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Electrochemical treatment of bilge wastewater

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ABSTRACT

Bilge water generated on sea ships is a mixture of water and hydrocarbons that must be further separated and treated. In this work, an innovative electrochemical reactor, with parallel plate electrodes, is operated to achieve separation and flotation of oily traces, electroreduction of contained metals and electro-oxidation of dissolved organic matter. All the environmental parameters measured in the study (i.e. colour, turbidity, COD and Pb–Zn concentration) were reduced by the process (average reduction for the 2-h experiences 80, 70, 50 and 40%, respectively). Increasing the imposed current favours all the processes occurring in the cell; however, there exists an optimum in terms of energy consumption for target organic load removal.

Keywords: Bilge wastewater; Electro-oxidation; Oily wastewater; Electrochemical flotation; Electrochemical remediation

1. Introduction

For decades, marine pollution caused by hydrocarbons has led to huge damage in aquatic ecosystems. In some cases, these hydrocarbons are discharged into the sea by oil tanker accidents; however, this corresponds to 10–15% of the total hydrocarbon discharge. The remaining percentage corresponds to small spills in loading and unloading operations, minor accidents, breakage of deposits, cleaning of tanks and waste discharge bilge [1]. The importance of this to governments and marine authorities led to the signing of international agreements to regulate the handling of hydrocarbons in sea lanes, that is, the MARPOL international convention (1973 and further modifications) that regulates the operation of bilge residues.

Bilge liquid is made up of oily residues generated from normal sea vessel operations. These residues are a mixture of water and hydrocarbons, and they are unloaded in port and transported to a hydrocarbon recovery plant, in which the oil and water are separated. The obtained aqueous phase has hydrocarbon traces as well as metallic impurities such as zinc, lead and vanadium and therefore requires additional purification treatment [1,2].

The conventional treatments of bilge wastewater are physicochemical and incineration methodologies. Physicochemical treatments consist of the phase separation and removal of the oil from the aqueous phase using sand filters, settlers and centrifugal filters, thus obtaining a hydrocarbon-rich “phase” and

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another rich in water. This last has hydrocarbon traces as well metallic impurities such as Zn and Pb, thus needing further purification treatment before final discharge [1–3]. The disadvantages of this method are high investment cost, high energy costs and the generation of exhausted filters that constitute a new solid waste to be disposed of. Incineration involves the combustion of the hydrocarbon fraction, and the disadvantages are the loss of the fuel and the generation of large amounts of unwanted CO_2, thus worsening the greenhouse effect.

It is for these reasons that have been proposed treatment techniques for aqueous wastes generated in the bilge water separation, including photocatalytic and electrochemical techniques [4–10].

In this work, an innovative electrochemical process to treat bilge wastewater is proposed. The method exploits the synergic effect encountered in the operation of a parallel plate electrochemical reactor, which is of particular interest for this type of residue, which is abundant in port cities, due to the following:

- Promotion of water-emulsified hydrocarbon traces by an applied electrical field.
- Concentration of hydrocarbon traces by froth flotation induced by electrogenerated hydrogen and oxygen microbubbles.
- Electro-oxidation of dissolved organic compounds derived from the degeneration of the high molecular weight of the original heavy fuel.
- Electroreduction of heavy metal impurities at the cathodes.

Separation of emulsions by an external magnetic field has proven effective due to magnetic forces interacting with the interfaces, separating emulsion water droplets. Currently, this technology is often considered for the separation of an aqueous phase dispersed in a dielectric oil phase with a significantly lower dielectric constant than that of the dispersed phase [11,12], for example, in removing water from diluted bitumen emulsions [13].

