Electrochemical treatment of plastic industry wastewaters powered by photovoltaic solar energy

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Abstract. Electrochemical processes combined with renewable energy sources are considered sustainable and efficient for wastewater treatment. The combined photovoltaic – electrochemical (PV-EC) method can produce electrolytic hydrogen and purify industrial wastewaters by combining solar energy with electrocoagulation and electrooxidation processes. The PV-EC system's adaptability resides in its capacity to modify wastewater flow rate in response to the PV array's current intensity and instantaneous solar radiation. Operating parameters that affect process efficiency include wastewater flowrate, applied current intensity, electroprocessing time and solar irradiance were examined and optimal conditions were identified. The experimental results revealed that the initial chemical oxygen demand (COD) of 19 460 mg L^{-1} of the plastic industry wastewater, were decreased to 8000 mg L^{-1}, after 2 h electroprocessing time using iron or aluminium electrodes at 600 mA current intensity. Further increase of COD removal efficiency was not possible either with increasing processing time, current intensity or using electrooxidation process. The results of our study indicate that the electrochemical treatment can reduce COD from wastewater generated during the production of plastic products. Moreover, the proposed method is applicable in decentralized areas without access to the electricity grid.

1 Introduction

Anthropogenic chemical / by-products generated by numerous industrial activities can cause major environmental damage when disposed without proper treatment. These substances are harmful to ecosystems because they are regarded as pollutants. Regrettably, effluents from the plastics industry are expected to cause major water pollution [1], thus it is urgent to redefine sustainable methods and technologies for wastewater treatment.

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Addressing this issue is critical since water quality is essential to human health, well-being, and environmental balance.

Since the implementation of European commission Wastewater Directive (1991) water quality has been improved [2]. Technologies suitable for wastewater treatment include physical, chemical and biological processes. Among them, electrochemical technologies, such as electrocoagulation, electro-flotation, and electrooxidation, have shown promising results for several water treatment applications [3].

1.1 Basic principles of electrocoagulation

Utilizing the concepts of flocculation and coagulation, electrocoagulation is an electrically powered wastewater treatment method. Using electrical current, metallic ions are discharged into the wastewater from the sacrificial electrodes. The required coagulant species are then formed by hydrolyzing these ions. In electrocoagulation, coagulants are produced in-situ as a result of the electro-dissolution of aluminium or iron anodes, in contrast to conventional procedures where they are introduced to the process externally [4]. Through the electrocoagulation procedure with electrodes from aluminium and iron, the next reactions arise:

$$\text{Electrodes from iron: } Fe \rightarrow Fe^{2+} + 2e^{-} \text{ (anode)} \quad (1)$$
$$Fe \rightarrow Fe^{3+} + 3e \text{ (anode)} \quad (2)$$
$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \text{ (cathode)} \quad (3)$$
$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \text{ (coagulant)} \quad (4)$$
$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3 \text{ (coagulant)} \quad (5)$$
$$\text{Electrodes from aluminum: } Al \rightarrow Al^{3+} + 3e^{-} \text{ (anode)} \quad (6)$$
$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \text{ (cathode)} \quad (7)$$
$$Al^{3+} + 3OH\text{-} \rightarrow Al(OH)_3 \text{ (coagulant)} \quad (8)$$

The generated metallic cations (Fe^{2+}, Fe^{3+} and Al^{3+}) from the relevant anodic reactions (1), (2) and (6) have as a result decrease of the colloidal matter's net surface charge consequential in destabilization afterwards coagulation. Also, Fe^{2+}, Fe^{3+} and Al^{3+} cations combined with the cathodically produced OH^{-} anions (see formulas (4), (5) and (8)) form coagulant precipitates such as $Fe(OH)_2$, $Fe(OH)_3$ and $Al(OH)_3$ that can absorb both organic and inorganic pollutants [5]. Concurrently microbubbles of hydrogen gas are formed for the duration of water electrolysis and released at the cathode. The microbubbles assist agglomerates to float and separated from the liquid phase by filtration. Therefore, the electrocoagulation process include mechanisms like oxidation-reduction, coagulation, absorption, flotation, and precipitation [6].

The electrocoagulation process is characterized as cost-effective, energy efficient, and friendly to the environment. The technology require less energy compared to treatment techniques such as chemical oxidation or filtration, which result in low operational expenses. In addition, electrocoagulation generates less sludge than conventional techniques such as chemical coagulation and flocculation.

