



Electrochemical treatment in relation to pH of domestic wastewater using Ti/Pt electrodes

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Abstract

This paper describes an electrochemical treatment of domestic wastewater (DW) using 0.8% (w/v) sodium chloride as electrolyte. In this technique, DW was passed through an electrolytic cell using Ti/Pt as anode and Stainless Steel 304 as cathode. Due to the strong oxidizing potential of the chemicals produced (chlorine, oxygen, hydroxyl radicals and other oxidants), the organic pollutants and nutrients (organic nitrogen, phosphorous) were wet oxidized to carbon dioxide, and nitrogen as well as phosphorous was precipitated as $\text{Ca}_3(\text{PO}_4)_2$. Experiments were run in a continuous, laboratory-scale, pilot plant, at 40 °C and the efficiency of oxidation was studied in relation to pH. It was found that in alkaline conditions the electrolysis was more efficient. At pH 9, NaCl concentration 0.8% (w/v), current density 0.075 A/cm² and for 1 h of electrolysis, COD was reduced by 89%, volatile suspended solids (VSS) by 90%, ammonia nitrogen by 82% and total phosphorous by 98%. The efficiency of electrolysis went up to 35 g COD_r/(h m² A) and the energy consumption to 12.4 kWh/kg COD_r. It is concluded that the application of electrolytic oxidation of DW is more advantageous compared to conventional biological treatment especially for small works. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Domestic wastewater; Electrochemical treatment; Organic oxidation; Nutrient removal

1. Introduction

Domestic wastewater (DW) is a complex mixture of suspended and dissolved materials; both categories constitute organic pollution. The strength and quality of DW effluent is described mainly in terms of its biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), total phosphorous (TP) and total nitrogen (TN) content. The total nitrogen contains the organic nitrogen (ON) and inorganic nitrogen (IN).

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The ON consists of nitrogen contained in nitrogenous organic compounds and ammonia (N–NH₄). The IN is comprised from the nitrogen in the form of nitrous and nitrates (N–NO₂ and N–NO₃). Ammonia is the main product either of reducing (anaerobic) or moderating oxidative (aerobic) biological decompositions of nitrogenous organic compounds, while IN is mainly the product of strong oxidative biological actions of nitrification of N–NH₄. The N–NO₂ is an intermediate product of biological oxidation of ammonia nitrogen to nitrates. The TP and TN content of DW constitute the so called “nutrients” due to their environmental effect on eutrophication of waters [1,2].

Biological waste treatment is currently the most widely used method for removing organic pollutants and nutrients from DW. The most versatile and efficient among the available processes is the A²/O activated sludge system where a combination of an anaerobic, an anoxic and an aerobic environment develops and maintains biological nitrification of excess ammonia, denitrification of produced nitrates and excess phosphorous uptake by phosphate-accumulating bacteria [3].

Generally A²/O systems are very complicated and difficult to stabilize and optimize and they are easy to fail down when there is a strong toxicity in the influent. There are many critical parameters of the system which respond dynamically to any influent disturbance, [4–9].

Recently there has been increasing interest in the use of electrochemical methods for the treatment of wastewaters [10]. Electrochemical methods have been successfully applied in the purification of wastewater from dye production [11], from alcohol production [12], from olive oil production [13], from tanneries [14–18], from textiles [19], wastewater containing cyanides [20], phenols [21,22], EDTA [23], landfill leachates [24] and domestic sewage [25,26].

This study deals with a physicochemical approach for the treatment of DW based on the principle of oxidative degradation of all its organic compounds in an electrolysis system.

2. Materials and methods

2.1. The laboratory pilot plant

The experimental plant consisted of the electrolytic cell, the recirculation system, the pH-correction system and the cooling system for the wastewater.

2.1.1. The electrolytic cell

The electrolytic cell consisted of the cathode, which was a Stainless Steel 304 cylinder of 20 cm diameter, and of the anode, which was located in the center of the cylinder and which was made of titanium alloy, measuring 48 cm in length and 2.54 cm in diameter, covered by platinum alloy foil approximately 0.25 mm thick. The electrodes were operated at 15 V dc and 100 A. The cylinder reactor volume was about 15 l.