The separation of the oil traces by flotation (by means of electrogenerated H_2 and O_2 bubbles) has many advantages. It has a fast rate of removal of pollutant particles, and the equipment needed is very compact and thus suitable for installation where the available space is limited. Furthermore, the convenience of dosing control (rate and dimension of bubbles) simply by adjusting the current makes automation relatively easy and offers simplicity and low capital and operating costs [14,15]. The main reaction in this mechanism is the electrolytic splitting of water according to:

$$2H_2O \rightarrow O_2\,(g) + 4H^+ + 4e^- \text{(at the anode)}$$

$$4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^-$$
(closing the electrochemical circuit at the cathode)

Electrochemical oxidation has been proved to be an environmentally friendly and economically viable solution for biorefractory of organic molecules [16,17]. There are two main routes by which dissolved organic molecules can be oxidized electrochemically, that is, direct electro-oxidation, where strong oxidants are generated from the dissociative adsorption of water over anodic surfaces: superior oxides MO_{x+1} in the case of conductive metal oxide anodes and hydroxyl radicals $OH^\bullet$ in the case of semiconductor anodes. Organic molecules then react with these oxidants at the electrode surface after diffusing to the anodic surface [18,19] according to the following generalized path:

$$R + MO_{x+1} \rightarrow RO + MO_x \quad \text{or}$$

$$R + MO(OH^\bullet)_{ads} \rightarrow ROH + MO$$

where R is a generic organic molecule which being oxidized to RO or ROH, MO_{x+1} is a superior metal oxide, and $MO(OH^\bullet)$ is a metal oxide with a superficial adsorbed hydroxyl radical. In both cases, the solid reactive surface is immediately renewed.

Alternatively, or even simultaneously, the organic molecules react through an indirect path with strong oxidants electrogenerated at the anode and then diffuse to the bulk of the solution reacting in the homogeneous phase with the organic molecules. These electrogenerated species are generally persulphates, peroxides and, of particular importance in this application, active chlorine species (i.e. hypochlorous ions) derived from the natural occurrence of chloride in the water contained in bilge residue coming from sea water infiltration.

The electroxidation techniques have been effectively applied to a variety of wastewater, and a large quantity of experimental results has been published so far [20–23].

Finally, when metallic cations are present in the residue in the form of organometallic compounds or salts, these, in contact with the cathodes, accept electrons and pass to the metallic zero-valent state [24]. When this process occurs together with extensive gas generation (hydrogen), the result is poor adhesion to the cathode and thus the generation of metallic powder that can be transported by the gas to join the hydrocarbon-rich froth or alternatively can be precipitated and further separated by filtration.

2. Materials and methods

2.1. Materials

The reagents used in this research were $Na_2SO_4 \cdot 10H_2O$ 99% (Merck) and ammonium chloride 99.5% (Sigma).

The bilge water was obtained after gravimetric separation of bilge waste collected from different origins discharged at Valparaiso and San Antonio ports in Chile. The different bilge residues were homogenized to obtain a representative sample of the real wastewater considering wide variation in typically identified residue characteristics in the shipping typology discharging at the ports.

2.2. Analytical method

Turbidity, colour (APHA Platinum Cobalt Colour Scale) and chemical oxygen demand (COD) were measured using an Orbeco-Hellige water analysis system model 975-MP. Heavy metals (Pb, Zn) were measured by atomic absorption spectroscopy (Thermo Electron Corporation M series AA Spectrometer). High-performance liquid chromatography (HPLC) analysis by Prominence UFLC, Shimadzu, was carried out in order to compare the profiles of kerosene, diesel and bilge residues.

2.3. Parallel plate reactor configuration and experimental procedures

This reactor (Fig. 1) is made of fibre glass and consists of four parallel plates: two anodes located at the centre and two cathodes, one at each external position. All plates are separated at 1 cm and measure 60 cm by 15 cm. The cathodes were stainless steel, and the anodes were made of oxidized titanium. The hydraulic circuit consists of PVC pipes of ½ inch, a centrifugal pump (0.5HP) and a turbine flow meter.

The pump recycles the bilge solution from a plastic container (8 L) and sends to the reactor. The froth formed was removed from the upper part of the reactor manually. Samples were taken regularly from the plastic container.

3. Results and discussion

3.1. Wastewater characterization

Bilge waste is a mixture of varying proportions of water, lubricating oils, fuel and wash-water generated during the operation of machines on board ships. HPLC analysis was carried out to compare the profiles of kerosene, diesel and bilge residues. As can be seen in Fig. 2, there is a high degree of similarity between bilge waste and diesel. However, it was possible to observe a marked difference in the range of low retention time; this variation is attributed to short-chain organic molecules ($C < 8$) generated by thermal or chemical degradation of initially high-weight hydrocarbons in the normal operation of the ship's machinery or by partial biological-chemical degradation.

