Mitigation of marine biofouling on tubes of open rack vaporizers using electromagnetic fields
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ABSTRACT
This study quantitatively evaluates the antifouling action of the continuous physical treatment with electromagnetic fields (EMFs) of seawater used as heat exchanger fluid in an open rack vaporizer (ORV) pilot plant to reduce the growth of biofouling on external rib-tube surfaces. The results demonstrate that the biofilm adhered on the treated rib-tubes was reduced by 33% in thickness and by 44% in dissolved solids regarding the biofilm adhered on the untreated control rib-tubes. The lower conductivity and Ca\(^{2+}\) and Mg\(^{2+}\) ionic content in the effluent of the treated seawater confirmed that the EMFs accelerated the process of ionic calcium nucleation and precipitation as calcium carbonate. The precipitation of ions dissolved affected the inter-molecular interactions among extracellular polymers, thereby weakening the biofouling film matrix and reducing its adhesion capacity. The drag of small particles by the flow of seawater had an erosive action and decreased the biofouling film thickness. Consequently, the antifouling methods treatment with EMFs allowed reduce the negative effect that the biofouling have for the heat transfer equipment used in the regasification process and keep the highest techno-economic operating conditions.

Key words | biofouling, calcium carbonate (CaCO\(_3\)), electromagnetic fields (EMFs), open rack vaporizer (ORV), regasification, seawater

INTRODUCTION
Natural gas (NG) is stored and transported on tankers as a liquid under atmospheric pressure and at \(-162\) °C, which reduces its volume 600 times, thereby making its transport profitable (Lu & Wang 2009). The liquefaction process uses common cooling systems based on the use of different refrigeration cycles (Remeljej & Hoadley 2006). Liquefied natural gas (LNG) reception terminals possess regasification plants that invert the process to provide gas to the consumer under the required pressure. The regasification process uses extended surface tube vaporizers (rib-tubes), open rack vaporizers (ORVs), which use large amounts of seawater as a heat exchanging fluid. Seawater flows in a cascade over the external surface of the tube, releasing latent heat through vaporization to the NG circulating upstream inside the tube. In the heat transfer process, the NG exits as a vapour at 5 °C and the seawater experiences heating of approximately 6 °C (Querol et al. 2010).

Seawater is a solution with a high concentration of dissolved ions and enormous biological activity (Trueba et al. 2015a). Its use in heat exchange industrial processes implies the rapid colonization of any metallic surface with which it is in contact by various physiologically versatile microbial organisms. These organisms are organized in a self-created polymeric matrix and develop micro-colonies, forming a microbiological film to which inorganic particles (salts and/or corrosion products) and the products of other types of biofouling can adhere. This biofilm formed by microorganisms (microbial biofouling or microfouling) can cause the accumulation of macro-organisms (macrofouling or macrofouling) (Eguía et al. 2008b). The adhesion of biofouling films to the external surface of vaporizer tubes in contact with seawater represents the biggest obstacle to maintaining the thermal performance of the ORV.

In most regasification plants, only global functioning parameters are supervised, and the instrumentation available cannot monitor the local conditions created by biofouling adhesion. Therefore, it is necessary to guarantee the efficiency of ORVs by developing small-scale laboratory
prototypes that allow the control of biofouling growth phases and the parameters involved in the biofouling process. These prototypes include insertion equipment (in situ) introduced inside the vaporization equipment, derived equipment (side-stream) arranged in parallel to the heat exchange process, or simulation equipment (ex situ) operating under laboratory conditions (Eguía et al. 2008a).

This equipment allows the optimization of antifouling methods (AF) and the prediction of optimal stopping times for equipment maintenance.

The AF method ‘on-line’ commonly used in regasification plants is the addition of chlorine obtained from the electro-catalytic reaction of a small volume of seawater produced in an electro-chlorination unit (Mahfouz et al. 2006). However, the use of chlorine is limited by current environmental laws (European Union 2006) regarding the discharge of free chlorine in effluents released into nature. Allowable concentrations can be lower than the effective concentrations, requiring the use of new AF methods as alternatives to chlorine.