1.2 Basic principles of electrooxidation

Organic matter may undergo anodic oxidation by two (2) major mechanisms:

A) Direct oxidation, where the pollutants are adsorbed on the anode surface and destroyed by the electron transfer reaction and

B) Indirect oxidation by the electrochemically generated intermediate oxidants, such as free hydroxyl radicals OH*, hydrogen peroxide H_2O_2, chlorine Cl_2 and peroxodisulfate, $S_2O_8^{2-}$, according to the reactions (9-12):

$$H_2O \rightarrow OH^* + H^+ + e^- \quad (9)$$
$$2OH^* \rightarrow H_2O_2 \quad (10)$$
$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (11)$$
$$2SO_4^{-2} \rightarrow S_2O_8^{-2} + 2e^- \quad (12)$$

The free hydroxyl radicals generated at the exterior of dimensionally constant anodes (like boron doped diamond (BDD), TiO_2, PbO_2, graphite, and Pt) are mostly responsible for organic pollutants oxidation. These radicals are used for oxidative destruction of organic materials in both chemical advanced oxidation processes (CAOP) and electrochemical advanced oxidation processes (electrochemical advanced oxidation processes (EAOP)). The higher efficiency for oxygen generation has been reported for BDD electrodes [7, 8]. Additionally, these electrodes show excellent mechanical and chemical stability. Consequently, BDD electrodes, in contrary to Ti/Pt are more suitable for producing free OH* radicals and performing EAOPs with high current efficiencies [9, 10].

2 Materials and methods

2.1 Wastewater origin and characteristics

Raw wastewater was acquired from a plastic industry in Greece producing polyethylene (PE) and polypropylene (PP) products. The basic features of wastewater are shown in Table 1. All measurements were performed in duplicate.

Table 1. Main characteristics of treated wastewater sample

Parameter	Value
pH	2.47
EC (mS cm^{-1})	3.06
Total Suspended Solids (TSS) (mg L^{-1})	510 ± 30
Volatile Suspended Solids (VSS) (mg L^{-1})	400 ± 20
VSS/TSS	0.8 ± 0.05
Total COD (mg L^{-1})	21240 ± 1100
Soluble COD (mg L^{-1})	19460 ± 800

2.2 Experimental study and equipment

Electrocoagulation experiments were realised at room temperature with the use of a cylindrical electrochemical reactor (with volume equal to 450 mL) which includes a magnetic stirrer (Thermodyne, Nuova II Stir Plate), functioned at 300 rpm. Two commercially iron (St 37-2 steel) (in keeping with German standard DIN 17100) or aluminum plates (2024 aluminum alloy) were react as electrodes with dimensions 8 cm x 5 cm x 0.3 cm offering an area equal with 25 cm^2 each. The electrodes were installed vertically parallel to one another, having an inter-electrode distance of 1 cm. Electrochemical oxidation was also studied using platinized titanium Ti/Pt cathode and boron doped diamond (BBD) anode (DiaCCom, Germany) electrodes. Na_2SO_4 and NaCl were used as supporting electrolytes. In both methods, the electrodes were supplied with DC current (STELLTRAFO, PHYWE Systeme Gmbh & Co, Germany) to offer constant current and a hand-held multimeter (Fluke 177) measuring voltage and amperage. The efficiency of the electrocoagulation process was studied for different current intensities (300, 600 and 900 mA), electro-processing time (60, 120 and 180 min), for both electrodes (iron and aluminum) and several initial pH values.

During the experiments, each 1 hour of electro-processing period, samples in liquid form were removed from the reactor medium, filtered with the use of whatman paper, and examined for 3 parameters, i) pH, ii) electrical conductivity and iii) chemical oxygen demand (COD). COD measurements were completed with a COD thermoreactor (Tr 420, Merk) and a spectrophotometer (Spectroquant Pharo100, Merk), consistent with the Standard Methods for analysis of water and wastewater.

2.3 Electricity supply system

In order to have zero emissions in the local area all the necessary electricity can supplied via solar photovoltaic panels. For the experimental procedure is needed 600 mA with 4.5 V (450 mL of water) for 60 min which means consumption 6 Wh (or 0.006 kWh) for every liter of wastewater. Bearing in mind that a medium sized company needs to applied this method for approximately 200 l per day an autonomous and ecological electrical system was evaluated with the use of Homer (Hybrid Optimization of Multiple Energy Resources) software. Homer is a renewable energy tool, which can evaluate many potential system configurations in order to find the optimum system. In this article a long term meteorological data from Xanthi city were used with intention to determine the best system.

Figure 1 depicts the simulated design of the examined renewable energy system in Xanthi (with average daily horizontal solar radiation equal with 4.16 kWh/m^2) that includes PV panels, converter and storage battery. The PV-batteries system was demonstrated flexible in relation to the instantaneous solar irradiation by regulating the wastewater flow rate to the current intensity supplied by the photovoltaic panels. The experimental set-up is shown in Figure 2 [11].