3.2. Colour removal

Colour was monitored during the electrolysis runs as it is a common and simple way to measure a parameter of the wastewater. The electrolysis was performed by varying the imposed current from 2 to 6 A without removing the froth. As a result, the froth is remixed with the bulk to a degree that depends on the level of turbulence that is in turn related to the flux rate. The results obtained are presented in Fig. 3, showing that the degradation kinetics is directly related to the imposed current. On the other hand, recording several runs at different flux rates (data not shown) confirms improved degradation performance at the maximum flux rate (60 L min^{-1}) and then is possible to conclude that the process is under mixed control (both charge transfer and diffusion control). Fig. 3 also includes a test carried out with the lowest imposed current (2 A) but with manual removal of the froth at the top of the reactor. The important effect of the froth removal can be seen, having the same effect on the removal of the colour parameter as that of doubling the current intensity (from 2 to 4 A).

3.3. Turbidity removal

From the results obtained by monitoring the turbidity parameter (see Fig. 4), it can be said that froth removal has a greater effect on this parameter. This is likely to be because the presence of the oil–water emulsion has more effect on the turbidity parameter than on the colour parameter. In this case, the effect of the current intensity enhances the bubble formation directly, and then the froth formation is enhanced; however, in the absence of froth removal, the parameter decreases very slightly and only by the action of the degradation of the organic molecules as in the case of the colour parameter.

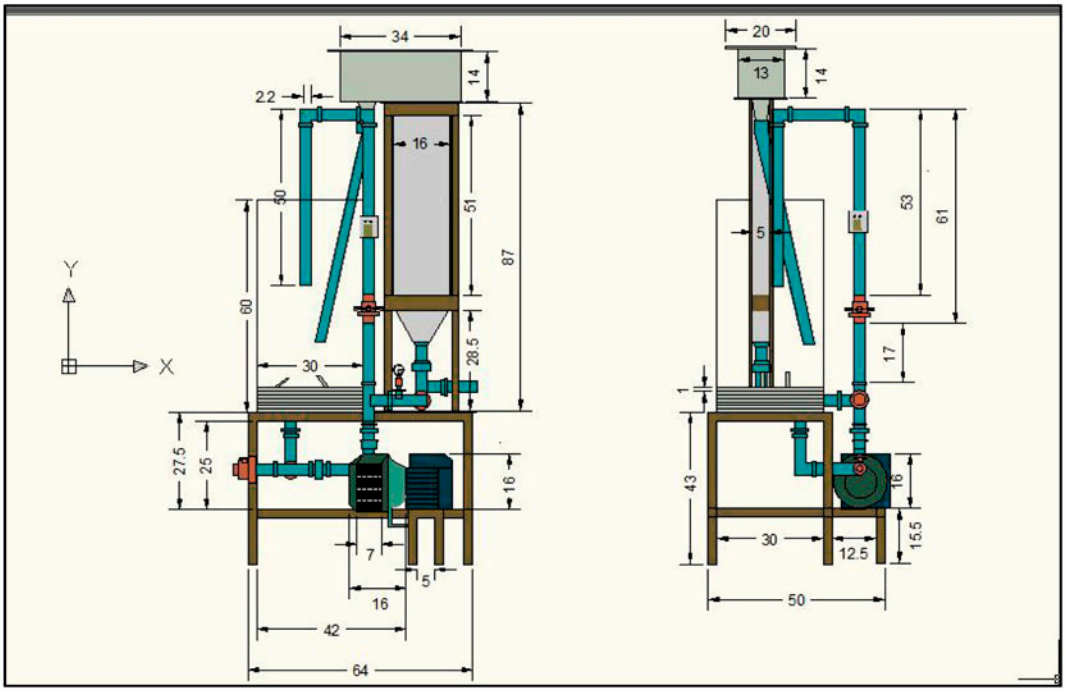

Fig. 1. Front (left) and side (right) views of the parallel plate electrochemical reactor (measurements in cm). At the bottom is placed the centrifugal pump, the liquid flows from the transparent container through the pump and enters the lower part of the reactor, and a bypass to the container in the line is used to regulate the flow rate. In the upper section of the electrochemical reactor is located a container that allows the froth removal.

