Removal of algae from biological cultures: a challenge for
electrocoagulation?

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Abstract

BACKGROUND: In the search for novel technologies for the treatment of urban
wastewater, combined anaerobic-algae membrane bioreactors have become a very
interesting choice, nowadays. Recovery of algae produced in these reactors has become
the key point to obtain a good economic efficiency with this technology. In this work,
electrocoagulation is studied as an alternative for the coarse removal of algae from a
biological culture.

RESULTS: Results demonstrate that the electrochemical technology is a suitable
technology for this purpose allowing the removal of more than 90% of the algae without
modifying significantly the pH and with an operating cost below 0.04 €/m³. The same
general trends are observed for applied current charge and current density supplied when Al or Fe are used as electrodes although aluminum was much more efficient.

CONCLUSIONS: The dose of coagulant reagents required is very low, indicating that coagulant generated in the process is very efficiently used. The best results in terms of algae and turbidity removals are obtained operating at low current densities with aluminum electrodes. According to pH and z-potential values, insoluble metal hydroxide and anion M(OH)₄⁻ seems to be the primary coagulation species involved in the electrocoagulation process.

Keywords: algae culture, electrocoagulation, electro-flotation, aluminum, iron

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INTRODUCTION

Nowadays, research on novel technologies for urban wastewater treatment is a hot topic. The main interest is to look for more efficient processes in terms of energy consumption. Anaerobic membrane bioreactors (AnMBR) are becoming a very interesting choice because they transform organic matter efficiently into biogas and avoid the huge aeration cost associated to the well-known bio-oxidation processes, such as the traditional activated sludge or the innovative biological nutrient removal processes. Main drawback of AnMBR technology is the reluctance to remove nutrients. This is a major concern nowadays because nutrient removal is a required standard in the treatment of urban wastewater in order to avoid eutrophication at the discharge point of treated wastewater.

For this reason, different technologies are being investigated in the recent years to be combined with AnMBR. Algae membrane bioreactors are clearly emerging as the most interesting choice because of the very promising results. However, scale-up of this technology should face a significant challenge: it requires an efficient separation of algae in order to obtain an efficient economic valorization. Algae cultures are characterized by the occurrence of colloids in large amounts. Hence, an efficient separation technology should be based on the destabilization of these colloids.

Electrocoagulation is a very exciting technology for the treatment of colloids dispersions and it has been the focus of many studies in the recent years with applications in the treatment of supply water and also for different types of wastewater. It combines into a single reactor many processes that may interact in a synergistic way if properly combined. The key for this technology is the application of current between a sacrificial anode (typically iron or aluminum) and an inert cathode (which could even be
of the same material to allow polarity reversal). This current produces the formation of many iron or aluminum species. The concentrations of each of these species depend on the resulting pH and total concentration of metal dissolved\(^\text{11}\). Electric current also produces bubbles of oxygen and hydrogen, as a consequence of the water oxidation and reduction on the surface of the anode and cathode, respectively. Bubbles are directly related to the mixing because they promote turbulence and help in the flocculation processes (so-called electro-flocculation\(^\text{12}\)). In addition, they can adhere to particles contributing to the separation by flotation (so-called electro-flotation). As a consequence of the addition of all these single processes in the same reactor, a very effective combined process is obtained, for which two additional advantages are:

1. the much lower increase in the conductivity as compared with a conventional coagulation (because no salts are added and no neutralizations are required after the treatment\(^\text{13, 14, 15}\) and
2. the buffering effect on the pH, which has been pointed out as the main advantage of the electrocoagulation\(^\text{16}\).

Regarding previous experiences found in the literature on the application of electrocoagulation technologies to the harvesting of algae, few information is available. Electroflocculation–electrofloation technology (without the chemical addition) has been studied to remove algae in several works with promising results\(^\text{17, 18, 19}\), but without taking advantage of the coagulation mechanisms associated with the dissolution of iron or aluminum. With electrochemical reagents addition, the removal of algae has been also studied\(^\text{20, 21}\) showing good results at acidic pHs and worse performance in alkaline conditions. However, the technological approach used was based on the application of very low current densities (1 mA cm\(^{-2}\)), looking for low energy requirements. Results demonstrated this low energy demand (only 0.4 kWh m\(^{-3}\)) but unfortunately, these
operation conditions may lead to a significant drawback during the later upscaling procedure: the need for very large electrode areas and so, of very high investment cost, pointing out the necessity of studying higher operation current densities. Regarding applications, it is worth also to take in mind that this technology has not only been used for environmental application but it has also been studied in the energy industry, particularly in concentration of algae cultures during the production of biodiesel 22-24.