2.1.2. The DW feeding system

The DW feeding system included a vessel of 100 l, which contained the wastewater to be treated, and a dosing pump (PP-3), which was continuously feeding the raw DW into the electrolytic cell.

2.1.3. The recirculation system

The recirculation system included a reactor of 5 l, which contained the DW to be treated, and a centrifugal pump (P) of 40 l/min flow rate, which continuously recirculated the reactor contents into the electrolytic cell.

2.1.4. The pH-correction system

The pH-correction system consisted of a pH indicator recorder (pHIR) which continuously measured the pH content of the surge vessel and with the help of the dosing pumps PP-1 and PP-2 which supplied HCl and NaOH, respectively, the pH was kept constant.

2.1.5. Cooling system

The cooling system included a temperature indicator controller recorder (TICR), an electric valve for the water and a cooling water jacket which was located in the reactor. The cylinder wall and the cooling jacket constituted the cathode. Whenever the temperature of the water exceeded 45 °C, cooling water was circulated in the jacket, until the temperature returned to the desired value.

The change of redox potential in the reactor was continuously recorded by a redox indicator recorder (RIR). The samples for analysis were drawn from the overflow of the recirculation reactor.

2.2. Material

The composition of the DW that was used in all experiments is shown in Table 1. Sodium chloride was added to DW so that its concentration reached 0.8% (w/v).

2.3. Methodology

The efficiency of the electrolytic cell was studied in relation to pH and to the residence time of DW into the reactor when the temperature remained constant at 45 °C during all experiments. Also, in all experiments NaCl has been used as electrolyte in a constant concentration of 0.8% (w/v). The effect of the electrochemical method on DW treatment was examined for pH 6, 7, 8 and 9.

Table 1
Composition of domestic wastewater (DW) used in all experiments

Characteristics	Value (mg/l)
pH	7.2
BOD ₅	385
COD	1047
Total suspended solids	870
Volatile suspended solids	628
Total soluble phosphorous	17.5
Ammonium nitrogen	150
Alkalinity as CaCO ₃	350
Fats and oils	45

All followed experiments were of continuous operation. The DW residence time into the electrolytic system was controlled by the flow rate of the dosing feeding pump PP-3. Every half an hour, samples were taken from the effluent of the reactor for a total residence time of 6 h. Soluble COD, volatile suspended solids (VSS), $N-NH_4$, nitrates, total soluble phosphorous, calcium ions, chlorides, hypochlorides, chlorine and total oxidants were measured.

Two experiments under the same conditions were run for each pH value and the results presented in this work are the average of the two separate measurements. The observed scale of error is based on duplicate experiments and no serious statistical results analysis can be presented.

2.4. Methods of analyses

The COD, VSS, $N-NH_4$, nitrates, total soluble phosphorous, chlorides, total chloramines, calcium cations and hypochlorides and free chlorine analysis were carried out according to the standard methods for the examination of water and wastewater [27]. The determination of the total oxidants except the chlorine was carried out according to Wilk et al. [28]. Chlorates were calculated from the chlorine balance.

3. Results and discussion

3.1. COD

Fig. 1 shows the change of COD versus pH and residence time. When the pH and the residence time increase, the efficiency of the electrolytic oxidation of COD increases. For residence time of 2.5 h and pH 6, the COD was reduced from 1047 to 780 mg/l. For residence time of 2 h and at pH 9, the COD was reduced from 1047 to 5 mg/l.

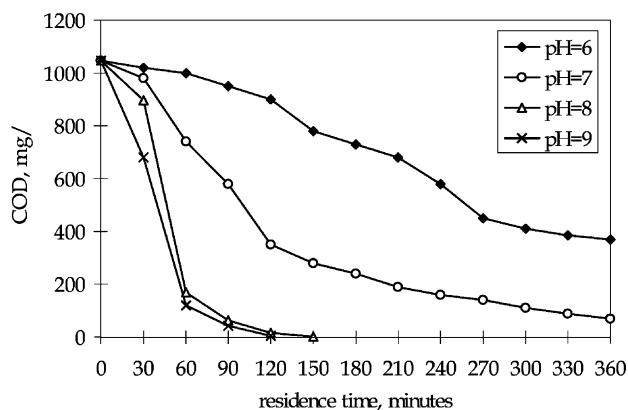


Fig. 1. Reduction of COD in relation to pH and residence time.

