possible to observe that the more amounts of Cl$^-$ ions are present, the more chlorophyll-a removal will be obtained.

As the effect of the hydrodynamic of the reactor is concerned, we can observe a decrease in the removal of the normalised absorbance as the flow rate increases.

This behaviour may be interpreted considering the different phenomena occurring during the process, and the possible mechanisms responsible for algae inactivation.

During the electrolysis of water with DSA, two main reactions occur at the anode surface: adsorbed and dissolved chlorine are generated from the oxidation of chloride ions (Comninellis and Nerini, 1995), while oxygen evolves from water discharge.

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (1)$$
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

The dissolved chlorine may in turn react with water to give hypochlorous acid and hypochlorite ions:

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \qquad (3)$$
$$HClO \leftrightarrow ClO^- + H^+ \qquad (4)$$

The distribution of the three forms of active chlorine depends on the conditions, at the neutral or weakly alkaline pH of the water processed in the electrolyses, the reaction of disproportionation is shifted towards HClO. Moreover, it is worth highlighting that in a previous work carried out with the same apparatus here used, appreciable amounts of other chlorinated compounds were not detected under conditions similar to those adopted in this work (Mascia et al., 2013).

At the cathode the main reactions are the reduction of active chlorine and the hydrogen evolution:

$$ClO^- + 2e^- + H_2O \rightarrow Cl^- + 2OH^- \qquad (5)$$
$$H_2O + e^- \rightarrow 1.5\ H_2 + OH^- \qquad (6)$$

the electrochemical reaction (5) is fast, so that the kinetic of active chlorine reduction may be assumed as controlled by the mass transfer towards the cathode surface (Vacca et al., 2011).

The ability of active chlorine to attack the proteins of the cell membrane, the protoplasm and the nucleus of the cell is well documented (Li et al, 2010), and the role of the active chlorine species was also investigated for algae removal processes (Gao et al., 2010).

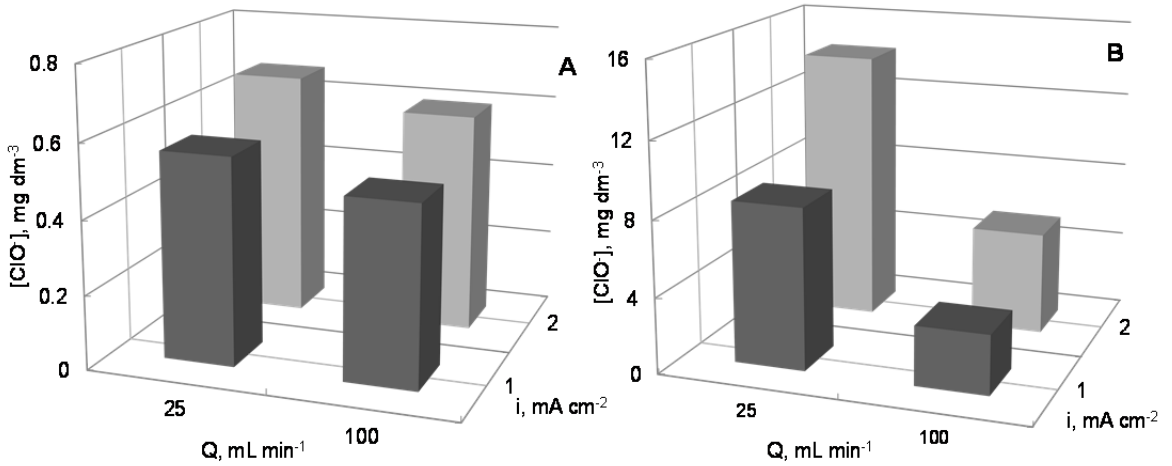

Figure 3: steady state concentrations of electro-generated oxidants, represented in mg dm^{-3} of ClO$^-$, in the outlet of the reactor. Data obtained from electrolysis under different flow conditions, applied current densities, and with 200 and 400 mg dm^{-3} of chloride ions

Moreover, when the algae are exposed to an external electric field permanent or transient pores in the membrane of the cells may be induced (Gao et al., 2010), which may increase the effectiveness of the electro-generated oxidants.

The behaviour of the system was investigated firstly with solutions only containing the growing medium, to which different amounts of chlorides were added. Electro-generated oxidants were measured in the outlet stream when the process achieved the steady state.

Figure 3 shows the concentration of active chlorine formed in the outlet stream as function of the flow rate and the applied current density with two different initial concentration of chlorides ions: 200 mg dm^{-3} (Figure 3 A) and 400 mg dm^{-3} (Figure 3 B). The generation of active chlorine increased with the current density and decreased with the flow rate. Under the conditions adopted in this work, the currents of migration and diffusion of chlorides are of the same order of magnitude, and the kinetic of chloride oxidation is under mixed current/mass transfer control (Mascia et al., 2012). The effect of current density and inlet concentration observed is expected, while the flow rate may differently affect the process.