Electromagnetic fields (EMFs) had been researched as AF treatment in a tubular heat exchanger (Shahryari & Pakshir 2008; Xiaokai 2008; Lipus et al. 2011; Trueba et al. 2014) but not in ORVs. EMFs are physical tensor fields, produced by electrically charged elements and affecting particles with electric charges, precipitating mineral ions dissolved in water as mineral salt crystals (Trueba et al. 2015a). In an aqueous medium with high ion concentrations (such as seawater), precipitates of calcium carbonate (CaCO₃) predominate, with smaller amounts of silicates and sulphates present (Trueba et al. 2014). After the crystallization process (involving the association of ions and the formation of stable nuclei to which other particles can aggregate, forming crystals), the CaCO₃ deposits on the solid–liquid interphase form a sludge that is easily removed by the effects of circulating water (Lipus et al. 2011). CaCO₃ is polymorphous, existing as calcite or aragonite (Xiaokai 2008). In heat exchangers refrigerated by fresh water, calcite is the main component of CaCO₃ crystals at temperatures below 35°C, and it adheres weakly and is easier to remove than aragonite. Aragonite precipitates at temperatures above 35°C and forms dense deposits that are difficult to remove (Trueba et al. 2015a). According to Shahryari & Pakshir (2008) or Trueba et al. (2014), it is difficult to remove aragonite crystals that grow directly on a heated surface, while it is easier to remove deposited particles originating from pre-precipitation during EMF treatment.

This study quantitatively evaluated the AF action of continuous physical treatment with EMFs of seawater used as heat exchange fluid on extended surface rib-tubes in a heat exchange-regasification pilot plant, applied under ‘clean tube’ conditions to avoid the development of biofouling on the external surface of the tubes. The objective was to maintain the ‘fouling factor’ of the heat exchange surface over time at similar values to those obtained in the initial ‘clean tube’ condition.

MATERIALS AND METHODS

Experimental setup

The pilot plant (Figure 1) consisted of a heat exchanger-regasificator formed by four independent tubes of extended surface (rib-tubes) made of aluminium, 1,050 mm in length (see dimensions in Figure 1) and arranged vertically. Seawater was pumped from Santander Bay (43°28'N, 5°48'W) to the laboratory (a distance of 250 m) by two centrifuge pumps (ITUR AU-M1 1.5/10) that were arranged in series. In the laboratory, the seawater was macro-filtered and decanted in a 1 m³ tank before being transferred by two circulation pumps (Grundfos CHI 4-50 AWG) at 1.2 bar toward untreated seawater distribution channels or through the EMF generator unit toward the treated seawater distribution channels, falling in a cascade over the external surface of the rib-tubes. The flow of seawater on each rib-tube was maintained at a constant rate using a rotameter flow meter, fixing the speed of the falling seawater at 0.5 m s⁻¹.

The EMF generator unit (Aqua-4D® 360 Serie, Planet Horizons Technologies, Switzerland) comprised two coils in series (separated by 100 mm) wrapped in a tube having a length of 804 mm and water path diameter of 50 mm. This unit generated EMFs with a strength of 15 mT and a 1 kHz (12 V) frequency under the control of the control unit. The working principle of EMFs is based on Faraday’s Law (Shahryari & Pakshir 2008; Xiaokai 2008; Lipus et al. 2011), in which the oscillation of a magnetic field induces an oscillating electric field that agitates dissolved ions, causing them to collide and crystallize into fine particles. These particles are then deposited on the surface of the tube and are easily removed by the effects of circulating water. Thus, the EMF unit produces a pulsing current to create a time varying EMF on the tube, precipitating calcium ions (Ca²⁺) and carbonate (CO₃⁻) as CaCO₃ (Trueba et al. 2014). According to Gabrielli et al. (2001), CaCO₃ precipitates erode biofilm. Likewise, according to Eguía et al. (2008b), the precipitation of dissolved ions affects the inter-molecular binding of
extracellular polymers, causing the destruction of the biofilm matrix and its detachment from the surface.

**Quantitative biofouling characterization**

The quantitative evolution of biofouling adhered to the external surface of the heat exchanger-regasification rib-tubes was followed using direct measurements (thickness and composition of the biofouling film), which depended on the solid matter deposited on the external surface of rib-tubes with known weights and dimensions. The biofouling thickness was calculated as (Eguía et al. 2007):

$$\varepsilon = \frac{\Delta M}{2\pi rl} \cdot 10^4$$

where, $\varepsilon$ is the biofouling thickness (μm), $\Delta M$ is the biofouling mass (g) or the difference between the weight of the wet biofouling and the initial unladen tube weight, $r$ is the mean tube external radius (cm), $l$ is the tube length (cm) and $\delta$ is the biofouling density (1.025 g cm$^{-3}$).