This work aims to determine whether electrocoagulation could exhibit suitable characteristic to be used to separate algae at slightly alkaline conditions and hence if it could be used as a complement to a MBR operating at large current densities (looking for a potential applicability because low current densities lead to huge electrochemical cells which would be inapplicable in large scale processes). In addition, some mechanistic information is also looked for, in particular the effect of pH and z-potential on results, because both parameters are strongly related to the potential reclaiming of the effluent of the treatment and of the algae culture. Taking into account the growing interest of MBR technology for municipal wastewater treatment, such a combination could become a reference technology in urban wastewater treatment if it helps to avoid the current drawbacks found.

**MATERIAL AND METHODS**

Electrocoagulation test were carried out in small flask of 100 cm³ equipped with square-shaped anode and cathode (4 cm²) of iron or aluminum (depending on the test) and filled with 75 cm³ of a solution of fresh algae prepared from an chlorella vulgaris inoculum, using tap water as solvent. pH of the solution was not modified (natural pH). Two current densities were studied: 5.0 and 50.0 mA cm⁻². Current was applied with a power supply
(DC Power Supply FA-376 PROMAX). The current flowing through the cell was measured with a 2000 Digital Multimeter KEITHLEY). Sampling times were chosen in order to obtain the same applied current charges at the end of the experiments in order to compare results obtained in the same conditions. When the electrolysis time of each experiment is obtained, the solution is kept without any disturbance for 30 minutes in order to allow the particles to settle or float according to its properties like in a full scale tank and do not obtain a simple transitory response. Prior to each experiment, the electrodes were treated with a solution of 1.30 M HCl in order to reject any effect due to the different prehistory of the electrodes.

Turbidity was measured using a multi parameter optical device type 115 Velp Cientifica. This is an indirect measurement of the concentration of colloids. Zeta potential determination was performed using Zetasizer Nano analyzer (Malvern, England) equipped with an automatic titrator MPT-2. Measurements of pH and conductivity were carried out with a pH-meter type GLP 22 (CRISON). To monitor the changes in the concentration of algae, in addition to the turbidity, a photometric measurement was carried out: the absorbance of light at 696 nm, because at this wavelength the maximum of the peak associated to chlorophyll is attained. This is an indirect measurement of algae and it was clear in all spectra carried out in this work. It allows us to have a rapid and robust value of the concentration of a marker directly related with algae. All samples were filtered with Whatman® prepleated qualitative filter paper before analysis. Photos were taken at different stages of the treatment although in this manuscript only those corresponding to the final solution are shown. It has been tried to keep light and position conditions in order to compare them properly.

RESULTS AND DISCUSSION
Figure 1 shows the changes in the concentration of algae and in the residual turbidity during the electrocoagulation of an algae suspension containing 800 mg dm$^{-3}$ of Chemical Oxygen Demand at pH 9 with iron and aluminum electrodes at two different current densities (5 and 50 mA cm$^{-2}$). This range of current densities is expected to lead to a significant difference in the results obtained during electrocoagulation because of the complex interactions between very different processes occurring during this electrochemical technology. Thus, electrocoagulation can be understood as a sequence of two processes:

(i) the electrochemical dissolution of the electrode and the production of oxygen and hydrogen bubbles by water decomposition (eqs. 1 and 2) which are going to be strongly influenced by current density and

(ii) the interaction between coagulants, pollutants and the solution components (pH changes, precipitations, etc.) which is not dependent on the electrolytic parameters but it has its own kinetics, which depend on non-electrolytic processes such as the adsorption of coagulant species on the surface of the algae, flocs formation, mixing rate, adhesion of bubbles to flocs, etc..

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^- \] (1)

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2\text{e}^- \] (2)

The lowest current density applied in this work is representative of mild operations conditions, with small production of bubbles and a very high efficiency in the dosage of coagulants. In full scale it would correspond to large cells in terms of electrode surface - influent flow rate ratio, and hence it would involve higher investment and lower operating cost than applying a higher current density. Regarding operation, interactions between the coagulant and the algae at low current densities are expected to be carried out more
efficiently because the production of coagulants is relatively slow and these reagents can interact for a longer time with algae. On the contrary, the highest current density means more compact reactors with an intense production of bubbles and a very rapid formation of flocs and hence lower time of interaction of the fresh coagulants with algae. Production of bubbles means that efficiency in the reagent dissolution is lower, but it has to be taken in mind that these bubbles help in the separation of algae by flotation and that this separation could be more efficient in the latter case.