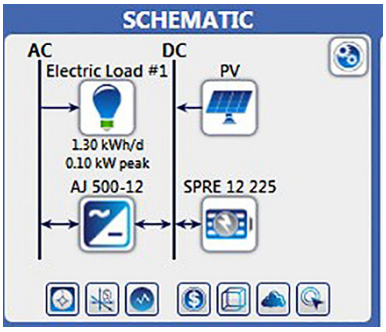

Fig. 1. The simulated system configuration in Homer software.

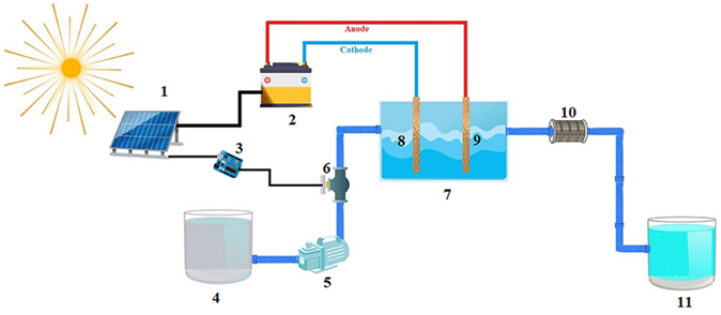

Fig. 2. Experimental setup of the combined electrochemical reactor supplied with solar energy (1. PV Solar panel, 2. Battery, 3. Regulator, 4. Wastewater tank, 5. Peristaltic pump, 6. Valve, 7. Electrocoagulation reactor, 8. Anode, 9. Cathode, 10. Filter, 11. Treated effluent.

3 Results and discussion

A variety of operational factors, such as electrode type, flow rate, and current intensity may affect the PV-EC process efficiency. This study evaluates the efficacy of a treatment technology intended to treat actual wastewater from plastic industry by examining all these factors.

3.1 Electrocoagulation using iron electrodes.

According to the results provided in Fig. 3, the COD removal increased with increasing operating time and current intensity. In the case of 600 and 900 mA current intensity, COD removal increased between 56 and 60% within 2 h electroprocessing time. Further increasing reaction time to 3 h did not improved overall process efficiency. According to [12] iron electrodes are fewer toxic and adequate in circumstance that the treated effluent is reused in agriculture. As can be seen from Figure 2 optimum results were obtained at a current intensity of 600 mA.

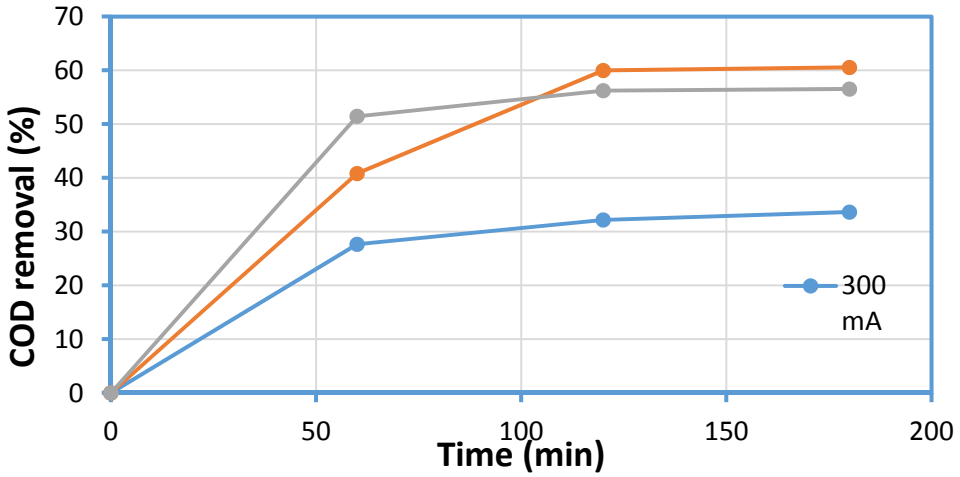

Fig. 3. Effect of electroprocessing time and current intensity on COD removal efficiency during electrocoagulation of plastic industry wastewater using iron electrodes.

3.2 Electrocoagulation using aluminium electrodes

Figure 4 illustrates the result of electroprocessing time on COD exclusion productivity based on electrodes constructed from aluminum with current intensity 600 mA. For comparison the results of COD removal efficiency using iron electrodes at the same current intensity are included. The data demonstrate that COD removal using aluminum electrodes is within the same range with iron. In this case, maximum COD removal was around 57% after 2 h processing time with a current intensity of 600 mA.