Once the total mass of biofouling was known, the water present in the composition of the biofouling film was determined as the difference between the weight of the wet biofouling and the biofouling dried at 105°C for 4 h. The amount of organic matter was determined as the difference between the weight of the dry biofouling and the biofouling incinerated at 550°C for 12 h. The rest was inorganic matter (Figure 2).
Experimental procedures

Experiments evaluated the AF action of continuous EMFs treatment applied from day one of experimentation (‘clean tube’ conditions) to avoid the development of biofouling on the external surface of the rib-tubes in a heat exchanger-regasification pilot plant using seawater as a heat exchanger fluid.

Continuous treatment with EMFs was used for 49 days on rib-tubes 1 and 2 of the heat exchanger (Figure 1). Tubes 3 and 4 were used as control rib-tubes with no AF treatment to compare the quantitative evolution of biofouling on treated and untreated rib-tubes. Therefore, as the assays were performed in duplicate, the results are expressed as the mean values of the data obtained from both rib-tubes. The accumulated weight of the deposits adhered to the tubes’ surface and their thicknesses were measured every seven days, while the composition of the biofouling film was determined at the end of the experiment, as this required the destruction of the accumulated biofouling. The experimental period extended from July to August 2012, matching the season of the year with the most biological activity in a marine environment (Eguía & Trueba 2007).

To explain the mechanism of action of EMFs and their influence on the physicochemical characteristics of seawater, measurements of pH (multimeter Crison® MM41), conductivity (multimeter Crison® MM41), and dissolved calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)) (ASTM D1126-12 2012) concentrations were taken every seven days in the influent and effluent. The sum concentrations of dissolved Ca\(^{2+}\) and Mg\(^{2+}\) is total hardness (Slowinski et al. 2012).

Statistical analysis

A Wilcoxon signed-rank test paired in statistical software IBM SPSS Statistics (22.0; http://www-01.ibm.com/software/analytics/spss/products/statistics/) was used to compare the mean difference (MD) and the standard derivation (SD) of the values to zero from direct measure (\(\Delta M\)) taken in untreated and treated rib-tubes. The test supposed that all sources of uncontrollable random variation will affect each tube equally and depended on the MD, the variability of the differences and the amount of data.

The simplest way to carry out a Wilcoxon signed-rank test was to compute the differences and then carry out a signed-rank test as follows: (1) calculate difference scores for the two variables; (2) calculate absolute values of difference scores; (3) calculate ranks for absolute values of difference scores; (4) create ranks of positive and of negative difference scores; (5) sum positive and negative ranks; (6) calculate the SD of the differences; (7) enter the appropriate confidence level (95%); (8) calculate the z-statistic (Z); and (9) obtain the p-value (Asymp. Sig. (2-tailed)) or the probability that the result was due to sampling error. A p-value of 0.05 was considered statistically significant.

RESULTS AND DISCUSSION

Evolution of biofouling on the untreated control rib-tubes

The weight evolution of the untreated control rib-tubes (Figure 3) followed a sigmoidal curve described by Eguía et al. (2007). In the initial colonization phase or induction phase, the accumulation of biofouling was barely significant (day 14 \(\Delta M = 2\%\)). In the second phase called exponential growth, the weight of the deposits increased exponentially, reaching values close to the maximum (day 35 \(\Delta M = 11\%\)). In the third phase or levelling phase, the biofouling adhesion process was stabilized at maximum values (day 49 \(\Delta M = 12\%\)). In accordance with Trueba et al. (2010), the accumulation of organic and inorganic deposits on a surface was the net result of several physical, chemical, and biological processes: (1) transport of soluble compounds and particles to the moist surface; (2) adsorption of cells by the moist surface; (3) chemical reaction with the surface; and (4) separation, detachment, or fractionation of the deposits. The sequence of these processes allowed the development and stabilization of a biofouling film.

At the end of the experiment, the average biofouling thickness taken on the untreated control rib-tubes was 2,183 \(\mu\)m. The biofouling was composed of 75% water, 20% inorganic matter and 5% organic matter (Figure 4). The concentration of dissolved solids was 55.9 mg cm\(^{-2}\). In accordance with Percival et al. (1999) and Tsai (2005), both the thickness and nature of the deposits forming the biofouling film depend on factors such as the surface roughness, the nutrient input, and the velocity of circulation of the seawater around the tube. It is not easy to associate the adhesion process of biofouling with any one of these factors. The surface roughness determines the level of bacterial adhesion. The rougher the surface is, the greater the initial amounts of microbial adhesion and the faster the subsequent colonization of the surface (Percival et al. 1998). According Vrouwenvelder et al. (2009) and Trueba et al. (2015b), the circulation velocity of seawater is determinant in the sedimentation of organic and inorganic matter,
increasing the substrate loading rate and directly influencing the composition of biofouling film. The shearing tension that water flow exerts on a wall increases proportionally to the squared velocity of the flow. In accordance with Wills et al. (2000), Battin et al. (2005) and Risse-Buhl & Küsel (2009), higher shearing tensions reduce the accumulation of microorganisms on a surface, eroding biofouling films by reducing their thickness, smoothing them, and affecting their structure by favouring the detachment of organic and inorganic deposits.

