



## ELECTROCHEMICAL TREATMENT OF VINASSE FROM BEET MOLASSES

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### ABSTRACT

In this work the results from a new technique are presented in which the vinasse from beet molasses is treated by electrolysis. By this technique, sodium chloride is added in the wastewater and the mixture passes through an electrolytic cell. A number of experiments was run in a laboratory scale pilot plant. In the electrochemical process chlorine, chlorates and other oxidants are produced. Because of the strong oxidizing potential of the chemicals produced the organic pollutants were wet oxidized to carbon dioxide and water. The results obtained have shown that the treatment depends on the catalytic activity of the anode used, the COD loading rates and the pH of the solution. The best results for sodium chloride concentration 4%, temperature 42°C, 72,000 mg/l influent COD conc were found to be the following: pH 9.5 and vinasse feed rate 30 ml/min. Under these conditions the COD reduction was 20 g/h/A/m<sup>2</sup> and the COD conc of the effluent was 8000 mg/l. These results have shown that the electrochemical treatment of beet vinasse can be efficient and feasible. © 1997 IAWQ. Published by Elsevier Science Ltd

### KEYWORDS

Beet molasses; distillery slop; electrolysis; treatment; vinasse; wet oxidation.

### INTRODUCTION

The liquid waste under examination is produced from alcohol industries that use beet molasses as primary raw material, it is named vinasse and is the residue from the fermentation and distillation processes. The primary raw materials for these processes in Greece are molasses, mainly from beets but also from raisins and wines. The alcohol distilleries are typical of traditional Greek agricultural industries, and are of great importance for the national economy (Vlyssides and Zouboulis, 1993). The nine Greek distilleries have a total production of 170,000 litres alcohol/day and 2000 m<sup>3</sup>/day of liquid wastes. Vlyssides (1986, 1987); Vlyssides *et al* (1988) calculated that for 1 t of anhydrous alcohol, 16 m<sup>3</sup> of vinasses are produced and 60 m<sup>3</sup> of cooling water are necessary.

Although beet vinasse is not characterized as toxic, because it does not contain toxic metals or other chemicals dangerous to the natural ecosystem, its free disposal creates a serious environmental problem due to its high organic load (25,000-45,000 mg BOD<sub>5</sub>/litre and 70,000-120,000 mg COD/litre), high nitrogen content (4000-6000 mg/l) and high sulfates content (7000-9000 mg/l) (Table 1). Several chemical or

biological treatment methods have been examined for the safe disposal of vinasses; among them, chemical or biological treatment (aerobic or anaerobic classical methods, trickling filters, lagoons, etc.), evaporation-condensation with or without combustion, direct dispersion on soil as a fertilizer, etc. (Sheehan and Greenfield, 1980; Rao, 1972).

A common feature of all these methods is their ineffective final results as well as their relatively high fixed and operational costs, and sometimes simultaneous creation of other hazardous byproducts/pollutants (Vlyssides and Zouboulis, 1993). Although anaerobic treatment presents a number of advantages including the quite high degree of purification with high-organic-load feeds, the low nutrient requirements and the generation of a combustible biogas that can reduce operational costs (Lettinga *et al.*, 1979, 1981; Espinosa *et al.*, 1995), Vlyssides *et al.* (1988) showed that anaerobic treatment alone is not a solution to the vinasse treatment problem. It is essential therefore that new techniques should be developed in order to solve the problem of the vinasse from beet molasses. The electrolysis technique presented in this work gives a new approach to the solution of the vinasse problem.

