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Combined adsorption and electrochemical processes for the treatment of acidic aqueous phenol wastes

P. CAÑIZARES, J. LOBATO, J. GARCÍA-GÓMEZ and M.A. RODRIGO*
Department of Chemical Engineering, Faculty of Chemistry, University of Castilla-La Mancha, Campus Universitario s/n, 13004 Ciudad Real, Spain
*(*author for correspondence, e-mail: Manuel.Rodrigo@uclm.es)*

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Abstract

This paper describes a combined adsorption/electrochemical reaction device for the treatment of acidic aqueous phenol wastes. The system works in batch mode. In each operation cycle there are two stages: (i) treatment of waste, in which the organic matter contained in the waste is removed from the aqueous solution and (ii) activated carbon regeneration, in which adsorbed organics are removed from the system and converted into carbon dioxide. The system leads to successful treatment of these wastes and transforms the organics contained in the waste into carbon dioxide and electrocoagulated solids. The granular activated carbon (GAC) bed of the system achieves rapid removal of the organics, with treatment time shorter than those reported for conventional electrochemical treatments. The regeneration of the GAC is achieved by electrochemical means and efficiencies close to 80% are obtained. The energy consumption of this system is similar to those reported for other electrochemical technologies used to treat aqueous wastes.

1. Introduction

Many industrial processes (including petrochemical refineries, pulp and paper mills, pharmaceutical industries, etc.) generate wastewater flows with high concentrations of phenols and other related compounds. This makes phenol a reference pollutant in the study of the treatment of industrial organic wastewater [1–4].

The treatment of highly concentrated phenolic wastes is not a complex matter and often recovery techniques, in cases where such an approach is economically viable, or incineration technologies [5, 6], in the remaining cases, are used. When the concentration of organic material is lower, the choice of treatment technology is more difficult and several treatment processes compete [7]. The use of biological processes is normally recommended for the treatment of industrial wastes on the basis of economic considerations. However, phenolic compounds are highly toxic and biological processes are normally unsuitable for their treatment. For this reason, the treatment of low concentration phenolic wastes has to be carried out using non-biological technologies such as ozonation or chemical oxidation [8]. Among these technologies, adsorption and electrochemical oxidation are frequently referred to in the literature [9, 10].

Granular activated carbon (GAC) adsorption is frequently used for the removal of hazardous organic pollutants from wastewater [11, 12]. This technology achieves a rapid removal of the organic pollutants from the wastewater and retains them on the GAC surface. The major disadvantage associated with this technique is saturation of the GAC, which makes it necessary to regenerate the activated carbon, normally by thermal or chemical processes [13]. This regeneration process leads to the loss of GAC and represents the main component of the operating cost for this technology. It has been reported [14] that activated carbon exhibits a high adsorption capacity for phenolic compounds and is cost-effective in their treatment.

Electrochemical oxidation of organic aqueous wastes is an emerging technology and has been widely reported [1, 2, 15–17]. The technique consists of the oxidation of the organic materials contained in the wastewater directly at the anode of an electrochemical cell and/or mediated by inorganic oxidants generated at this surface. High energy consumption is the main drawback, although recent studies have shown operating costs comparable with those obtained for currently used technologies such as ozonation.

Electrochemical phenol oxidation has been widely studied [18–20]. It has been determined that the nature of the anode material is the main factor that affects the process [21–23] and that, regardless of the material used, electrochemical oxidation converts phenol into carbon dioxide through several aromatic (hydroquinone and benzoquinone) and aliphatic intermediates (maleic, fumaric and oxalic acids) [24, 25]. The most widely accepted reaction pathway is shown in Equation 1.

$$\mathrm{PhOH} \rightarrow \mathrm{HQ} \leftrightarrow \mathrm{BQ} \rightarrow \overset{\mathrm{C_4acid}\rightarrow\mathrm{C_2acid}}{\underset{\mathrm{C_2acid}}{+}} \rightarrow \mathrm{CO_2} \qquad (1)$$