For comparison purposes, sample times during the electrolysis were selected at both current densities \( j \) in order to apply on the treated algae culture the same electric charges when the samples are taken regardless of the \( j \) applied. This procedure allows us to make a direct comparison of results. As the highest current density is ten times higher than the lowest, the electrolysis time and the sampling periods were ten times higher in the experiments carried out at the lowest current density. Hence, total electrolysis time was 3 minutes for the 50.0 mA cm\(^{-2}\) tests and 30 minutes for the 5.0 mA cm\(^{-2}\). This means that slow non-electrochemical processes could develop in a greater extension at lower current densities. One important point is that previous to the sampling, treated solution was kept without current application for 30 minutes in order to allow flocs formed to settle and/or float in suitable conditions and to avoid the effect of transitory responses.

Regarding results shown in Fig.1, as it can be observed, the best results in terms of turbidity and algae removal are obtained for very low applied current charges (around 0.02 Ah dm\(^{-3}\)). In addition, it may be pointed out that aluminum performs better than iron. About iron, and taking into account that dissolution of iron is a two electron transfer reaction (eq. 3), because it is not iron (III) but iron (II) the product of the electrochemical dissolution of iron anodes, the stoichiometric conversion between applied current charge and iron dissolved can be fixed in 1 Ah dm\(^{-3}\) for 1041 mg dm\(^{-3}\) of iron dissolved. This
means that optimum conditions when iron is used as electrode are obtained for a stoichiometric dosage of 20.8 mg dm$^{-3}$. As it is known, in electrocoagulation processes iron (II) is the initial species formed but it is not the coagulant because it is further oxidized by oxygen in the solution to iron (III), which is always considered as the final product of the dissolution of the electrode. This explains the formations of foaming flocs of iron (III) hydroxyde precipitates, which are going to be discussed afterwards (eqs. 4-7). Regarding results obtained, removal of algae clearly becomes less efficient at higher applied charge per volume unit of electrolyzed solution ($Q$), suggesting a less efficient use of coagulant reagents and that floc enmeshment (promoted at high dosage of coagulant) may not be a good mechanism for the removal of algae. Regarding turbidity, low current densities lead to a less efficient process as compared to high current densities and a clear increase in the residual turbidity is observed when the dose of iron dissolved increase. This worsening of the residual turbidity is not observed operating at higher current densities and it points out the large mechanistic differences observed at two current densities.

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (3)
\]

\[
\text{Fe}^{2+} (aq) + 2\text{OH}^- (aq) \rightarrow \text{Fe(OH)}_2(s) \quad (4)
\]

\[
4\text{Fe}^{2+} (aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{Fe}^{3+} (aq) + 4\text{OH}^- (aq) \quad (5)
\]

\[
4 \text{ Fe(OH)}_2(s) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{Fe(OH)}_3 \quad (6)
\]

\[
4\text{ Fe}^{2+} (aq) + 4\text{H}^+ (aq) + \text{O}_2(g) \rightarrow 4\text{Fe}^{3+} (aq) + 2\text{H}_2\text{O}(l) \quad (7)
\]

For aluminum dissolution a three-electron transfer is expected (eq. 8) and resulting stoichiometry between electric charge and aluminum dose is 1 Ah dm$^{-3}$ for 334.5 mg dm$^{-3}$. Taking into account that optimum current charge applied is 0.02 Ah dm$^{-3}$ as well, this value corresponds stoichiometrically to a dose of aluminum of 6.7 mg dm$^{-3}$.

\[
\text{Al} \rightarrow \text{Al}^{3+}+3e^- \quad (8)
\]
In this case, and opposite to it was observed with iron, higher dosages of aluminum that those required to meet almost depletion does not worsen the results in terms of removal of algae and it is kept at the maximum level, regardless of the increasing dose of aluminum. However, turbidity changes shows exactly the same pattern in the case of aluminum electrocoagulation that in the case of iron electrocoagulation: in the case of the low current density experiment it becomes worse as the dosage of coagulant increase and this behavior is not observed operating at high j. Main differences between both conditions are the increased production of bubbles at large j, which seems to have a very important role in the mixing and hence in the flocculation stage of algae. This is more clearly seemed when the production of coagulant is larger and it explains the higher turbidity in the case in which low bubbles production is obtained. Better performance of aluminum over iron was also shown in a previous work focused on the removal of algae in which after 45 min of treatment the removal efficiencies attained using iron and aluminium electrodes were 78.9% and 100% respectively.