Table 1. The composition of vinasse from beet molasses (Vlyssides and Zouboulis, 1993)

Parameters	Total	Liquid Phase	Solid Phase
Total Solids, mg/l	81200		
Total Volatile Solids, mg/l	60226		
Suspended Solids, mg/l	3837		
COD, mg/l	72000		
Hydrocarbons, mg/l	5526.1	5264.9	261.1
Lipids, mg/l	3813.6	3633.3	180.2
Proteins, mg/l	27656.7	26349.7	1306.9
Unknown Substances, mg/l	23229.6	22131.8	1097.7
Inorganic Substances, mg/l	20973.9	19982.8	991.1
Total Phosphates, mg/l	91		
Inorganic Nitrogen (Total), mg/l	840		
Total Sulfates, mg/l	4520		
Total Nitrogen, mg/l	7340		

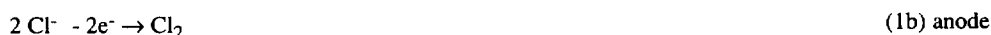
#### THEORETICAL APPROACH

The electrochemical reactions which take place during the electrolysis are complicated and not entirely known. For the time being only assumptions can be made, based on the products that can be determined ( $\text{Cl}_2$ ,  $\text{ClO}_2$ ,  $\text{O}_3$ ,  $\text{OH}^-$ ,  $\text{O}^-$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ).

A possible mechanism of electrolysis is described below. The electrolytic evolution of hydrogen in acid and alkaline solutions occurs in different ways. In acid solutions, the source of hydrogen is hydroxonium ions which are discharged at the cathode to form hydrogen gas (Antropov, 1977; Prentice, 1991).



At the anode, chloride ions are oxidised:



For alkaline solutions it is assumed that electrons are directly added on to water molecules which then decompose to yield hydrogen and hydroxyl ions :



It is believed that reaction (2a) may also proceed in acid solutions but at high current densities (Antropov, 1977).

At the anode, chloride ions are oxidised:



The anodic dischargement of the water takes place simultaneously, forming hydroxyl radicals which are absorbed on the active sites of the electrode surface M [ ] (Comminellis, 1992).



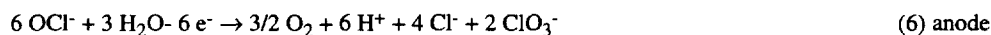
The main by-reaction during this procedure is the oxygen formation according to the following reaction:



The reaction that takes place in alkaline solutions in the electrolytic cell is as follows (Prentice, 1991):



At high  $\text{OCl}^-$  concentrations, elevated temperature and turbulent flow conditions, the mass transport reactions are the following (Pletcher and Walsh, 1990) :



The electrochemical oxidation of aqueous solutions which contain organic matter, by the use of traditional anodes (Ti/Pt, Ti/PbO, Ti/IrO<sub>2</sub>...) proceeds in two steps (Comminellis, 1992).

The first step is the reaction (3). After this, the absorbed hydroxyl radicals oxidize the organic matter:



where RO represents the oxidized organic matter which can be oxidized continuously from the hydroxyl radicals which are formed continuously too, since the anodic dischargement of the water goes on.

Therefore it is concluded that in acid solutions, chlorine is the main oxidative agent for the oxidation of organic matter. In alkaline solutions a cycle of chloride - chlorine - chloride takes place, which produces  $\text{OCl}^-$ ,  $\text{ClO}_3^-$  and free hydroxyl radicals. These radicals are strong oxidative agents and have a dominant presence and action in alkaline solutions.

## MATERIALS AND METHODS

### Description of the laboratory pilot plant

The experimental plant (Figure 1) consists of the electrolytic cell, the recirculation reactor, the wastewater feed system, the pH correction system, and the cooling system of the wastewater.

**Electrolytic cell.** The electrolytic cell consists of the cathode, which is a stainless steel 304 cylinder of 20 cm diameter and of the anode, which is located in the centre of the cylinder and which consists of titanium alloy, measuring 48cm long and 2.54 cm diameter, covered by platinum alloy foil approximately 0.25mm. The electrodes were operated under 15 D.C. voltage and 100 amperage.

**Recirculation reactor.** The recirculation reactor (V) includes a vessel of 15 litres, which contains the wastewater to be treated, and a submerged centrifugal pump (P) of 40 l/min flow rate, which recirculates continuously the reactor content into the electrolytic cell.

**Wastewater feed system.** The wastewater feed system consists of a storage vessel of the wastewater and a dosing pump (PP-1).

