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Electrolytic Pretreatment of Olive Mill Wastewater (OMW) for Methane to Hydrogen Production

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Olive mill wastewater (OMW) is an abundant agro-industrial effluent in the Mediterranean countries where the biggest olive oil production occurs. OMW can be used as a renewable energy source for hydrogen production. Hydrogen can be steam reformed from biogas produced by biodegradation of the waste. Olive mill wastewater has high content of chemical oxygen demand (COD) and phenols which render it from being used directly to anaerobic treatment. In this study filtration followed by electrochemical oxidation is being evaluated as pretreatment strategies for COD reduction and Total Phenols removal from typical olive mill wastewater for subsequent utilization in hydrogen production. Undiluted OMW electrolyzed with Ti/Ta/Pt/Ir anode for 3 h showed that Energy consumption can be as low as 8.97 kWh/kg CODr achieving 50.7% TPh reduction and 62.85% COD reduction.

Keywords electrooxidation; hydrogen production; olive mill wastewaters; phenols; pretreatment

INTRODUCTION

Hydrogen has been recognized as a clean energy carrier, has a high specific energy on a mass basis, and can be generated from various sources among which are biomasses from agricultural wastes (1). Olive mill wastewater (OMW) is heavy polluted and hence it cannot be disposed into the environment without any treatment. Olive mill wastewater can be used as a renewable energy source for biogas to hydrogen production. Hydrogen can be produced directly from OMW through microbial treatment with the combination of wastes (2) or the combination of methods (3) and can be steam reformed from biogas produced from anaerobic digestion of OMW. Olive mill wastewater has a high content of chemical oxygen demand (COD) and phenols which render it from being used directly to anaerobic treatment, where methane and carbon dioxide are produced. Pretreatment of OMW is a prerequisite for biological treatment as there is evidence that the phenolic compounds present in the waste inhibit biogas production (4). Many researchers acknowledge physicochemical pretreatment as a necessity prior to anaerobic treatment. Mantzavinos and Kalogerakis review integrated approaches which combine the main anaerobic treatment to a chemical pretreatment step (5). Electrochemical oxidation is an energy intense process for complete mineralization of Olive mill wastewater (OMW). Many studies (6–9) have been employed combining various conditions of current density, dilution, filtration, addition of different electrolytes at various concentrations, and different electrodes. They report that even though it is a costly process for money and energy it can be effective as a pretreatment step (6,7) when it is coupled with a biological process. It can be used to partially oxidize OMW aiming at the phenolic fraction, which renders it recalcitrant to microorganisms. Electrochemical oxidation, with BDD anodes, can successfully treat phenolic aqueous wastes, achieving lower energy consumptions for complete removal compared to other electrochemical and non-electrochemical technologies (8).

It has been reported that for high initial concentrations of phenols the conversion increases with increasing salinity and current over Ti/Pt anodes (6). At higher initial concentrations of COD (9,11) and lower salinity (9) energy consumption per unit of organic load removed is lower, thus the process is more efficient. Chatzisymeon et al. (11) report that 96 kWh/kg COD removed for undiluted OMW with initial COD 40000 mg/L and operating conditions 15 h at 20 A which led to 19% COD and 36% TPh removal over BDD anode. In another study Israilides et al. (7) report that 4.73 g-COD/h*m^{2}*A and 12.3 kWh/kg COD removed for undiluted OMW with initial COD 17.8220 mg/L and operating conditions 10 h at 0.26 A/cm^2 which led to 93% COD and almost complete %TPh removal over Ti/Pt electrode. Panizza and Cerisola (10) report that the specific energy consumption for the complete removal of aromatics is lower than that for COD removal, which is 0.18 kWh/L and 0.8 kWh/L respectively after 15 hours of electrolysis.

In this work undiluted OMW is used in order to investigate the parameters that would suggest electrolysis to be a feasible pretreatment technique in terms of energy

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TABLE 1
Characteristics of raw olive mill wastewater and filtered OMW

	TCOD (kg/m^3)	TS (kg/m^3)	COD (kg/m^3)	STP (kg/m^3)	STP reduction %
Raw OMW	88.3	76	52.3	2.4	
Filtered OMW	–	73–43	46.8–49.1	1.8–1.5	37.5

consumption and anode efficiency. The aim is to reduce the phenolic fraction that stresses anaerobic consortia by electrolysis. Such a pretreatment step is recommended for enhanced biogas production when OMW is treated anaerobically.