3.4. Metal removal

Lead and zinc were taken as the metals mainly present in bilge residues and hence in the wastewater derived from the mechanical separation of oily water. The concentrations of both metals before electrolysis were low, corresponding to 20 mg L^{-1} for zinc and 0.1 mg L^{-1} for lead. The results of the metal monitoring are presented in Figs. 5 and 6. In the case of zinc (Fig. 5), the concentration decreases at rates proportional to the imposed current, and the use of manual removal of the froth also helps with the remediation. It is important to note that to favour the froth elimination (avoiding remixing) a fabric filter was employed, and it is probable that part of the reduced metal powder may also have been detained by the filter. The case of lead is homologous to that of zinc; the difference here is the lower removal percentage which may be attributed to a very low initial concentration and the diffusive limitation that implies.

3.5. COD behaviour

The wastewater obtained after mechanical separation of the oily fraction from the bilge residue presented an average level of COD equal to 2,500 mg L^{-1}. This key parameter was effectively reduced in all the runs performed as shown in Fig. 7 (representative results of all electrolysis performed). The data were fitted to a first-order reaction kinetics in order to estimate specific energy consumption, considering that kinetics analysis in this process is complex since none depends on only one mechanism but rather on different synergic effects between electro-oxidation, flotation and destabilization of emulsion by electric field, and then the fitting of the data is merely to compare and give a quantitative estimation. In this case, the performance is similar to the colour and metal parameters; the main difference is the lower removal after the same time considered to measure all the parameters. This could be explained by the fact that flotation is the main process that is producing rapid decay in the parameters and, after this initial decay, the process is principally the electro-oxidation of the dissolved organic molecules where the mechanism of electro-oxidation seems to be direct oxidation with some contribution of indirect oxidation promoted by the inherent amount of chlorides of this kind of wastewater (no measured) resulting in a process controlled mainly