**pH correction system.** The pH correction system consists of a pH indicator controller (pHIC), two vessels that contain hydrochloric acid and sodium hydroxide, and two dosing pumps (PP-2) and (PP-3) respectively. Depending on the desirable pH value, the (PP-2) and (PP-3) pumps supply the reactor content with alkali or acid. The recirculation of the (P) pump is high enough so that additional stirring for the homogenisation of the chemicals added is not required.

**Cooling system.** The cooling system includes a temperature indicator controller (TIC), an electric valve for the water and a water cooling coil, which is located in the reactor. When the temperature of the water increases over the desirable value, then cooling water circulates in the coil, until the temperature returns to the desirable value.

The change of redox potential in the reactor is continuously recorded by the RI indicator. The treated wastewater is discharged through the reactor's overflow.

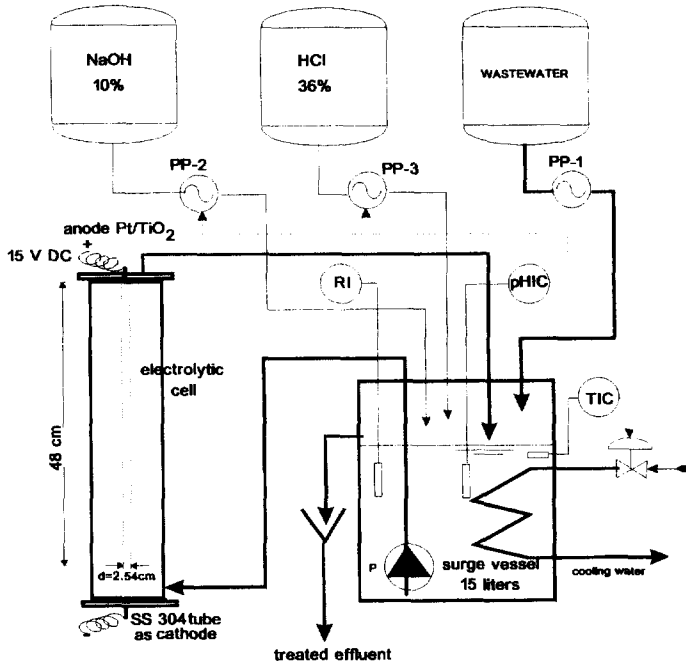


Figure 1. Experimental laboratory pilot plant. (P = submerged recirculating pump, PP = peristaltic dosing pumps, TIC = temperature indicator controller, pHIC = pH indicator controller, RI = redox indicator).

## Methodology

The efficiency of the electrolytic cell was studied in relation to the wastewater feed rate (10, 20, 30 ml/min) and the pH values (4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5). Both NaCl consistency of the wastewaters and temperature at which the experiments were carried out, remained stable during all the experiments and equal to 4% (w/v) and 42°C respectively. The experiments were of continuous operation and each one lasted until

the steady state was approached. This was accomplished after 12 to 20 hours. Every half an hour samples were taken from the reactor and COD, free chlorine, the total oxidants except the chlorine and the chlorate ions were measured. When the concentrations of the former were stabilised, the experiment was stopped.

### Methods of analyses

The COD and free chlorine analyses were carried out according to the Standard Methods for the Examination of Water and Wastewater. The determination of the total oxidants except the chlorine was carried out according to Wilk (1989), and the chlorate ions were determined according to Vogel (1969).

## RESULTS AND DISCUSSION

As shown in Figure 2 the COD concentration of the effluents decreases as the pH increases. At the wastewater flow rate 10 ml/min, COD effluent was reduced from 60,000 mg/l at pH=4.5 to 8000 mg/l at pH=9.5. The decrease of COD at the flow rate 20 ml/min was not so intensive, as COD effluent was reduced from 50,000 mg/l at pH=4.5 to 28,000 mg/l at pH=9.5. At the wastewater flow rate 30 ml/min finally COD declines from 62,000 mg/l at pH=4.5 to 28,000 mg/l at pH=9.5. The COD reduction at pH=9.5 is 88%, 44% and 55% for 10, 20 and 30 ml/min wastewater feeding respectively.