MATERIALS AND METHODS

Olive Mill Wastewater

Olive mill wastewater was taken from a three-phase olive mill in the region of Chania. It was centrifuged and filtered before being subjected to electrochemical treatment. Parameters of initial and conditioned waste are presented in Table 1.

Equipment

The electrochemical experiments were performed over a titanium–tantalum–platinum–iridium (Ti/Ta/Pt/Ir) anode and a Boron Doped Diamond (BDD). The surface of the anode area of the first is 58 cm^2. A schematic of the experimental set up is presented in details elsewhere (9). The second electrochemical apparatus is a DiaCell (type 100) single compartment electrolytic flow-cell manufactured by Adamant Technologies (Switzerland). Two circular electrodes made of BDD on silicon were used as the anode and cathode; each electrode area was 70 cm^2 and the distance between them was 0.01 m.

Experimental Plan

A total of 16 experiments were conducted using the two different electrodes. In Table 2 the conditions of all experiments are summarized. The variables used are;

a) Current density (A/cm^2) 0.214 A/cm^2 and 0.428 A/cm^2 for BDD and 0.518 A/cm^2 and 1.034 A/cm^2 for Ti/Ta/Pt/Ir,
b) Concentration of Cl^- (gr-ion/L) 0.171 M, 0.342 M, 0.684 M, and 1.026 M,
c) pH neutral whenever NaCl was used and acidic whenever HCl was used ranging from below 1 up to 3.7.

Analytical Methods

Chemical Oxygen Demand (COD)

COD concentrations were measured with a Hach spectrophotometer using the dichromate method with vials for COD range of 0–1500 mg/L. In all cases the dissolved COD was measured and hence all samples were filtered through a 0.45 μm nylon filter. Equally treated control sample with distilled water was used. Total COD measurements were performed, without filtering the samples through 0.45 μm pore size filters, for determination of COD removal after filtration treatment. Appropriately diluted samples were mixed with the digestion solution which contained potassium dichromate, sulfuric acid, and mercuric sulfate. It was incubated for 120 minutes at 150°C in a COD reactor. COD concentrations were measured colorimetrically. The absorbance of the digested solution was measured at 620 nm on a DR/2010 spectrophotometer.

Total Phenols (TPh)

Total dissolved phenols were estimated with the Folin Ciocalteau micro-method for Total Phenol. Samples were taken periodically during the electrochemical experiments,

TABLE 2
Experimental design of electrolytic experiments with undiluted OMW of each independent variable x

	Level of factor in each experimental run			
Run	x_1 Electrode	x_2 D Current density	x_3 M Cl^-	x_4 pH
1	1	3	3	4
2	1	3	4	4
3	1	4	3	4
4	1	4	3	1
5	1	4	2	2
6	1	4	2	4
7	1	3	2	4
8	1	3	1	3
1	2	1	3	4
2	2	1	4	4
3	2	2	3	4
4	2	2	3	1
5	2	2	2	2
6	2	2	2	4
7	2	1	2	4
8	2	1	1	3

x_1, Electrode: 1: Ti/Ta/Pt/Ir, 2: BDD.
x_2, D Current density (A/cm^2): 1: 0.214, 2: 0.428, 3: 0.518, 4: 1.034.
x_3, M [Cl^-]: 1: 0.171, 2: 0.342, 3: 0.684, 4: 1.026.
x_4, pH: 1: <1, 2: <1.5, 3: 3.7, 4: 7.

to follow the degradation of phenols, and were filtered through 0.45 pore size filter. Samples were also taken from raw olive mill wastewater for the determination of phenolic content change before and after filtration treatment. The sample or gallic acid standard (20 μL) was mixed with the Folin Ciocalteau reagent (100 μL), water (1580 μL), and Sodium Carbonate (300 μL). After being left for 2 hours in the dark at room temperature, the absorbance of the solution was measured at 725 nm on a Shimadzu UV 1240 spectrophotometer. The calibration curve was prepared using 0, 50, 100, 150, 250, 500 mg/L gallic acid standards. TPh is reported at Gallic Acid Equivalent, GAE (mg/L).

Total Suspended Solids (TSS), Total Solids (TS)

TS and TSS were measured according to the standard method for water and wastewaters (12).

Color

The color reduction was measured photometrically with the absorbance of samples at 725 nm wavelength at sample dilutions (1/5) on a Shimadzu UV 1240 spectrophotometer.