In addition to electro-oxidation, there are several other electrochemical technologies available for wastewater treatment, although understanding of these processes is less advanced. One of these technologies is assisted electrochemical coagulation. This technique can be applied to wastes containing particulate matter as the contaminants and is based on the continuous production of a reagent (generated by the dissolution of the anode) that causes coagulation of the particles. The electrochemically generated coagulant destabilizes the particles and allows them to link and form flocs (flocculation process). The gas-forming side reactions that occur at the electrodes (evolution of oxygen and hydrogen) provide turbulence that improve the flocculation process and the subsequent solid/liquid separation by flotation. Clearly, the nature of the anode material, the waste characteristics and the operating conditions are the main factors that influence the efficiency of the process.

The work described here concerns a system that combines adsorption onto a GAC bed, electrochemical oxidation and coagulation of organics and electrochemical regeneration of the GAC bed. The goal of the work was to achieve the rapid removal of organics by GAC adsorption and to combine this with the final treatment using electrochemical technology.

2. Experimental

2.1. *Analytical procedures*

Carbon concentration was monitored using a Shimadzu TOC-5050 analyzer. Organic compounds were identified and quantified by liquid chromatography (HPLC). The separation and analysis of carboxylic acids was performed on a Supelcogel H column, with a mobile phase of 0.15% phosphoric acid solution at a flow rate of 0.15 $\mathrm{cm^3\ min^{-1}}$. The UV detector was set at 210 nm. Aromatics were monitored using a Nucleosil C_{18} column, with a mobile phase of 40% methanol/60% water at a flow rate of 0.50 $\mathrm{cm^3\ min^{-1}}$. In this case the UV detector was set at 270 nm. In order to quantify the total amount of iron in solution, atomic absorption measurements were performed using a SpectrAA 220FS spectrophotometer. Prior to measurement, samples containing insoluble compounds were dissolved in sulfuric acid and diluted to the measurement range.

2.2. *Experimental setup*

Figure 1 shows the experimental setup used. The apparatus consisted of a combined adsorber – electrochemical reactor inserted into a hydraulic circuit comprising one peristaltic pump, one electrolyte reservoir (3.0 $\mathrm{dm^{-3}}$), a heat exchanger, a cyclone for gas–liquid separation and a gas absorber to collect the CO_2 contained in gases evolved from the reactor into sodium hydroxide.

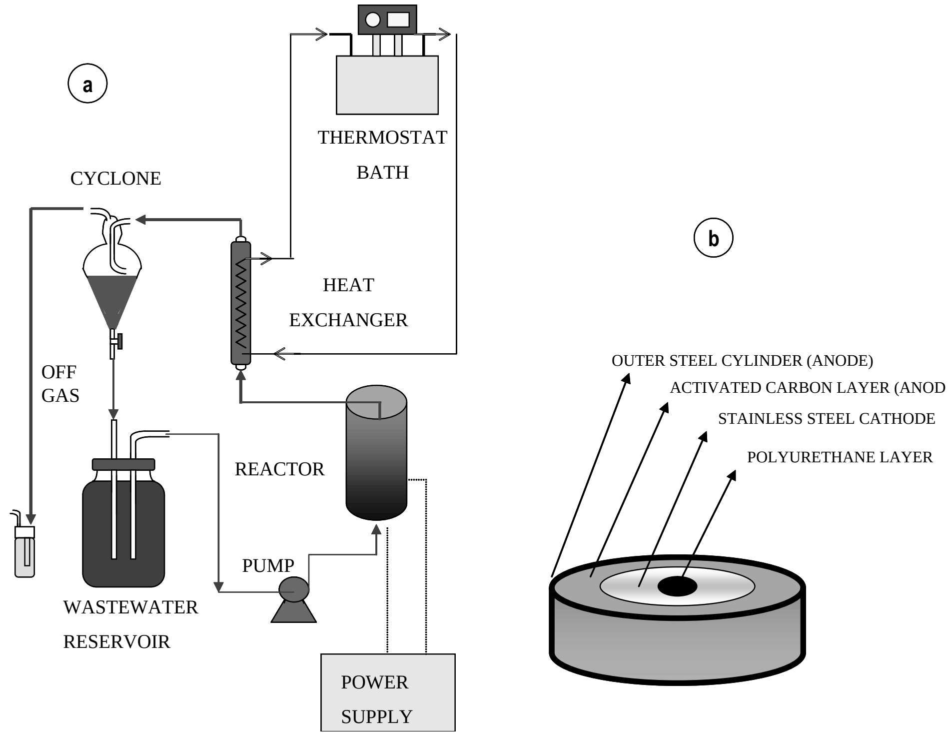

Fig. 1. (a) Lay out of the pilot plant; (b) detail of the electrochemical cell section.