At low flow rate, the residence time of the electrolyte inside the cell is relatively high in both the electrode compartments. In the anode packing high contact times favour the formation of active chlorine.

At the cathode we have to consider the negative effect due to the increased residence time for active chlorine reduction (reaction 5), but also the positive effect of low mass transfer rate, which is the controlling step of reaction 5.

High values of flow rate lead to low contact times, which may reduce the formation of active chlorine, but also balance the increase of the specific rate of reaction 5. Active chlorine formation was also investigated with *M. aeruginosa* in the inlet of the reactor. Figure 4 shows the comparison of active chlorine concentrations measured in the outlet stream from electrolysis both in presence and in absence of *M. aeruginosa*. The concentration of chloride ions in the inlet stream was 400 mg dm^{-3} or 600 mg dm^{-3}. The experiments were performed with a current density of 2 mA cm^{-2} and a flow rate of 25 mL min^{-1}. It is worth observing that only under these conditions of relatively high current density and high chloride ions concentration the active chlorine was present in detectable amount.

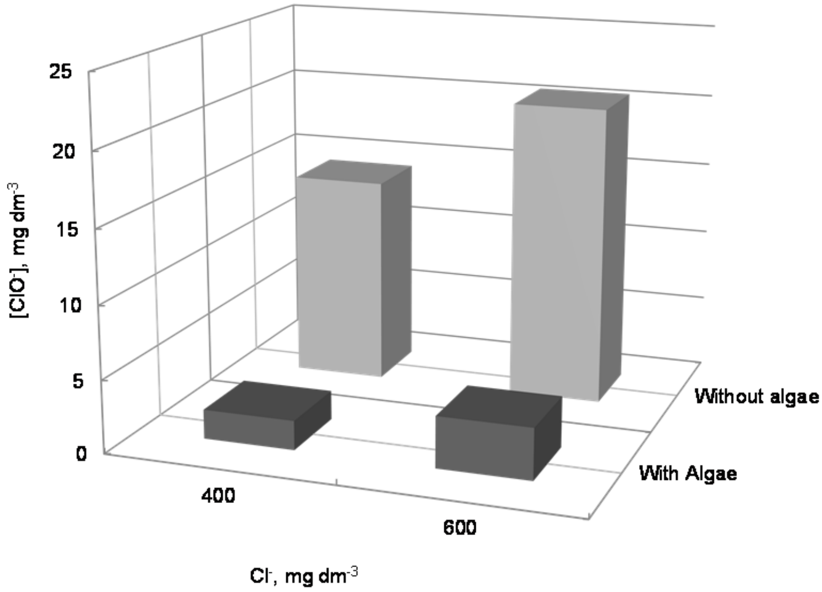

Figure 4: steady state concentrations of electro-generated oxidants, represented in mg dm^{-3} of ClO$^-$, in the outlet of the reactor under different Cl$^-$ concentrations, current density of 2 mA cm^{-2}, and flow rate of 25 mL min^{-1} with and without M. aeruginosa in the inlet stream

Active chlorine concentrations below 2 mg dm^{-3} were obtained with 400 mg dm^{-3} of chloride ions, while higher values were obtained with 600 mg dm^{-3}, but in any case, the presence of algae strongly reduced the active chlorine concentration in the outlet stream. This result leads to the conclusion that the bulk phenomena are prevalent in the algae removal process, under the conditions adopted in this work.

The active chlorine formed at DSA anode may react with the high organic load originated by the presence of microalgae, so that the difference in oxidants concentration detected with and without algae, may be attributed to the consumption of the oxidising species by *M. aeruginosa*. This may be confirmed by the trend of removal efficiency with the flow rates: passing from 25 mL min^{-1} to 100 mL min^{-1}, chloride ions concentration and current density being the same, the removal efficiency resulted reduced by 60 %.

4. Conclusions

The inactivation of *M. aeruginosa* by electrochemical treatment was studied in continuous mode in a fixed bed reactor with 3-dimensional electrodes. The results showed that with the DSA anode used in this work a high efficiency could be achieved only under conditions of high current density and low flow rate. Moreover, at least 400 mg dm^{-3} of chloride ions should be contained in the inlet stream to achieve an appreciable inactivation of algae.

The most remarkable removal efficiency of chlorophyll-a was obtained with the initial Cl^- concentration of 600 mg dm^{-3}, at current density value of 2 mA cm^{-2} and at flow rate of 25 mL min^{-1}. The removal efficiency of the *M. aeruguinosa* in the water disinfection process may be related to the synergistic effect of electro-generated oxidants produced from the chloride ions and electric field, but results have shown that the main mechanism is the killing by long life oxidants electro-generated at the anode surface.

The obtained results will constitute the basis for further work in which the direct electrolysis process for the removal of this type of algae will be focused on the study of other influential parameters involved in the process.

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