Statistical Analysis

Statistical analysis of variance (ANOVA) was performed using the SPSS (SPSS.Inc 17.0) statistical software package. The effects of each factor where processed separately and the responses where analyzed statistically. Thus one way ANOVA was performed for each independent variable separately according to the experimental designs. The factors that where studied in this work were: x_1 the type of electrode, x_2 current density, x_3 Cl^- concentration and x_4 the pH. The responses were: Y_1 specific energy consumption (SEC), Y_2 Energy Consumption, Y_3 Anode efficiency, Y_4 percentage COD removal, Y_5 percentage TPh removal, and Y_6 percentage TS removal.

RESULTS AND DISCUSSION

Analysis of variance (ANOVA) was conducted with the statistical software package SPSS. In Tables 3 and 4 are presented values of characteristics for each experimental run for Ti/Ta/Pt/Ir and BDD electrode respectively.

TABLE 3
Initial COD, initial TS, initial TSS, percent TSS removal and color reduction, pH, and final TPh of electrolytic treatment of OMW over Ti/Ta/Pt/Ir electrode

Run	COD initial (mg/L)	Initial TS (g/L)	Initial TSS (g/L)	TSS % removal	pH	Color reduction %	TPh final (mg/L)
1	28150	67.5	3.6	27.77	7.2	67.02	524.09
2	36850	92.8	4.8	16.66	7.2	81.33	410.00
3	45050	72.8	3.6	66.66	7.2	84.49	1109.04
4	45050	41.2	7.6	60.52	0.3	98.86	1016.08
5	49000	62.2	2.2	72.72	1.1	93.06	821.09
6	44650	43.1	4.4	72.72	6.4	60.19	660.65
7	43700	61.2	4.6	13.04	6.1	30.77	1372.59
8	39450	39	1	60	3.9	83.96	1477.04

TABLE 4
Initial COD, initial TS, initial TSS, percent TSS removal and color reduction, pH and final TPh of electrolytic treatment of OMW over BDD anode

Run	COD initial (mg/L)	Initial TS (g/L)	Initial TSS (g/L)	TSS % removal	pH	Color reduction %	TPh final (mg/L)
1	42450	72.1	2.8	0	6.6	6.6	1728.6
2	40500	91.5	2.6	76.92	6.9	15.3	1236
3	40300	70.7	2.4	58.33	6.4	24.2	1238.6
4	38150	47.6	1.4	57.14	0.9	88.7	1231.5
5	40550	41.3	0.8	25	1.4	91.6	1290.2
6	38800	53.4	1.4	14.28	7	33.7	1070.1
7	54450	53.9	1.8	44.44	6.2	47.3	1304
8	42650	42.3	20	95	3.6	44.3	1194.1

TABLE 5
Observed responses for all experiments, total mean and standard deviation for each Y variable

Run	Y1 SEC KWh/m^3	Y2 Energy consumption KWh/KgCODr	Y3 Anode efficiency gr CODr/h*m^{2}*A	Y4 COD % removal	Y5 TPh % removal	Y6 TS % removal
1	87.862	20.008	67.301	15.6	46.63	47.4
2	81.319	17.941	60.781	12.3	62.71	1.61
3	227.894	30.401	53.853	16.64	25.99	0.54
4	142.067	17.520	58.254	18	32.08	4.61
5	276.404	8.975	221.239	62.85	50.7	81.99
6	371.293	12.503	213.338	66.51	63.52	9.97
7	95.607	13.284	103.411	16.47	30.73	36.11
8	122.980	13.368	132.180	23.32	30.59	15.64
1	105.802	35.913	65.467	6.94	2.3	50.48
2	96.814	97.173	22.140	2.46	13.2	60.54
3	266.302	50.753	58.301	13.02	26.03	48.51
4	203.000	30.528	73.884	17.43	27.58	23.94
5	270.410	47.872	62.762	13.93	20.04	13.8
6	313.296	152.929	22.763	5.28	22.4	40.44
7	112.543	10.004	249.986	20.66	11.11	30.24
8	140.341	26.240	118.851	12.54	27.39	13.23
Mean	182.120	36.588	99	20.247	30.812	29.940
SD	93.315	38.152	70.68	18.182	17.323	23.598

In Table 5 the values of the dependent variables for all experiments over the two electrodes with undiluted olive mill wastewater are presented. In Table 6 the results of the analysis of variance for all 16 experiments are shown according to the experimental design in Table 2 for each factor separately. The level of significance is provided whenever it was above 95%.