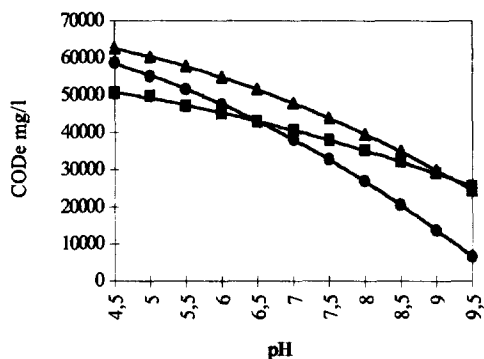


Figure 2. Steady state COD effluent concentrations against pH in different wastewater flow rates. ● 10 ml/min; ■ 20 ml/min; ▲ 30 ml/min.

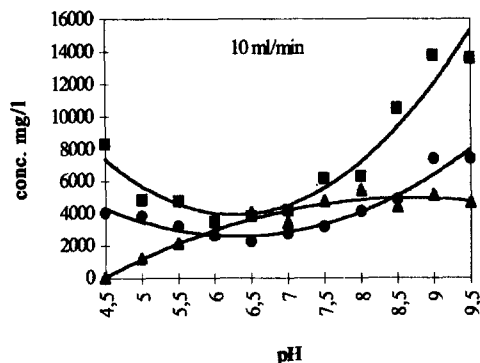


Figure 3. Steady state effluent concentrations against pH in 10 ml/min wastewater flow rate. ■ total oxidants except chlorine; ● free chlorine; ▲ chlorate ions.

In Figures 3, 4 and 5 the concentrations of the oxidants are presented for wastewater flows 10, 20 and 30 ml/min respectively.

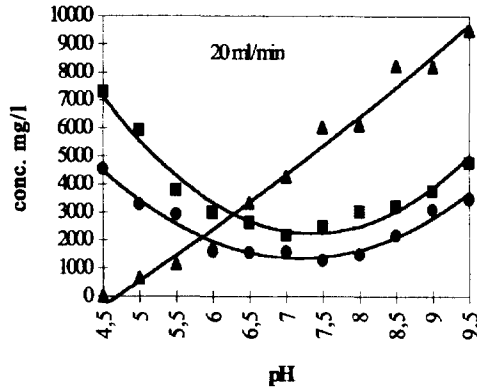


Figure 4. Steady state effluent concentrations against pH in 20 ml/min wastewater flow rate. ■ total oxidants except chlorine; ● free chlorine; ▲ chlorate ions.

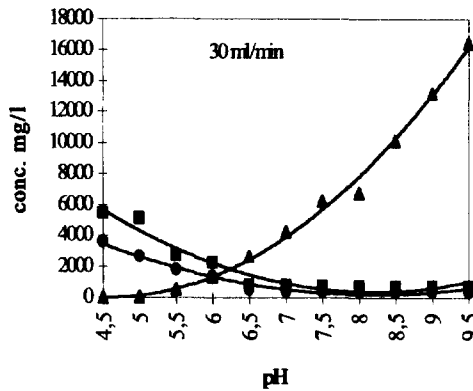


Figure 5. Steady state effluent concentrations against pH in 30 ml/min wastewater flow rate. ■ total oxidants except chlorine; ● free chlorine; ▲ chlorate ions.

The concentration of free chlorine ( $\text{Cl}_2 + \text{OCl}^-$ ) and the rest of the oxidants decrease when the solution was acid. As soon as it entered the alkaline range the oxidants concentration started to increase as much as the pH was rising. This is observed in the case of 10 and 20 ml/min flow rate of the wastewater. In the case of 10 ml/min and at pH=4.5 to 7.5 chlorates increased from 0 to 4000 mg/l and then this value remained stable to pH-9.5. At the rate of 20 ml/min chlorates increased proportionally with the pH from 0 to 9500 mg/l, while at the rate of 30 ml/min chlorates increased from 0 to 16,000 mg/l respectively.

The experimental results seem to follow the mechanism proposed in the Theoretical Approach. In acid solutions the products of the electrolysis are hydrogen and chlorine only, while in alkaline solutions  $\text{OH}^-$ ,  $\text{O}_2$ ,  $\text{Cl}^-$ ,  $\text{OCl}^-$  and  $\text{ClO}_3^-$  are also formed.