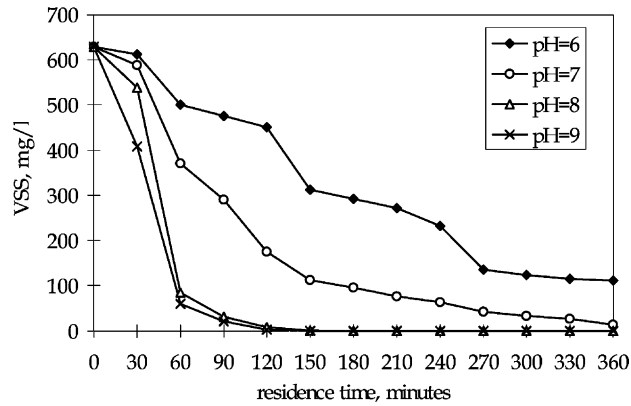


Fig. 2. Reduction of VSS in relation to pH and residence time.

3.2. Volatile suspended solids (VSS)

There was a similar to COD change in VSS as shown in Fig. 2. The VSS were reduced only by 28% (from 628 to 450 mg/l) for pH 6 and residence time 2 h, while for pH 9 and the same residence time, the VSS reduction was almost 100%.

3.3. Ammonia nitrogen ($N-NH_4$)

As it is depicted in Fig. 3, $N-NH_4$ was reduced quickly in all pH values exempt pH 7. Thus, for pH 6, 8 and 9 and 2 h residence time of DW in the reactor, $N-NH_4$ was reduced by almost 100%, while at pH 7 and the same residence time, $N-NH_4$ reduction was only 30% (from 150

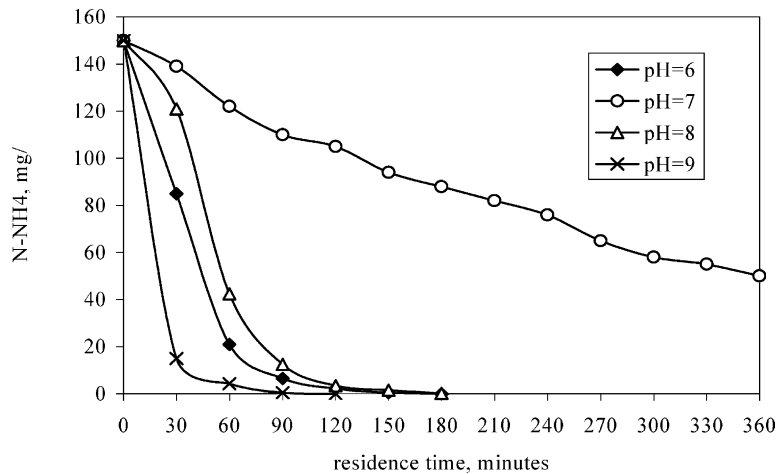


Fig. 3. Reduction of $N-NH_4$ in relation to pH and residence time.

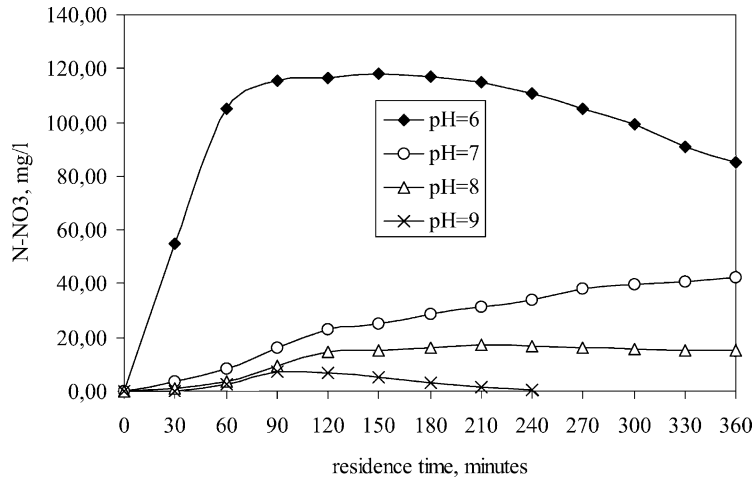


Fig. 4. Production of N-NO_3 in relation to pH and residence time.