The two electrodes differ statistically significantly for energy consumption, the %COD removal and the %TPh removal. The Ti/Ta/Pt/Ir electrode shows lower Energy Consumption and greater %COD removal and %TPh removal comparing to the BDD. Thus it is considered more suitable for the purpose of this study, which is partial removal of COD and TPh at the lowest possible level of energy consumption.

Exploring the factors affecting these variables (%COD removal and %TPh removal), ANOVA showed that current density is a factor which affects statistically significantly SEC, %COD removal, and %TPh removal (Table 6). As current density increases so do all three variables for each variable. This gives a suitable explanation as to why the two electrodes differ significantly for variables Y2, Y4, and Y5. The BDD electrode could not reach the current intensity of the Ti/Ta/Pt/Ir electrode, which could reach 60A.

The other two factors, Cl^- concentration and pH of the waste, tested for all experiments did not show any statistical significance and tests where the run for each electrode separately for analyzing the results.

Undiluted OMWW Electrolyzed over Ti/Ta/Pt/Ir Electrode

In Fig. 1 the percentage of COD removal versus electrolysis time is presented. Experiments 1 to 4 were conducted with OMW produced in January while experiments 5 to 8 were conducted with waste produced later in the same season (May).

The results of the parameters estimated from 8 electrolytic experiments over Ti/Ta/Pt/Ir electrode are presented in Tables 3 and 5. In Table 8 the results of the analysis of variance for all 8 experiments according to the experimental design in Table 7 for each factor are shown separately. The level of significance is provided whenever it is above 95%.

Current Density appears to have statistically significant effect on Y1, which means that the specific energy consumption (SEC) increases greatly when the current density is doubled from 0.518 A/cm^2 to 1.034 A/cm^2. Cl^- concentration appears to have a statistically significant effect on Energy Consumption (Y2) and Anode efficiency (Y3), for Ti/Ta/Pt/Ir electrode. There is a positive effect of Cl^- concentration on Energy Consumption and a negative effect on Anode efficiency. The level of pH, neutral or acidic, has no significant effect on any of the variables tested.

TABLE 6
Means, standard deviation, and level of significance between levels of each X variable (Table 2) for Y variables (Table 5), analyzed with SPSS

	Y1	Y2	Y3	Y4	Y5	Y6
x_1						
Mean 1	175.67	16.75	113.8	28.96	42.87	24.733
sd	105.61	6.56	69	22.28	15.1	28.65
Mean 2	188.56	56.43	84.3	11.53	18.76	35.15
sd	86.09	46.65	73.58	6.21	9.11	17.62
Sign.	–	0.032	–	0.051	0.002	–
x_2						
Mean 1	113.87	42.33	114.1	10.65	13.5*	38.62
sd	18.78	38.09	98.84	7.84	10.395	21.10
Mean 2	263.25	70.52	54.4	12.42	24.01	31.67
sd	45.44	55.660	22	5.12	3.42	15.7
Mean 3	96.94	16.15	90.9	16.92	42.67*	25.19
sd	18.32	3.37	33.29	4.63	15.34	20.492
Mean 4	254.41	17.35	136.7	41	43.07*	24.28
sd	95.69	9.38	93.16	27.39	17.213	38.67
Sign.	0.001	–	–	0.043	0.016	–
x_3						
Mean 1	131.66	19.80	125.5	17.93	28.99	14.44
sd	12.27	9.10	9.42	7.62	2.26	1.70
Mean 2	239.92	40.93	145.6	30.95	33.08	35.43
sd	111.31	56.82	94.8	26.63	20.05	25.83
Mean 3	172.15	30.85	62.8	14.61	26.77	29.25
sd	71.183	11.98	7.36	4.14	14.31	22.85
Mean 4	89.06	57.56	41.5	7.38	37.96	31.08
sd	10.95	56.03	27.32	6.96	35.01	41.67
Sign.	–	–	–	–	–	–
x_4						
Mean 1	172.53	24.02	66.1	17.72	29.83	14.28
sd	43.09	9.20	11.05	0.40	3.18	13.67
Mean 2	273.41	28.42	142	38.39	35.37	47.90
sd	4.24	27.50	112.1	34.59	21.68	48.22
Mean 3	131.66	19.80	125.5	17.93	28.99	14.44
sd	12.28	9.10	9.42	7.62	2.26	1.70
Mean 4	175.87	44.09	91.7	17.59	30.46	32.58
sd	108.66	46.35	77.72	18.11	20.99	21.48
Sign.	–	–	–	–	–	–

In Fig. 2 the negative effect of increasing salinity on the %COD removal at Ti/Ta/Pt/Ir electrode is depicted. Energy Consumption for experiments 1, 2, and 7, which were conducted at the same current density for three hours with NaCl as electrolyte at neutral pH, is plotted against initial COD and TPh in Fig. 3.