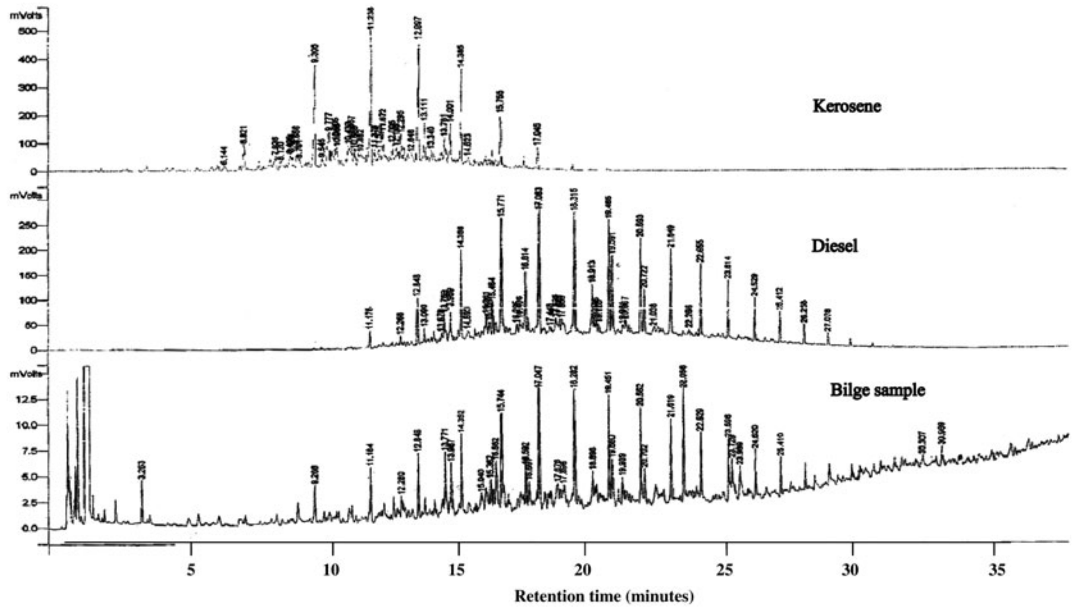

Fig. 2. HPLC profiles of kerosene, diesel and bilge sample. Principal peaks (minutes of retention time): kerosene [6,821; 9,305; 11,238; 12,897; 13,111; 14,385; 15,765; 17,045]; diesel [11,176; 12,848; 14,386; 15,771; 16,614; 17,083; 16,315; 18,913; 19,485; 20,593; 21,649; 22,655; 23,614; 24,529; 25,412; 26,258; 27,078]; bilge sample [3,263; 9,666; 11,164; 12,280; 12,846; 13,771; 13,987; 14,352; 15,744; 17,047; 18,898; 19,939; 20,562; 20,702; 21,619; 22,056; 22,629; 23,596; 24,220; 25,410; 30,307; 30,989].

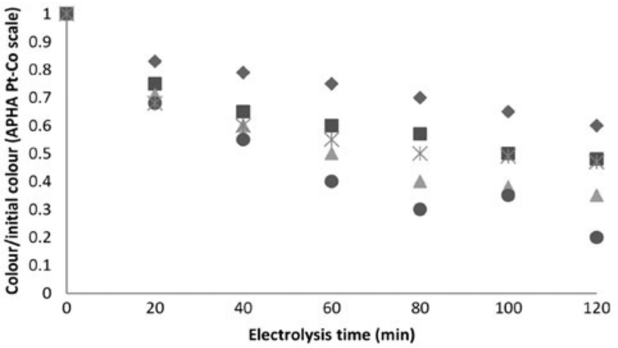

Fig. 3. Colour parameter (APHA Platinum Cobalt Colour Scale) without froth removal, diamond: 2 A; square: 4 A; triangle: 5 A, circle: 6 A; and asterisk: 2 A with froth removal.

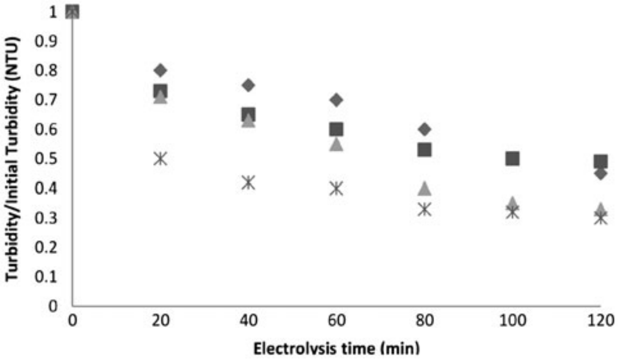

Fig. 4. Effect of current intensity on turbidity, without froth removal, diamond: 2 A; square: 4 A; triangle: 5 A and asterisk: 2 A, with froth removal.

by diffusion that follows a pseudo-first-order kinetics reaction. Fig. 7 also includes the comparison between electrolysis with and without froth removal, obtaining the same results discussed above for the other parameters. This figure also shows results with froth removal at different current intensities where it is possible to identify the effect of current on the flotation process since the increased current means that more bubbles are generated.

The difference in the results for colour and COD leads to the idea that after the first hour of electrolysis a conversion of the organic molecules occurs, reducing the colour intensity but not mineralizing out from the water.

The effect of temperature was not studied in this work; however, during the experiments, it was observed that temperature control (by means of a metal coil immersed in the agitation tank whereby cooling

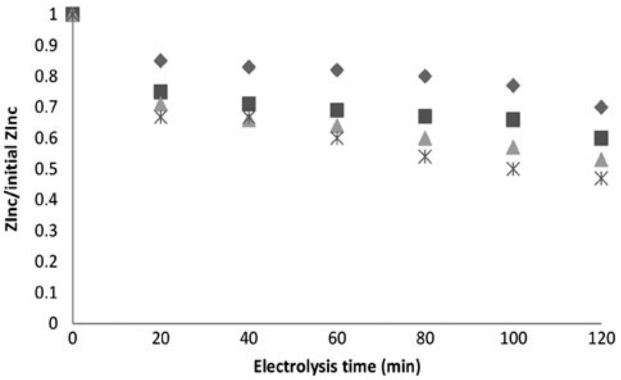

Fig. 5. Effect of current on zinc removal, without froth removal, diamond: 2 A; square: 3 A; triangle: 5 A and asterisk: 5 A, with froth removal.