The reactor consisted of two carbon steel concentrically disposed cylinders. The inner cylinder was solidly made and the outer one void. A polyurethane layer (155 cm^3 volume) was fixed around the inner cylinder and the space between this layer and the outer cylinder was filled with a GAC layer. The polyurethane layer did not allow direct contact of the GAC layer with the inner steel cylinder, but did allow wastewater to pass through it. The outer cylinder (internal surface, 288 cm^2) and the GAC (volume of the bed, 160 cm^3) were the anodes of the system. The inner cylinder was the cathode (cathode surface, 73.5 cm^2). In this system, the current flow was perpendicular to the wastewater flow. The length of the electrochemical cell was 20 cm.

2.3. *Adsorption assays*

To determine the adsorption isotherms of phenols and their main oxidation products on GAC, different quantities of GAC (in the range 0.25–1.50 g) were added to flasks containing 220 cm^3 of solutions of different concentrations (C_{s0}) of the compounds in question (phenol, hydroquinone, maleic and oxalic acids) with 5000 mg dm^{-3} of Na_2SO_4, and H_2SO_4 in appropriate amounts to give a pH of 2. The flasks were submerged in a thermostatically controlled bath that maintained the temperature at 20 ± 0.1 °C and the samples were stirred (130 r.p.m) by means of a multiple stirrer (model Ro 15, IKA-Werke Gmbh & Co, Staufen, Germany). These experimental conditions were maintained for 100 h in order to attain equilibrium. The equilibrium time had been determined previously from preliminary kinetic studies. After this time the solutions were filtered through a 0.45 μm PTFE syringe filter (Millex-HN, Millipore) and injected into the HPLC to determine the concentrations of organics in the solution (C_{se}). The quantity of organics adsorbed into the GAC was then calculated using Equation 2.

$$q_s = \frac{(C_{s_0} - C_{se})V_{solution}}{m_{GAC}} \qquad (2)$$

Prior to use the GAC was rinsed repeatedly with deionized water and then dried in an oven at 110 °C to constant weight. The GAC used in this work was supplied by PANREAC (PANREAC activated charcoal no.1). The main characteristics of this material are: surface area, 750 m^2 g^{-1}; density, 200 kg m^{-3} and particle size, 1.25–3.0 mm.

2.4. *Electrolysis assays*

Galvanostatic electrolysis was carried out to study the behavior of the system. The average composition of the wastewater used in the experiments was 1340 mg C dm^{-3} (phenol), 5000 mg Na_2SO_4 dm^{-3} and H_2SO_4 in appropriate amounts to give a pH of 2. In each experiment the pH was kept constant at 2.0 ± 0.1 during electrolysis by the continuous introduction of sulfuric acid (or sodium hydroxide) to the electrolyte reservoir, the temperature was maintained at 20 ± 0.5 °C and the electrolyte flow rate through the cell was 600 cm^3 min^{-1}. The volume of wastewater treated was 3 dm^3.