As initial COD and Total Phenols initial concentration increases the energy consumption per COD removed decreases. The electrode is more efficient when the waste is concentrated and has a greater organic load.

Undiluted OMW Electrolyzed over Boron Doped Diamond Electrode

In Fig. 4 the percentage of soluble COD removed versus electrolysis time is presented. All eight experiments were conducted with the same waste which was produced in May.

The results of the parameters estimated for the 8 electrolytic experiments over BDD electrode are presented in Tables 4 and 5. In Table 9, the experimental design for the BDD electrode is presented. In Table 10 the results of

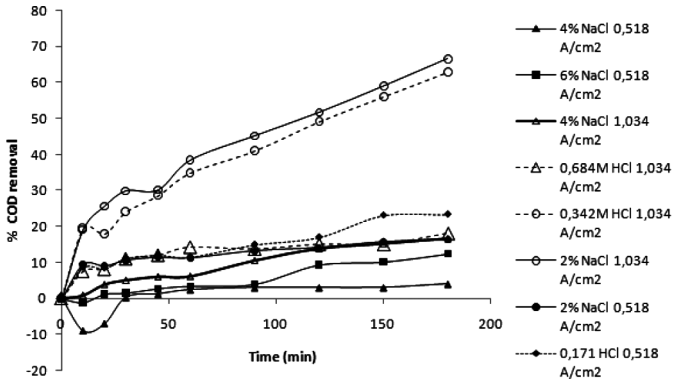

FIG. 1. Cumulative COD percent removal of each experiment conducted on Ti/Ta/Pt/Ir anode with recirculation rate 15.36 L/min.

the analysis of variance for all 8 experiments according to the experimental design in Table 9 for each factor are shown separately. The level of significance is shown whenever it is above 95%.

Experiments run at a low current density of 0.214 A/cm^2 and a high salinity of 6% and 4% NaCl, show an increase of soluble COD through electrolysis time compared to the initial COD of the waste. This phenomenon is attributed to the solubilization of solids which appear to have the highest percent TS removal as shown in Table 5 for experiments 1 and 2. This phenomenon is less pronounced at a higher current density of 0.428 A/cm^2, and occurs only during the first half hour of the experiment (experiment 3 conducted at 4% NaCl and 0.428 A/cm^2 as shown in Fig. 4).

TABLE 7
Experimental design of electrolytic experiments with undiluted OMW of each independent variable X for Ti/Ta/Pt/Ir electrode

	Level of factor in each experimental run		
	x_2	x_3	x_4
Run	D	M Cl^-	pH/electrolyte
1	3	3	N
2	3		N
3	4	3	N
4	4	3	A
5	4	2	A
6	4	2	N
7	3	2	N
8	3		A

x_2, D Current density (A/cm^2): 3: 0.518, 4: 1.034.
x_3, M [Cl^-]: 2: 0.342, 3: 0.684.
x_4, pH/electrolyte: N: Neutral/NaCl, A: Acid/HCl.

TABLE 8
Means, standard deviation, and level of significance between levels for each X independent variable (Table 7) for Y variables (Table 5) analyzed with SPSS for Ti/Ta/Pt/Ir electrode

	Y1	Y2	Y3	Y4	Y5	Y6
x_2						
Mean 3	96.94	16.15	90.90	16.92	42.67	25.19
sd	18.31	3.37	33.29	4.63	15.34	20.49
Mean 4	254.41	17.35	136.7	41.00	43.07	24.28
sd	95.69	9.38	93.16	27.39	17.21	38.67
Sign.	0.018	–	–	–	–	–
x_3						
Mean 2	247.77	11.59	179.3	48.61	48.32	42.69
sd	140.06	2.30	65.87	27.89	16.52	36.46
Mean 3	152.61	22.64	59.8	16.75	34.90	17.52
sd	70.61	6.83	6.86	1.20	10.61	25.96
Sign.	–	–	0.035	–	–	–
x_4						
Mean A	180.48	13.29	137.2	34.72	37.79	34.08
sd	83.62	4.27	81.61	24.50	11.21	41.86
Mean N	172.79	18.83	99.70	25.50	45.92	19.13
sd	126.47	7.19	66.32	22.99	17.47	21.35
Sign.	–	–	–	–	–	–

At neutral pH the TS% removal is statistically significantly greater compared to the acidic pH. Hence, the differences of the means at different levels of salinity are affected by the pH. This suggests the investigation of the differences at neutral pH.