Figure 2 shows a photo with the final solution obtained after 30 minutes of setting time in the different test carried out with Al electrodes. As it was pointed out in Figure 1, clearly the best results are obtained operating at low current densities and low applied charge because the clearest solution is obtained with a very small layer of floated sludge and no settle sludge is observed. This means that coagulant generated in the process has been used very efficiently. Regarding effect of Q, width of the floated sludge layer increase with the Q because of the higher amount of coagulant dosed and hence of the higher amount of insoluble aluminum hydroxide precipitate formed. In addition, the highest the current density applied the less dense is the floc layer, meaning that flocs becomes bulky and less compacter at higher j. This could be explained by the much higher production of bubbles under those conditions. As pointed out in Figure 1, the worst
removal of turbidity is clearly observed in the low current densities experiments at high
Q. This can be clearly seen when photos at 0.068 and 0.133 Ah dm$^{-3}$ are compared to
those obtained for the same Q but larger j because in the latter case no turbidity is
observed. Just on the contrary, in those cases, the occurrence of flocs which do not settle
or float at the conditions used seems to be greater. Larger production of bubbles by water
decomposition at larger j could explain this observation by an improve flocculation
(because of the mixing effect of bubbles). Excess of bubbles can also help to explain the
greater amount of suspended solids observed for larger Q and j.

It is also of interest the differences observed between the sludge formed at low and high
j for the lowest Q: it is more compacted the sludge formed at low j and in addition it only
floats. Opposite, the sludge formed at high j and low Q seems to be more bulky and it is
less efficiently splitten. The occurrence of surplus hydrogen and oxygen bubbles into the
flocs which being stripped with time can be responsible for this observation. In addition
the larger bubbles produced at large current densities can also explain the better
flocculation and the worse flotation (because flotation becomes less efficient as the
bubble size increase)

Regarding iron coagulation, photos corresponding to the last stage of the
electrocoagulation (after 30 minutes of settling time) are shown in Figure 3. The same
general trends are observed for Q and j than those discussed for aluminum
electrocoagulation. However, in this case, the floc enmeshment seems to be the main
removal mechanisms because the amount of sludge is perceptively much higher, less flocs
are suspended and width of the floated sludge layer is higher, while a significant layer of
settled sludge appears. As in aluminum electrocoagulation, the higher j leads to a better
removal of turbidity (although some suspended particles can be clearly observed) and low
leads to a high turbidity at high Q because of the less important floc formation (worsen flocculation because of a lower production of bubbles in the reaction system).

Figure 4 focuses on the changes observed in the pH and z-potential during the electrocoagulation tests carried out in this work. Regarding changes in the z-potential, results show that charge neutralization is not occurring in a great extension and that only a significant decrease in this parameter towards the zero point charge is observed for aluminum electrocoagulation at low current densities in the complete range of Q (the best electrode and the best operating conditions found in this work for the removal of algae).

Regarding the other tests carried out, the most interesting observation is that for a Q of 0.02 Ah dm$^{-3}$ the lowest z-potential (in absolute value) is obtained. For higher Q, z-potential becomes more negative suggesting that the best removal obtained in the turbidity during these tests has to be explained in terms of a floc-enmeshment mechanism and that the most efficient removal of algae is obtained when a slight charge neutralization is obtained. Small interactions between coagulant species and algae (reflected in the very small surface changes according to the z-potential) suggest that algae should not be significantly disturbed by the electrochemical addition of coagulation reagents.

Regarding pH changes, as expected for the very low current charges applied and taking into account the well-known buffering effect of electrocoagulation, pH only suffer a small decrease towards neutralization. This decrease is higher in the case of the electrocoagulation tests carried out at higher current densities and this is in agreement with the greater extension in which reactions 1 and 2 develops. As it has been discussed before, these reactions are important in the separation of algae, because production of bubbles of oxygen and hydrogen is directly related to the mixing (and hence to the flocculation) and to the separation (flotation) stages. The small change in the pH means that life conditions for algae are not changing importantly and this fact opens the
possibility of using this technology for the recovery of algae culture which is a topic of a great interest because of the current price of algae.