to 105 mg/l). For residence time half an hour, N-NH_4 reduction for pH 6, 7, 8 and 9 reached 43, 7, 20 and 90%, respectively, which strongly suggests that the highest rate of reduction occurs at pH 9 and that between pH 6.5 and 7.5 the oxidation of N-NH_4 is reduced drastically.

3.4. Nitrates

The production of nitrates is shown at Fig. 4. The highest production was observed at pH 6 where for retention time of 90 min the concentration of nitrates reached its highest value which was 118.2 mg/l, while for pH, 7, 8 and 9 and the same retention time, the corresponding concentrations came up to 16.4, 9.4 and 7.2 mg/l indicating that the rate of nitrate production was much higher in acid than in alkaline environment (105 mg/(l h) for pH 6 against only 2.5 mg/(l h) for pH 9). It was also observed that at pH 6 nitrates concentration remained for a long period at its highest point before it started to decline in contrast to pH 9 where the reduction of nitrates started immediately. This may be due to the fact that, at pH 9 all the easily oxidizable organic compounds have been oxidized from nitrates, while at pH 6 high concentrations of more reducing compounds continued to remain, which until they were oxidized, the nitrates remained constant [29].

3.5. Total soluble phosphorous

Fig. 5 shows the changes in total soluble phosphorous in relation to pH and the retention time of DW in the reactor. In the acid and neutral region there was a partial removal of phosphates with sedimentation, while in the alkaline region there was a complete precipitation of soluble phosphates. Thus, for pH 6 and 7 there can be a marginal removal of phosphates 26 and 60%, respectively, while for pH 8 and 9 there is a complete removal of phosphates in 1 and 2 h, respectively. The highest rate of phosphate reduction for pH 6, 7, 8 and 9, reached 1.4, 5.4, 13.8 and 29.6 mg/(l h). The precipitation of phosphates is due to

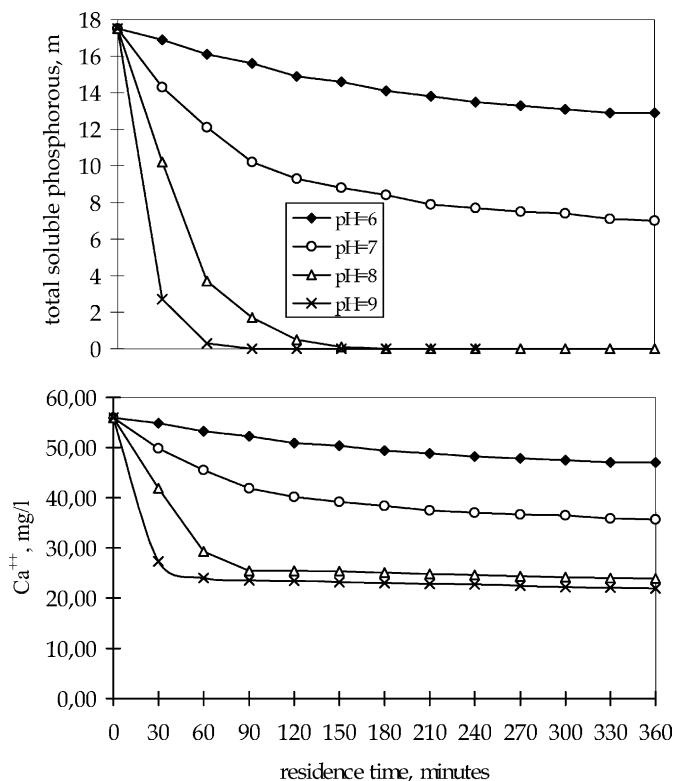


Fig. 5. Changes of total phosphorous and calcium ions concentration in relation to pH and residence time.

the formation of calcium insoluble salts. This is confirmed from the elemental reduction of the concentration of calcium cations as it is depicted in Fig. 5. The mechanism of precipitation of phosphates is probably due to the pH shift to the alkaline region rather than to special oxidative actions. The marginal concentrations of phosphates in relation to pH are in agreement with the reports by [30–33].