In Fig. 6 the relation between %TS removal and the pH is depicted. The relation between Cl^- anions and the

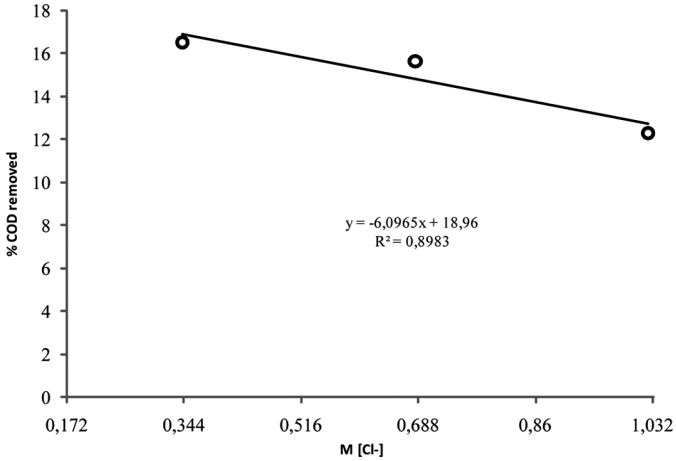

FIG. 2. Effect of salinity on % COD reduction at Ti/Ta/Pt/Ir electrode at constant current density 0.518 A/cm^2 and pH neutral.

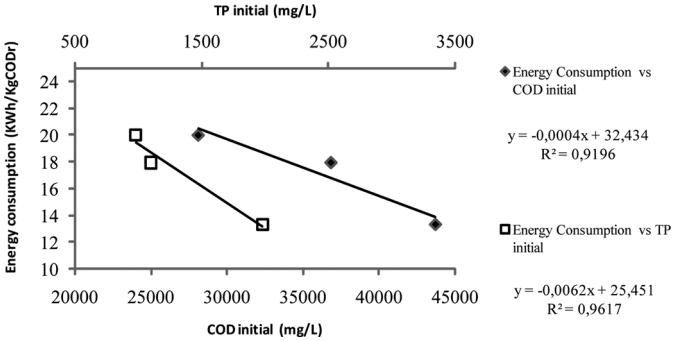

FIG. 3. Effect of COD initial and TPh initial on energy consumption at 0.518 A/cm^2 at Ti/Ta//Pt/Ir electrode with neutral pH.

%removal of TS is presented in Fig. 5. When the Cl^- ion concentration is increasing so does the %TS removal. From the same figure it the opposite effect of Cl^- concentration on %COD removal can be seen which also causes the Energy Consumption to increase significantly. In Figure 6, the relation between %TS removal and the pH is depicted. As shown in Fig. 7, the initial concentration of TS affects the percentage of COD removal, the TS removal and the Energy Consumption.

Energy Consumption and Anode Efficiency

Energy Consumption and Specific Energy Consumption (SEC)

Energy consumption (kWh/CODr) was estimated by dividing the SEC by the concentration of COD removed in kg/m^3. The specific energy consumption (kWh/m^3) was estimated using the Eq. (1) and the results are presented in Table 5.

$$\mathrm{SEC} = (\mathrm{D} * \mathrm{S} * \mathrm{U} * t_f)/\mathrm{v} \quad (1)$$

where D is the current density (A/m^2), S is the electrode surface area (m^2), U is the cell potential (V), t_f is the duration electrolysis (h), and v is the electrolyte volume (m^3).