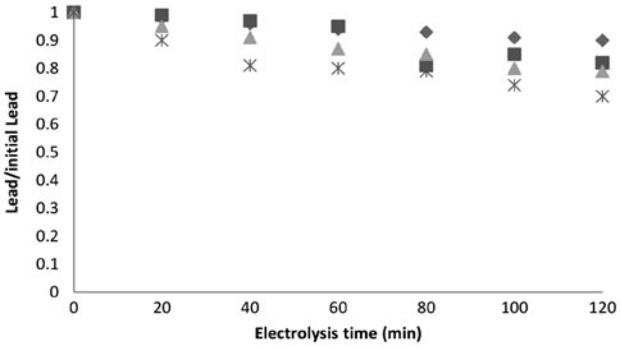

Fig. 6. Effect of current on Pb removal, without froth removal, diamond: 2 A; square: 3 A; triangle: 5 A and asterisk: 5 A, with froth removal.

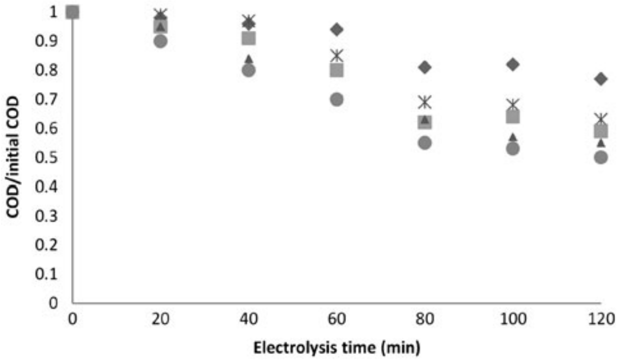

Fig. 7. Effect of current on average initial COD: diamond: 2 A without froth removal; asterisk: 2 A with froth removal; square: 4 A without froth removal; triangle: 4 A with froth removal; circle: 6 A without froth removal.

water was circulated) is very important for maintaining good froth production; otherwise, any possible improvement in kinetics related to increasing temperature is counteracted by the destabilization of the froth.

Specific energy consumption (electrical only) was calculated and tabulated (Table 1). The average cell voltage was collected for each run, and pseudo-first-order kinetics constant was estimated from the experimental results (all at 25˚C and considering froth removal). This constant was used to calculate the time for 90% COD removal, and this was in turn used to determine the electric power theoretically needed to attain degradation (at a fixed current). The results presented in Table 1 show the existence of an optimum with regard to energy consumption. This fact must be considered in the whole design of the process since, although a lower imposed current limits the specific energy consumption, it also implies the use of high electrolysis times which in turn imply higher pump times (and higher operational costs) and higher residence times and tank volumes (higher capital costs).

4. Conclusions

A parallel plate electrochemical reactor was used to treat a particular wastewater derived from the separation of the oily phase from bilge residues. All environmental parameters measured (i.e. colour, turbidity, COD and Pb–Zn concentration) were reduced by the process. The proposed treatment demonstrates the concurrence of four synergic

Table 1
Energy consumption at different current intensities (estimate values based on the behaviour shown up to the 2 h and observed pseudo-first-order kinetics)

Current (A)	Cell Voltage (V)	Time (90% removal)	Kinetic constant k (h^{-1})	Energy consumption (kWh)/(COD $_{\text{removed}}$)
3	5.4	12.4	0.186	0.08
4	6.5	9.8	0.234	0.10
5	11.0	9.5	0.240	0.21
6	12.0	9.5	0.240	0.27

phenomena: promotion of de-emulsification by electric field; electroreduction of metal compounds and formation of metallic powders; electro-oxidation of dissolved organic matter and electroflotation of oil-emulsified traces, where the latter two are the predominant mechanisms of the remediation. Increasing the imposed current favours all the processes occurring in the cell; however, there exists an optimum in terms of energy consumption for target organic load removal. A further study must be undertaken in order to find optimum conditions for the operation of the reactor that would allow the application of the technology on an industrial scale, where it may be considered as a possible pre-treatment to more typically used treatments (such as biological treatments) due to the diffusive restriction encountered at prolonged electrolysis times.

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