The normal operating procedure of the experimental bench-scale plant consisted of two stages: (i) treatment of the wastes, in which organic matter was removed by adsorption and electrochemical processes and (ii) GAC regeneration, in which adsorbed organics were oxidized electrochemically. This operation was studied by supplying a current intensity of 1 A to the electrochemical cell. The adsorption kinetics of the system were studied by carrying out one assay without supplying charge. The influence of the GAC bed was ascertained by conducting one assay in the experimental bench-scale plant without GAC. Finally, the influence of current was determined by performing assays with currents ranging from 1 to 10 A. Samples were taken from the electrolyte reservoir and from the absorber during electrolysis. The efficiency of the regeneration stage was studied by collecting small quantities of activated carbon (0.25 g) during the regeneration treatment and using these samples later in an adsorption experiment with 220 cm^3 of the synthetic waste used in the electrolysis study. The GAC regeneration efficiency was then calculated by Equation 3.

$$r(\%) = \frac{q_{used}}{q_{fresh}} \times 100 \qquad (3)$$

where q_{used} represents the phenol adsorbed onto the used activated carbon and q_{fresh} is the same parameter obtained for fresh activated carbon.

3. Results and discussion

3.1. *Adsorption of phenol and its oxidation products onto the GAC*

Figure 2 shows the adsorption isotherms of phenol and its typical oxidation products (hydroquinone and the carboxylic acids maleic and oxalic) onto the GAC used in this work. A typical type I adsorption isotherm can be

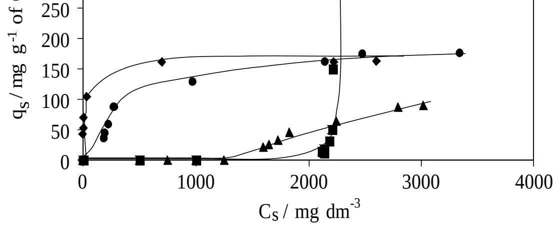

Fig. 2. Adsorption isotherms of phenol and typical oxidation intermediates: (●) phenol; (◆) hydroquinone; (■) oxalic acid; (▲) maleic acid ($T = 20$ °C).

observed for the aromatic compounds (phenol and hydroquinone) and a more unusual type III adsorption isotherm for the two carboxylic acids.

The main conclusions that can be drawn from these isotherms is that, within the range of carbon concentrations studied in this work, only phenol and hydroquinone can be adsorbed onto the activated carbon. The adsorption capacity of hydroquinone and benzoquinone is around 170 and 180 mg organic (g of GAC)$^{-1}$, respectively. Conversely, carboxylic acids are almost totally not adsorbed onto the GAC within the range of concentrations studied. Only for concentrations higher than 2000 mg dm^{-3} of carboxylic acids are some organics retained on the GAC. The resulting adsorption isotherm type is difficult to assign and further research is required. To a first approximation, however, it can be assumed that this isotherm type is due to the competitive adsorption of the carboxylic acids with sulfates present in the waste solution.

3.2. *General behavior of the batch combined adsorption/electrochemical system*

The experimental system described previously works in batch mode. In each operating cycle there are two stages. In the first stage (treatment of the waste) the waste is pumped cyclically to the reactor from the waste reservoir. In the second stage (activated carbon regeneration) this reservoir is bypassed and only a small volume is recirculated, mainly to favor evolved gas–liquid separation.

The concentration trends of phenol, intermediates, and carbon dioxide during the treatment stage (experimental conditions: $T = 20.0$ °C; $I = 1.0$ A; pH = 2.0) are shown in Figure 3. There is rapid removal of the phenol and this does not correspond with the generation of carbon dioxide. Likewise, hydroquinone was the only intermediate detected and the maximum concentration measured (20 mg dm^{-3} of C) was very small in comparison with the initial concentration of phenol contained in the waste. The presence of carboxylic acids was not detected by HPLC in the treatment process.

In addition to the species shown in Figure 3, yellow insoluble compounds were formed in the electrolysis. These solids can only be dissolved in very strongly acidic media (pH < 1). The concentration of the materials was low (<300 mg dm^{-3} of suspended solids at the end of the treatment stage) and they were mixed with activated carbon detached by erosion from the bed, a situation that made it difficult to quantify these materials. The volatile content of the solids was 25% (measured gravimetrically after combustion in an oven at 550 °C), indicating that the solid contained inorganic materials as well as carbon compounds.

Figure 4 shows the evolution of the soluble, total, and particulate iron concentrations during electrolysis treatment. The total iron concentration increased in a linear manner with the charge passed. The same trend for the soluble iron is observed, although lower values are reached. The particulate iron concentration (difference between total and soluble iron concentration) increases with the charge up to 15 A h dm^{-3} and thereafter remains constant.