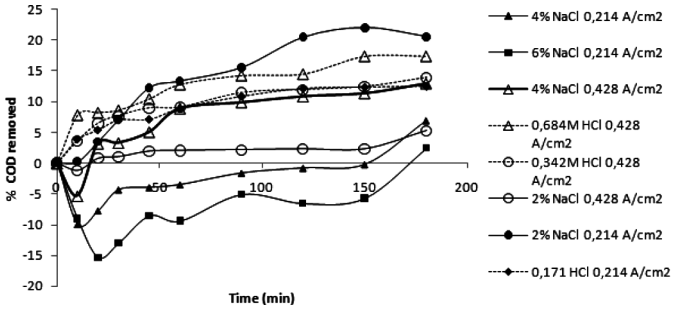

FIG. 4. Cumulative COD percent removal during electrolysis time of each experiment conducted over BDD anode with recirculation rate 10 L/min.

TABLE 9
Experimental design of electrolytic experiments with undiluted OMW of each independent variable X for BDD electrode

	Level of factor in each experimental run		
	x_2	x_3	x_4
Run	D	M Cl^-	pH/electrolyte
1	1	3	N
2	1		N
3	2	3	N
4	2	3	A
5	2	2	A
6	2	2	N
7	1	2	N
8	1		A

x_2, D Current density (A/cm^2): 1: 0.214, 2: 0.428.
x_3, M [Cl^-]: 2: 0.342, 3: 0.684.
x_4, pH/electrolyte: N: Neutral/NaCl, A: Acid/HCl.

Energy consumption (kWh/CODr) elsewhere sited as SEC was found to be very effective for both electrodes (average values of 16.750 and 56.427 kWh/CODr for

TABLE 10
Means, standard deviation and level of significance between levels for each X independent variable (Table 9) for Y variables (Table 5) analyzed with SPSS for BDD electrode

	Y1	Y2	Y3	Y4	Y5	Y6
x_2						
Mean 1	113.87	42.33	114.1	10.65	13.50	38.62
sd	18.78	38.09	98.84	7.84	10.40	21.10
Mean 2	263.25	70.52	54.4	12.42	24.01	31.67
sd	45.44	55.66	22.1	5.12	3.42	15.70
Sign.	0.001	–	–	–	–	–
x_3						
Mean 2	232.08	70.27	111.8	13.29	17.85	28.16
sd	105.72	74.05	121.3	7.71	5.96	13.44
Mean 3	191.70	39.06	65.9	12.46	18.64	40.98
sd	80.84	10.47	7.8	5.27	14.17	14.79
Sign.	–	–	–	–	–	–
x_4						
Mean A	204.58	34.88	85.20	14.63	25.00	16.99
sd	65.05	11.45	29.70	2.52	4.30	6.03
Mean N	178.95	69.35	83.70	9.67	15.01	46.04
sd	102.70	56.45	95.04	7.26	9.44	11.37
Sign.	–	–	–	–	–	0.007

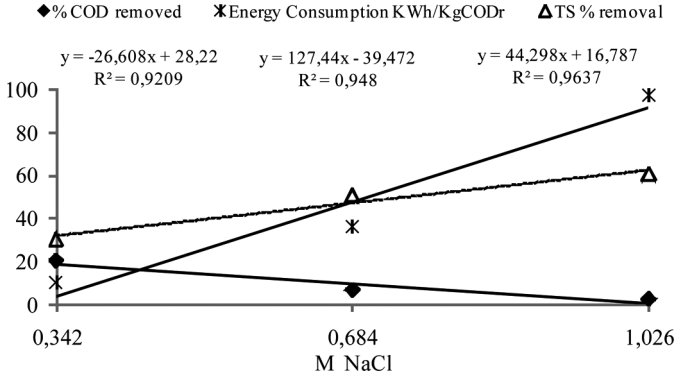

FIG. 5. Effect of salinity on energy consumption and % COD removal at 0.214 A/cm^2 at BDD electrode with neutral pH.

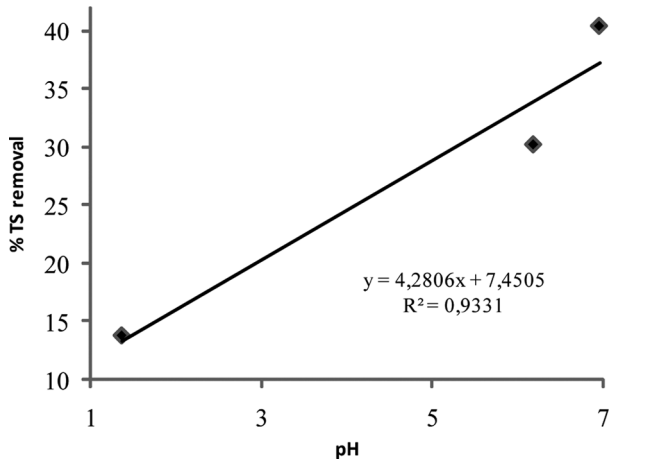

FIG. 6. Effect of pH on % TS removal at BDD electrode at 0.342 M Cl^- concentration.