A final remark is that according to the literature, the value of pH suggests that insoluble metal hydroxide and anion M(OH)\(^{4-}\) are the primary coagulation species playing a role in this electrocoagulation process. Occurrence of both species is also supported by the negative value of the z-potential.

Regarding operating cost, the low current charge required to attain the optimum conditions implies very low energy consumption. Cell voltage was under 4.0 V for aluminum and under 3.0 V for iron electrocoagulation in the experimental setups used. These values could be significantly decreased in a commercial electrocoagulation cell. However, even with those optimized values, energy requirements are below 0.1 kWh m\(^{-3}\). This value is even lower than that obtained by Gao et al. (2010) (0.60 kWh m\(^{-3}\) at pH 10)\(^{21}\). Considering a cost for electricity of 0.1€/kWh it means that energy cost associated to the coarse removal of algae are below 0.01 € m\(^{-3}\). On the other hand, price of aluminum sheets for electrocoagulation is around 3.85 €/kg \(^{26}\). Taking into account that optimum dose is 6.7 g m\(^{-3}\), a reagent cost because of the sacrificial electrodes of 0.026 € m\(^{-3}\) can be estimated, giving a total cost for the harvesting of algae below 0.04 € m\(^{-3}\).

3. Conclusions

From this work, the following conclusions can be drawn:

- Electrocoagulation is a suitable technology for the coarse removal of algae from biological culture. It attains a high efficiency 98-100 % for iron and aluminum
electrodes, respectively, in the separation of algae from the mixed liquors without
modifying significantly the pH and with a very low dose of coagulant reagents.

Aluminum electrodes seem to perform better than iron ones, although the same general
trends are observed for applied current charge and current density supplied with both
electrodes. Operating at low current densities and low applied charge allow obtaining the
best results in terms of algae and turbidity removals, meaning that coagulant generated in
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- Aluminum electrodes seem to perform better than iron ones, although the same
general trends are observed for applied current charge and current density
  supplied with both electrodes. Operating at low current densities and low applied
  charge allow obtaining the best results in terms of algae and turbidity removals,
  meaning that coagulant generated in the process is very efficiently used. As a
  result, the energy consumption for complete algae removal obtained was only 0.10
  kWh/m³.

- Main differences between both current densities used are the increased production
  of bubbles at large j which seems to have a very important role in the mixing and
  hence in the flocculation stage of algae.

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References

Figure captions

Figure 1. Changes in the concentration of algae and turbidity during the electrocoagulation of an algae suspension with aluminium and iron electrodes. Algae removal according to color depletion at 696 nm: ▲ Al j=50 mA cm$^{-2}$; ■ Al j=5 mA cm$^{-2}$; ● Fe j=50 mA cm$^{-2}$; ◆ Fe j=5 mA cm$^{-2}$. Residual turbidity: △ Al j=50 mA cm$^{-2}$; □ Al j=5 mA cm$^{-2}$; ○ Fe j=50 mA cm$^{-2}$; ◇ Fe j=5 mA cm$^{-2}$.

Figure 2. Photos with the final solution obtained after 30 minutes of setting time in the different test carried out with Al electrodes.

Figure 3. Photos with the final solution obtained after 30 minutes of setting time in the different test carried out with Fe electrodes.

Figure 4. Changes in pH and z-potential during the electrocoagulation of an algae suspension with aluminium and iron electrodes. pH: ▲ Al j=50 mA cm$^{-2}$; ■ Al j=5 mA cm$^{-2}$; ● Fe j=50 mA cm$^{-2}$; ◆ Fe j=5 mA cm$^{-2}$. Z-potential: △ Al j=50 mA cm$^{-2}$; □ Al j=5 mA cm$^{-2}$; ○ Fe j=50 mA cm$^{-2}$; ◇ Fe j=5 mA cm$^{-2}$. 
Figure 1.
Figure 2.

- $j=5 \text{ mA cm}^{-2}$
- $j=50 \text{ mA cm}^{-2}$
- $0 \text{ Ah dm}^{-3}$
- $0.022 \text{ Ah dm}^{-3}$
- $0.067 \text{ Ah dm}^{-3}$
- $0.133 \text{ Ah dm}^{-3}$
Figure 3.
Figure 4.