Given the fact that some Fe^{3+} ions are dissolved from the carbon steel anode and that the solids contained iron, and also taking into account the characteristics of the solids, it seems reasonable that these compounds were formed by electrochemically assisted coagulation involving the organic compounds presented in the waste (phenol and organic intermediates) upon treatment with ferric ion. It has been reported that phenol [21, 26, 27] and organic acids [28, 29] can interact chemically with trivalent cations to form insoluble species by combined complexation, precipitation and/or coagulation processes. This explains why carboxylic acids were not detected in the treatment, in spite of these compounds being typical intermediates in the oxidation of phenol.

When the concentration of organic matter decreases to a value close to zero, it is assumed that stage 1 is complete. At this moment all organics are transformed into electrocoagulated solids or adsorbed onto the GAC. Only a small amount of organics was, at this stage, transformed into carbon dioxide. The second stage in the batch operation mode of the combined adsorption/electrochemical system consists of the elec-

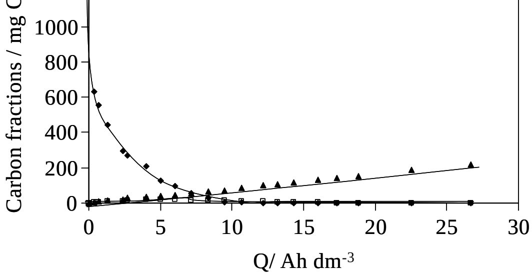

Fig. 3. Variation of soluble carbon compounds in the treatment stage: (◆) phenol; (□) hydroquinone; (▲) carbon dioxide.

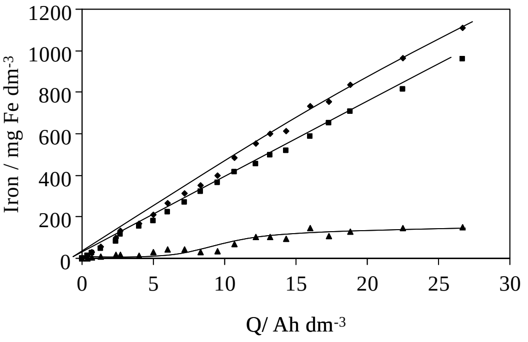

Fig. 4. Variation of the different iron fractions during electrolysis treatment of the wastewater: (◆) total iron; (■) soluble iron; (▲) particulate iron.

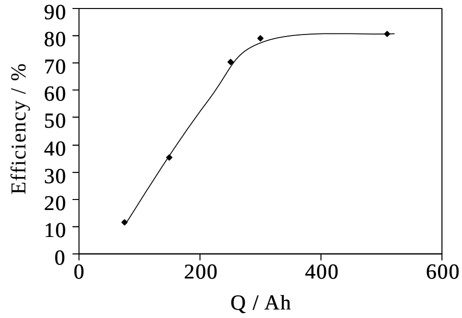

Fig. 5. Variation of the regeneration efficiency of the GAC with the specific current charge passed.

trochemical regeneration of the GAC. This is achieved through by passing the treated waste contained in the reservoir and circulating only a small volume (about 10%) through the reactor to favour gas–liquid separation. A current of 1 A was supplied.

Several samples of activated carbon were taken during this stage in order to measure the GAC regeneration efficiency. Figure 5 shows the trend of this parameter with charge passed. The efficiency increases in a linear manner to reach a value of 80% of the adsorption capacity of fresh GAC.

The effect of running for several cycles was assessed by measuring the maximum GAC regeneration efficiency for four consecutive cycles. Results are shown in Figure 6. A linear decrease in regeneration efficiency occurs on increasing the number of operation cycles.