The increased presence of inorganic matter in the biofouling film showed that the natural precipitation process of salts dissolved in seawater was associated with microbial fouling processes. According to Sudmalis & Sheikholeslami (2000), the precipitation of salts is caused by an alteration in a solution equilibrium as a consequence of the aeration of seawater in the heat exchanger. The aeration reduces the content of carbon dioxide (CO₂) in the seawater, thereby increasing its pH (Wu et al. 2010). The mean increase in the pH in the effluent compared to the influent (8.12 ± 0.04) after passage through the control rib-tubes was 0.11. Therefore, the stages of nucleation, growth, and re-crystallization that induce CaCO₃ crystallization depend on the CO₂ content and pH of the solution. According to Chong & Sheikholeslami (2001), the distribution of CO₂ ions and gases in a solution is a function of pH. The natural precipitation of
salts dissolved in seawater was also revealed by variations in conductivity and Ca\(^{2+}\) and Mg\(^{2+}\) ions in seawater after its passage through the heat exchanger. Seawater conductivity is directly proportional to the temperature and to the concentration of dissolved ions and their mobility in a solution (Trueba et al. 2014). The mean conductivity in the influent was 52.8 ± 1.1 mS cm\(^{-1}\), with a mean decrease in the control tubes effluent of 0.8 mS cm\(^{-1}\). The average Ca\(^{2+}\) and Mg\(^{2+}\) ionic content in the influent during the experimentation phase was 2.59 g L\(^{-1}\), decreasing approximately 6% after its passage through the exchanger (Figure 5). In agreement with Abdel Tawab et al. (2014), this result indicated that CaCO\(_3\) naturally precipitated under experimental conditions, forming an inorganic component of the biofouling film.

These results demonstrated that biotic and abiotic factors inherent to the heat exchanger-regasification pilot plant favoured the process of biofouling adhesion to the rib-tubes, allowing to test the effectiveness of AF treatment using EMFs under conditions of maximum demand.

**Evolution of biofouling on rib-tubes treated with EMFs**

The weight evolution of rib-tubes treated with EMFs followed a similar progression to the untreated control rib-tubes (Figure 3). In the initial colonization phase or induction phase, the accumulation of biofouling was 0.6%. In the exponential growth phase, the \(\Delta M\) was 5.5%. At the end of the experiment, a mean \(\Delta M\) of 8% was measured. The accumulation of deposits resulted in an average biofouling thickness of 1,467 \(\mu\)m, which was a reduction of 33% compared to biofouling on the untreated control rib-tubes. The biofouling was composed of 79% water, 18% inorganic matter and 3% organic matter (Figure 4). The concentration of dissolved solids was 31.6 mg cm\(^{-2}\). Therefore, compared to the untreated control rib-tubes, AF treatment using EMFs removed 44% of dissolved solids. These results demonstrated the capacity of the treatment to precipitate mineral ions dissolved in seawater as crystals of mineral salts, thereby avoiding their adhesion to the tubes. According to Lipus et al. (2011), EMFs caused Ca\(^{2+}\) and CO\(_3^{2-}\) to crystallize and precipitate as CaCO\(_3\) at the solid–liquid interphase of the tube. EMFs also suppressed the formation of calcite and increased the precipitation of aragonite. Calcite is a less troublesome form of CaCO\(_3\) than aragonite because it is less adhesive and more kinetically favourable (Cho et al. 1991). CaCO\(_3\) precipitation had two effects on the adherence of biofouling film to the tube surface: (1) the precipitation of ions dissolved in seawater affected the inter-molecular interactions among extracellular polymers, thereby weakening the biofouling film matrix and reducing its adhesion capacity (Eguaña et al. 2008b); and (2) the drag of CaCO\(_3\) by the flow of seawater had an erosive action and decreased the biofouling film thickness (Gabrielli et al. 2001).