3.6. Total chloramines

The production of chloramines is shown in Fig. 6. Chloramines are produced due to the presence of ammonia and free chlorine in the electrolysis system and can be regarded as an undesirable byproduct of the oxidation process. The higher production of chloramines happens at pH 6, where for retention time 330 min the chloramine concentration reached its peak, that is 36.5 mg/l. For pH 7, 8 and 9 the chloramine concentrations reached their highest values at 90, 32 and 30 min at 5.5., 1.7 and 0.4 mg/l, respectively. This shows that in acid environment the rate of chloramine production is much higher compared to alkaline. The production of chloramines ceases when all TKN has been oxidized (Figs. 3 and 5). At pH 7, 8 and 9 there was a slow reduction of chloramines due to their oxidation with the

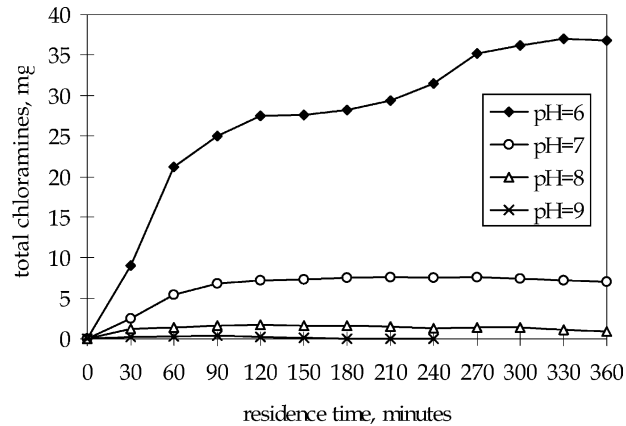


Fig. 6. Chloramines production in relation to pH and residence time.

increase retention time of DW in the reactor. At pH 9 their concentration is reduced to zero and for retention time higher than 240 min.

3.7. Chlorides and production of oxidants

Fig. 7 shows the concentration of chlorides, free chlorine, hypochlorides, chlorates and other oxidants as a whole in relation to pH and to the residence time of DW in the reactor. Among other oxidants, various free radicals that cannot be measured directly are believed to play a significant role in the electrochemical oxidation process [13,18,22]. The concentration of chlorides for pH 6 and 7 was reduced in the first 60 and 30 min from 4800 to 2650 and 3740 mg/l, respectively and was stabilized in these concentrations. On the other hand, for pH 8 and 9 the concentration of chlorides was reduced continuously in relation to residence time with constant rates of 415 and 505 mg/(l h), respectively. Also, the production of total chlorine (free chlorine + hypochlorides) for pH 6 and 7 was increased in the first 60 and 30 min from 0 to 2200 and 1060 mg/l, respectively and was stabilized in these concentrations. On the other hand, for pH 8 and 9 the concentration of total chlorine was increased continuously in relation to residence time with constant rates of 425 and 542 mg/(l h). The other oxidants, except from chlorine, were increased continuously as residence time was increasing for all pH. So for 360 min of residence time and pH 6, 7, 8 and 9 the steady state concentrations of other oxidants exempt chlorine were 1950, 1450, 2220 and 2460 mg/l, respectively. Among the oxidants, the presence of O_3 and H_2O_2 was also detected. Chlorates were detected only at pH 8 and 9 with increasing concentration in relation to residence time reaching 180 and 540 mg/l, respectively after 6 h of residence time.