The operating cost was estimated by considering both the energy required for the treatment and the regeneration step. The cell potential was maintained at 3.5 V. Taking into account the COD of the waste (4165 mg dm^{-3}) and that the volume of the treated waste was 3 dm^3, the energy consumption in the treatment stage was 21.01 kWh kg^{-1} COD and the energy required in the regeneration was 63.02 kWh kg^{-1} COD. The total energy required (84.03 kWh kg COD^{-1}) is within the range [22, 30] of energy consumptions for electrochemical processes, making this a promising technique for waste treatment since rapid decontamination of water can be achieved with total costs similar to those for other electrochemical technologies.

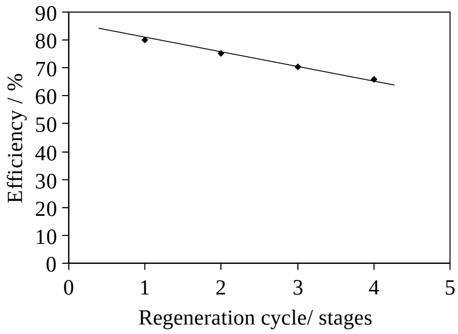

Fig. 6. Influence of the number of cycles in the total regeneration efficiency of the GAC bed.

3.3. *Improvements in adsorption processes*

Figure 7 shows the performance of the system both with (system 1) and without (system 2) the GAC bed (experimental conditions: $T = 20.0$ °C; $I = 3.0$ A; $pH = 2.0$). A more rapid removal of the organics in the presence of GAC is evident due to adsorption processes. In both systems the removal of organics does not correspond with the carbon dioxide generation. This can be explained by taking into account that oxidation processes are not the only ones occurring. Thus, in system 2 organics can be oxidized or electrocoagulated and in system 1 these compounds can also be adsorbed onto the GAC bed. The concentration of carbon dioxide increase in a linear way in system 1 and in an inverse exponential way in system 2. For this reason, although the initial formation rates of CO_2 are lower in system 1, both systems reached the same concentration at the end of the assays. Likewise, iron(III) arising from anode dissolution was measured in both systems. The evolution of this parameter in system 2 was linear, as was that obtained for the system with the activated carbon bed, and the iron generation rate is also very similar: the system without activated carbon generates 46.54 mg iron $(A\ h)^{-1}$, while the system with activated carbon generates 44.02 mg iron $(A\ h)^{-1}$ under the same operating conditions.

In both systems, the similar carbon dioxide and iron generation rates indicate that most of the electrochemical processes occur on the steel surface and that the GAC bed acts mainly as an adsorbent and not as an electrode.

In spite of these similarities, the amount of solids formed in system 1 was considerably lower than that formed in system 2 (300 mg dm^{-3} in system 1 and 600 mg dm^{-3} in system 2). This can be explained by bearing in mind that the GAC bed acts as a filter and retains some proportion of the solids formed. For this reason the filter needed to be cleaned (by back-flush) after the regeneration stage before starting a new cycle.

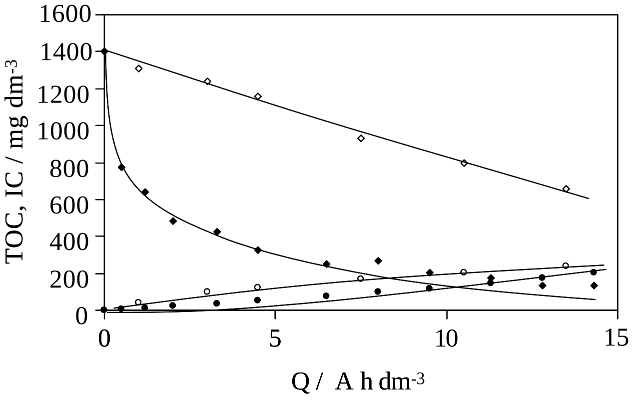

Fig. 7. Comparison of the evolution of the treatment process with and without the GAC bed. system 1: (◆) TOC, (●) IC; system 2: (◇) TOC, (○) IC.

3.4. *Influence of current*

In order to study the effect of the main operating parameter of an electrochemical oxidation process, several assays were carried out at different currents (ranging form 0.0 to 10.0 A). In all experiments the cell potential remained constant during the assay, indicating that passivation did not take place. Figure 8 shows the relation between applied current and the resulting voltage. As expected, the voltage increases almost linearly with current.