The mechanism of action of EMFs was also evident in their influence on the physicochemical characteristics of the analysed seawater. The mean pH in the influent during the experimental phase was 8.12 ± 0.04, with an average increase of 0.14 in the effluent after its passage through treated tubes. The pH of seawater depends on the pressure, temperature and carbonate (CO\(_3^{2-}\)), bicarbonate (HCO\(_3^{-}\)), borate (BO\(_3^{3-}\)), and hydrated metallic ion contents. Thus,
for certain pressure and temperature conditions, inorganic matter in general, and carbonates in particular, act as indicators and regulation mechanisms (Trueba et al. 2015a). In a saline medium, pH is a determining factor in the formation of biofouling film, according to Alimi et al. (2006), and in more alkaline water the nucleation probability increases; therefore, AF treatment with EMFs is more effective in alkaline and hard water. According to Tijing et al. (2009), the conductivity of a solution is directly proportional to the temperature and to the concentration of dissolved ions and their mobility. The mean conductivity in the influent was 52.8 ± 1.1 mS cm⁻¹, with an average decrease of 1.2 mS cm⁻¹ in the effluent after its passage through rib-tubes treated with EMFs. Therefore, EMFs demonstrated the capacity to precipitate ions dissolved in seawater, which crystallized in fine suspended particles that were not dissolved in the aqueous medium. The agitation experienced by dissolved ions treated with EMFs compensated for the decrease in conductivity caused by the precipitation of dissolved ions. Thus, the mean variation of the seawater conductivity in the effluent compared to the influent was not as significant as suggested by the final concentration of Ca²⁺ and Mg²⁺ ions in the effluent compared to the initial value. The analysis of the Ca²⁺ and Mg²⁺ ionic content allowed us to understand the physicochemical processes that occur in seawater during treatment with EMFs. The average concentration of Ca²⁺ and Mg²⁺ in seawater during the experimental period was 2.59 g L⁻¹, which decreased approximately 14% in the effluent from treated tubes (Figure 5). According to Banejad & Abdosalehi (2009), the lower concentration of Ca²⁺ and Mg²⁺ in treated seawater confirms that EMFs accelerated the nucleation process of ionic calcium and its precipitation as CaCO₃, which is easily removed by the flow of seawater, as shown by the lower concentration of inorganic matter on treated tubes.

According to Sriyutha Murthy et al. (2005), the biofouling adhered on surfaces in contact with seawater implies reduction in thermal performance, acceleration of microbiologically influenced corrosion, loss of production and increase in the maintenance cost of heat exchange equipment. The growth of biofouling in the piping systems increase the fluid frictional resistance and the pressure drop in the tube. This implies that, to maintain constant hydraulic conditions inside the tube, the energy consumption of the circulation pump must be increased (Vrouwenvelder et al. 2009). With regard to the thermal efficiency of the heat transfer process, the thermal conductivity of the biofouling film depend on the thickness, composition and the different concentrations of solids in the biofilm. In the absence of solids, the thermal effect of the biofilm is the same as that of an immobile water film with the same thickness. The deposits represent an isolation film that increase the thermal conduction resistance and decrease the overall heat transfer coefficient, which may further lead to significant loss of thermal exchange capacity (Trueba et al. 2015b). Therefore, the reduction in the thickness of the biofouling film and the reduction in the dissolved solids that partially compose the biofilm as consequence of the AF action of continuous EMFs treatment allowed keep the highest techno-economic operating conditions of the equipment.

**Statistical analysis of direct measures**

The statistical analysis of ΔM taken in untreated and treated tubes, z-statistic (Z = 2.36) and p-value (0.018 < 0.05) results, indicated a very small probability that the results occurred by chance, from a statistical standpoint. If this experiment were performed 100 times, the true value for the difference would lie in the 95% confidence interval 95 times. The 95% confidence interval confirms that the difference was statistically significant.

**CONCLUSIONS**

Under the conditions of this study, the EMFs minimized the adherence of deposits on the external surface of a rib-tube in contact with seawater, resulting in a significant difference between the weight of deposits accumulated on treated and untreated tubes.

EMFs stimulated the nucleation of ions dissolved in seawater, causing their crystallization mainly as CaCO₃, and determined the morphology of the resulting precipitates by suppressing the formation of calcite and increasing the precipitation of aragonite, which is less adhesive and more kinetically favourable. CaCO₃ present as aragonite eroded and weakened adhered deposits, resulting in a thinner biofouling film with fewer dissolved solids than films that formed without EMF treatment. Consequently, the AF treatment with EMFs allowed keep the highest techno-economic operating conditions of the equipment.

The physicochemical characteristics of the medium determine the AF capacity of EMFs, which are more effective in hard and alkaline water and are thus appropriate for use as an AF treatment in a marine medium.
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