Figure 5 shows that at flow rate of 30 ml/min the oxidants and the free chlorine concentration decline at increasing pH, while the chlorates tend to increase as indicated previously.

The oxidants reduction could be explained if we consider the mechanism of organic matter reduction.

As proposed above (Theoretical Approach) the organic matter is oxidised by the hydroxyl radicals which are formed in the intermediate stages of hydroxyl anions formation. Thus, the oxidants decline may be correlated with the COD reduction. This is confirmed by Figure 6.

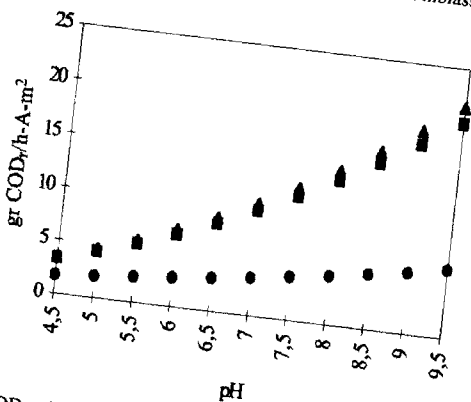


Figure 6. COD reduction/h/A/m<sup>2</sup> against pH in different wastewater flow rates. ● 10 ml/min; ■ 20 ml/min; ▲ 30 ml/min.

The efficiency of the anode in terms of grams of COD reduction per hour, per ampere and per m<sup>2</sup> of electrode surface increased with increasing flow rate as depicted in Figure 6. At pH value 4.5 the efficiency of the anode is independent of the COD loading. The efficiency of the anode increases proportionally with pH, but the gradient depends on the feed rate. Thus, at feed rate 10 ml/min, the efficiency increased from 1 g CODreduction/h/A/m<sup>2</sup> at pH value 4.5 to 4 g CODreduction/h/A/m<sup>2</sup> at pH value 9.5, while at feed rate of 20 and 30 ml/min the efficiency increased from 2 at pH value 4.5 to 20 at pH value 9.5. From Figure 6 it is concluded that the electrode efficiency increases slightly above the feed rate of 20 ml/min.

From Figure 5, it is shown that the free chlorine and total oxidants except chlorine decline, while the chlorates concentration increases. It is also deduced that free chlorine and oxidants, except the chlorates, play an active role in the oxidation of the organic matter.

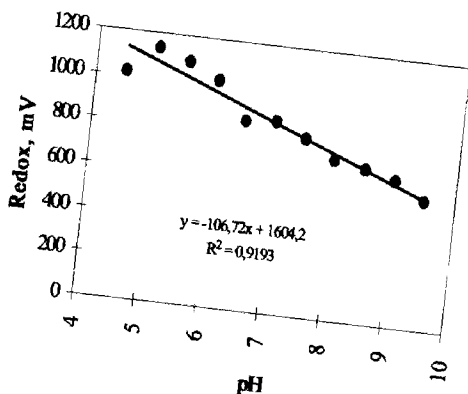


Figure 7. Steady state redox values against pH.

In Figure 7 the relation of pH values to the redox measurements is shown for all feed rates. From this and from the good fitting of the experimental data it is deduced that the redox value is independent of the feed rate and depends on pH.

### CONCLUSIONS

From the investigation run in the laboratory scale pilot plant it can be proved that the electrolytic oxidation of vinasse is effective. For NaCl electrolytic agent concentration 4% (w/v) the efficiency of the electrolysis depends on pH and the COD loading in g/min. The most effective oxidation conditions for 4% NaCl

concentration were found to be at pH value 9.5 and at feed rate of 30 ml/min (2.16 g COD/min). Under these conditions the efficiency of the electrolysis was measured at 20 g CODreduction/h/A/m<sup>2</sup> and the COD concentration in a continuous operation system was reduced from 72,000 in the influent to 8000 mg/l in the effluent. These results can be considered encouraging for the application of the method for the distillery slop.

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