Ti/Ta/Pt/Ir and BDD respectively). Kotta et al. (6) report 246 kWh/CODr for almost complete TPh removal after 72 h of electrolysis with raw undiluted and unfiltered OMW at 4% salinity and 20 A current over Ti/Ta/Pt/Ir anode.

The effect of salinity was investigated on %COD removal and Energy consumption on BDD electrode and the results are depicted in Fig. 5. At a constant current density of 0.214 A/cm^2 an increase in salinity is followed by an increase of Energy consumption and a decrease of %COD removal.

Anode Efficiency

Anode efficiency of the electrode was estimated in g-COD removed per hour per m^2 of anode surface and per Ampere applied (g-CODr/h*m^{2*}A). Values for each experiment as well as average values are presented in Table 5. Electrolysis over Ti/Ta/Pt/Ir/anode appears to be more efficient than BDD anode (in 5 experiments out of 8) in terms of Anode efficiency (Table 5).

CONCLUSIONS

- Electrolytic pretreatment of OMW with Ti/Ta/Pt/Ir electrode shows lower energy consumption per Kg of COD removed in the area of current density studied (0.518 and 1.034 A/cm^2) comparing to BDD electrode which was studied for lower current densities (0.214 and 0.428 A/cm^2).
- Increasing salinity, at 0.214 A/cm^2 current density in BDD electrode, energy consumption, and %TS removal increases while the percentage of COD removal decreases, with great significance.
- Increasing salinity, at 0.518 A/cm^2 current density in Ti/Ta/Pt/Ir electrode, %COD removal decreases too.
- Initial TS concentration affects the %COD removal, Energy Consumption, and the %TS

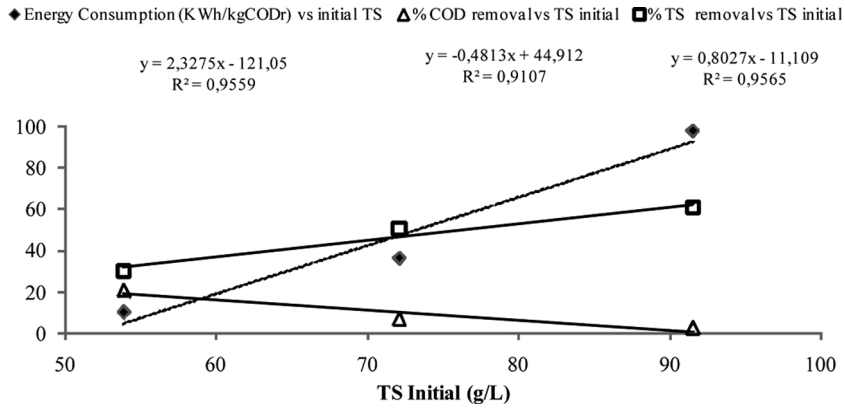

FIG. 7. Effect of TS initial on energy consumption, % COD removal and % TS removal at 0.214 A/cm^2 at BDD electrode with neutral pH.

removal. Thus for greater efficiency of BDD, the electrode reduction of initial TS is recommended.

- The pH is a factor which showed to have statistically significant impact on %TS removal of BDD electrode but not of Ti/Ta/Pt/Ir.
- Electrolytic oxidation of undiluted OMW for 3 hours under various conditions (of current density, electrolyte concentration and electrolytic cell) can reduce TPh to a final concentration that is not prohibiting for anaerobic digestion as a posttreatment considering a dilution will occur for the introduction of the waste to a biological process.
- Initial COD and Total Phenols concentration is affecting the energy consumption per COD removed and the more concentrated the waste the more efficient the Ti/Ta/Pt/Ir electrode appears to be.
- Dealing with undiluted OMW provides the advantage of fewer occupied space for storaging the waste until treatment. It also provides the advantage of higher efficiencies in terms of energy consumption per kg of COD removed.
- Undiluted OMW is recommended for electrolytic pretreatment prior to biological treatment. Energy consumption can be as low as 8.97 kWh/kg CODr achieving 50.7% TPh reduction and 62.85% COD reduction after 3 h of electrolysis with the Ti/Ta/Pt/Ir anode.

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