3.8. Anode efficiency

Fig. 8 shows the anode efficiency of the electrode in relation to pH and residence time of DW in the reactor measured in kg COD removed per hour per square meter of anode surface and per ampere applied ($kg\ COD_r / (h\ m^2\ A)$). For pH 6 there was almost a constant efficiency

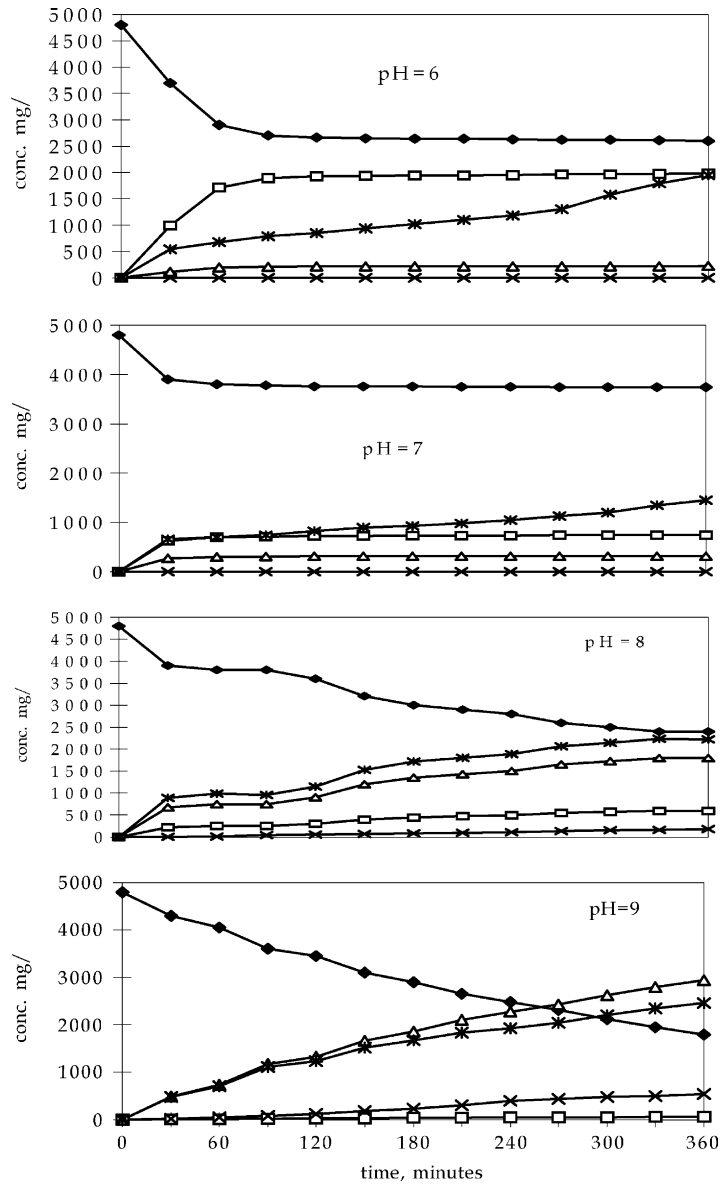


Fig. 7. Chlorides reduction and oxidants production in relation to pH and residence time: (◆) chlorides; (□) free chlorine; (△) hypochlorides; (✱) other oxidants; (✕) chlorates.

for all residence times of 3–4 kg $COD_r/(h\ m^2\ A)$. For the other pH, 7, 8 and 9 there was a peak of the efficiency at about 60 min of residence time reaching at 11.5, 32.5 and 34.3 kg $COD_r/(h\ m^2\ A)$, respectively. When the residence time was increased then the efficiency for all pH values was decreased rapidly and met the value of pH 6 after 6 h of residence

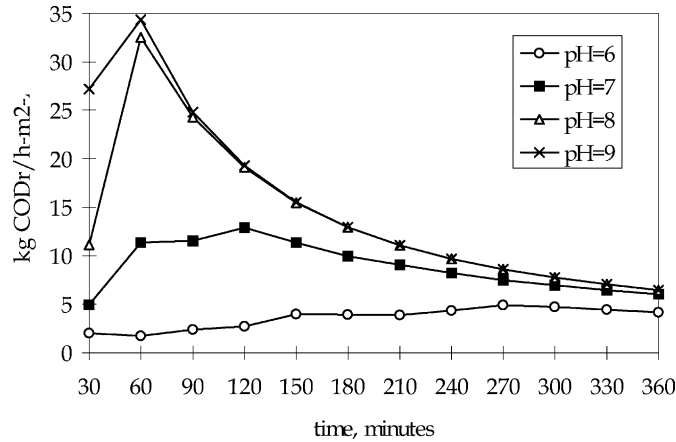


Fig. 8. Anode efficiency in relation to pH and residence time.

time (4.3 kg COD_r/(h m² A)). The gradual decrease of electrode efficiency indicates the increasing difficulty for oxidation of residual organics and inorganics in the waste.