Figure 9 shows the total organic carbon (TOC) variation. TOC decreases to a constant value (equilibrium) when no current is passed, since under these conditions only adsorption onto GAC occurs. Conversely, TOC decreases linearly (after the initial rapid adsorption) when current is passed. The oxidation rates increase with current and, as a consequence, smaller concentrations of TOC are reached at lower oxidation times. However, the small increase in oxidation rate with current, together with the large increase in the resulting cell voltage, ruled out the use of high currents from an economic point of view.

Figure 10 shows the variation of total suspended solids and carbon dioxide at the end of stage 1 as a function of current. It can be observed that high currents (consequently high voltages) favor carbon dioxide formation over electrochemically assisted coagulation.

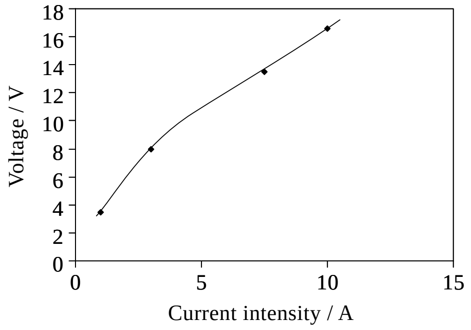

Fig. 8. Voltage of the experimental setup obtained for each current intensity applied.

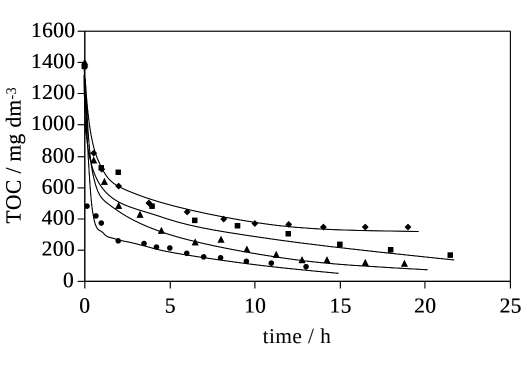

Fig. 9. TOC variation with current: (◆) 0.0 A; (■) 1.0 A; (▲) 3.0 A; (●) 10.0 A.

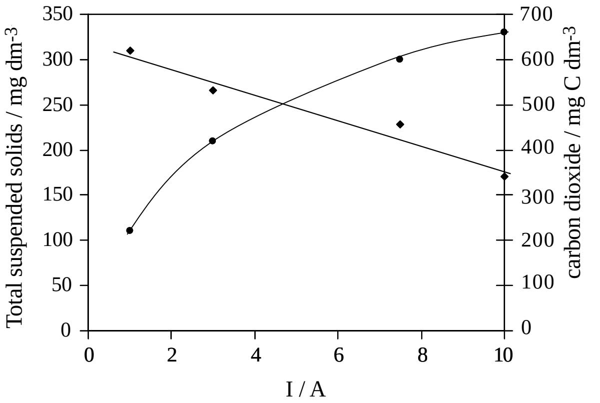

Fig. 10. Variation of the total suspended solids and carbon dioxide at the end of stage 1 as a function of the current: (◆) total suspended solids; (●) carbon dioxide.

4. Conclusions

A combined electrochemical reactor/GAC adsorber has been studied for the treatment of acidic aqueous phenol wastes. The following conclusions can be drawn:

1. The combined system can successfully treat acidic aqueous phenol wastes, transforming the organics into electrocoagulated compounds and carbon dioxide.
2. The GAC bed achieves a rapid removal of the organics. The bed has a high adsorption capacity for phenol and hydroquinone but almost no adsorption capacity for carboxylic acids.
3. The oxidation of phenol is practically a direct conversion of the compound into carbon dioxide.
4. Energy costs associated with this system are similar to those reported for other electrochemical treatment technologies.
5. High currents favor carbon dioxide formation over electrochemically assisted coagulation.
6. The small increase in oxidation rate with current, together with the large increase in the resulting cell voltage, ruled out, from an economic point of view, the use of high currents in the operation of the process.

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