3.9. Specific energy consumption

Fig. 9 shows the specific energy demand in relation to pH and residence time of DW in the reactor measured in kWh consumed per kg COD removed. The graphs of specific energy demand change for pH 7, 8 and 9 are in their lowest values when the residence time of DW in the reactor was 60 min. These values for pH 7, 8 and 9 are 38.54, 13.66 and 12.94 kWh/kg COD_r, respectively. The greater the retention time, the higher the specific energy demand in linear correlation reaching at 6 h values of 73.36, 68.76, 68.2 kWh/kg COD_r for pH 7, 8 and 9, respectively. On the other hand, at pH 6 the specific energy demand curve reached

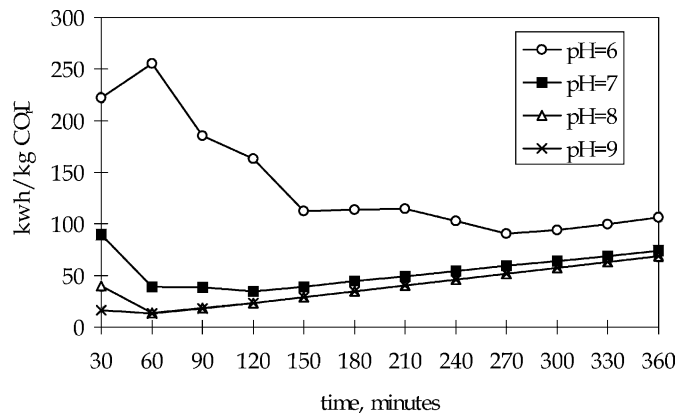


Fig. 9. Energy consumption in relation to pH and residence time.

Table 2
Finally results of electrochemical treatment of DW at pH 9

Residence time (min)	Effluent's COD (mg/l)	Effluent's VSS (mg/l)	Effluent's N-NH ₄ (mg/l)	Effluent's N-NO ₃ (mg/l)	Effluent's phosphorus (mg/l)	Energy consumption (kWh/kg COD _r)
0	1047	628	150	0	17.5	
30	680	408	19.4	0.2	2.7	16.34
60	120	60	27.0	2.5	0.3	12.94
90	42	21	34.7	7.2	0	17.91
120	5	2.5	42.0	7	0	23.03

a maximum value of 255 kWh/kg COD_r at 1 h retention time, and then it was reduced to 102 kWh/kg COD_r at 3 h in which value it stayed constant at further waiting. The minimum values of specific energy demand found in this study are in agreement with the theoretical approach referred by Comninellis [10].

Due to electrochemical reactions of the cathode, the brine solutions shifted the pH during electrolysis to the alkaline region [34] and equilibrated at pH about 9 [13]. Therefore, without pH control, the electrochemical treatment of DW with brine solution in practice has a buffer at pH 9. Table 2 shows some results of the electrochemical treatment of DW at pH 9.

4. Conclusions

The electrochemical oxidation is an integrated and effective method for the treatment of DW because it can reduce all pollutants (COD, VSS, TKN, phosphorus) almost to zero. Although the energy demand is about ten-fold compared to what is required for an aerobic biological reactor with the same treatment results, this method seems to be more feasible than a conventional biological treatment system for the following reasons:

- it is more simple to operate, control and maintain;
- as a physicochemical system it is more reliable for the results;
- there is no biosolids byproduction;
- probable toxicities in the entrance (phenols, pesticides, detergents, etc.) do not interfere with the process.

The electrochemical treatment of DW seems to be favored for small communities by the sea.

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