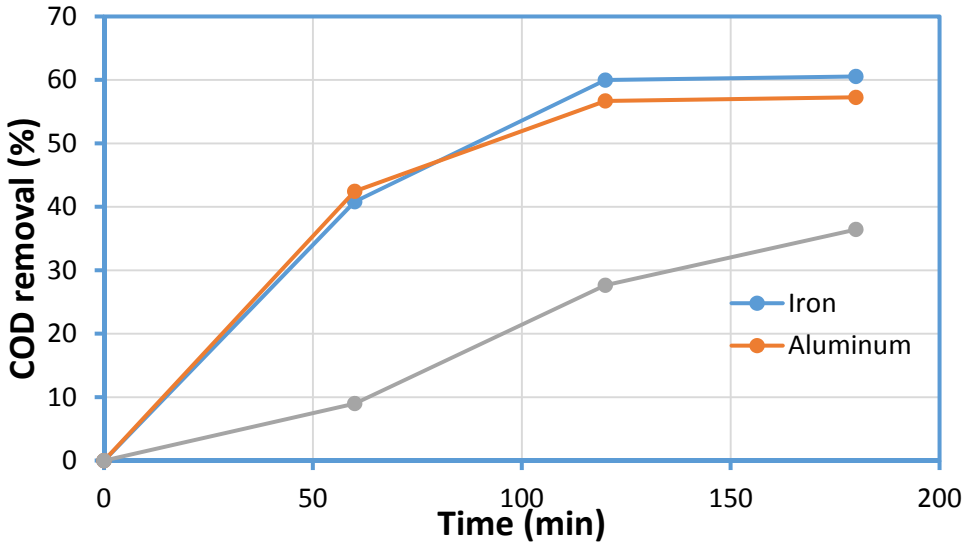

Fig. 4. Effect of electroprocessing time and current intensity on COD removal efficiency during electrocoagulation of plastic industry wastewater using iron, aluminum or Ti/Pt – BDD electrodes at current intensity 600 mA.

3.3 Electrooxidation using Ti/Pt and BDD electrodes

The electrodes used for the electrooxidation experiments were BDD serving as anode and Ti/Pt plate electrode serving as cathode. As shown in Figure 4, the electrooxidation treatment of the plastic industry wastewater sample with BDD anode was not efficient compared with iron or aluminum electrodes. In this case, COD removal remained maximum at 36% after 3 h electroprocessing time.

The maximum COD in all experiments is not very high, but similar with other works [12, 13]. It must be noticed that most published work uses municipal waste with few plastics while in this work have waste from plastic production plants that contain a lot of complex waste (plastics, microbicides, dyes). Furthermore in this work the current density (24 mA/m^2) it was really lower in comparison with the typical experiments (15 A/m^2) fact which reveals the advantage pf the proposed procedure. For better results in the next step will be combined with another method.

3.4 Renewable energy system

The optimum renewable energy system includes 0.595 kW PV panels, 3 Trojan SPRE 12 225 batteries and one Struder AJ 500-12 convertor 1 kW. Figure 5 shows the monthly electricity production of the system. From this Figure 5 is obvious that during the summer months the electricity production is higher while the minimum occurs in winter months. The charge daily profile of the batteries for every month is shown in Figure 6 and reveals that batteries is necessary mainly during the winter months. The total cost of energy for a 20 years project is approximately 0.4 /kWh which is a competitive cost for an autonomous system.

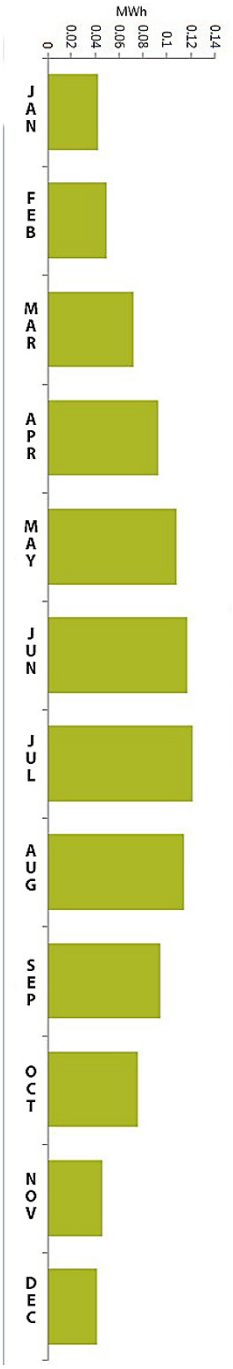

Fig. 5. Monthly electricity production of the suggested PV system.

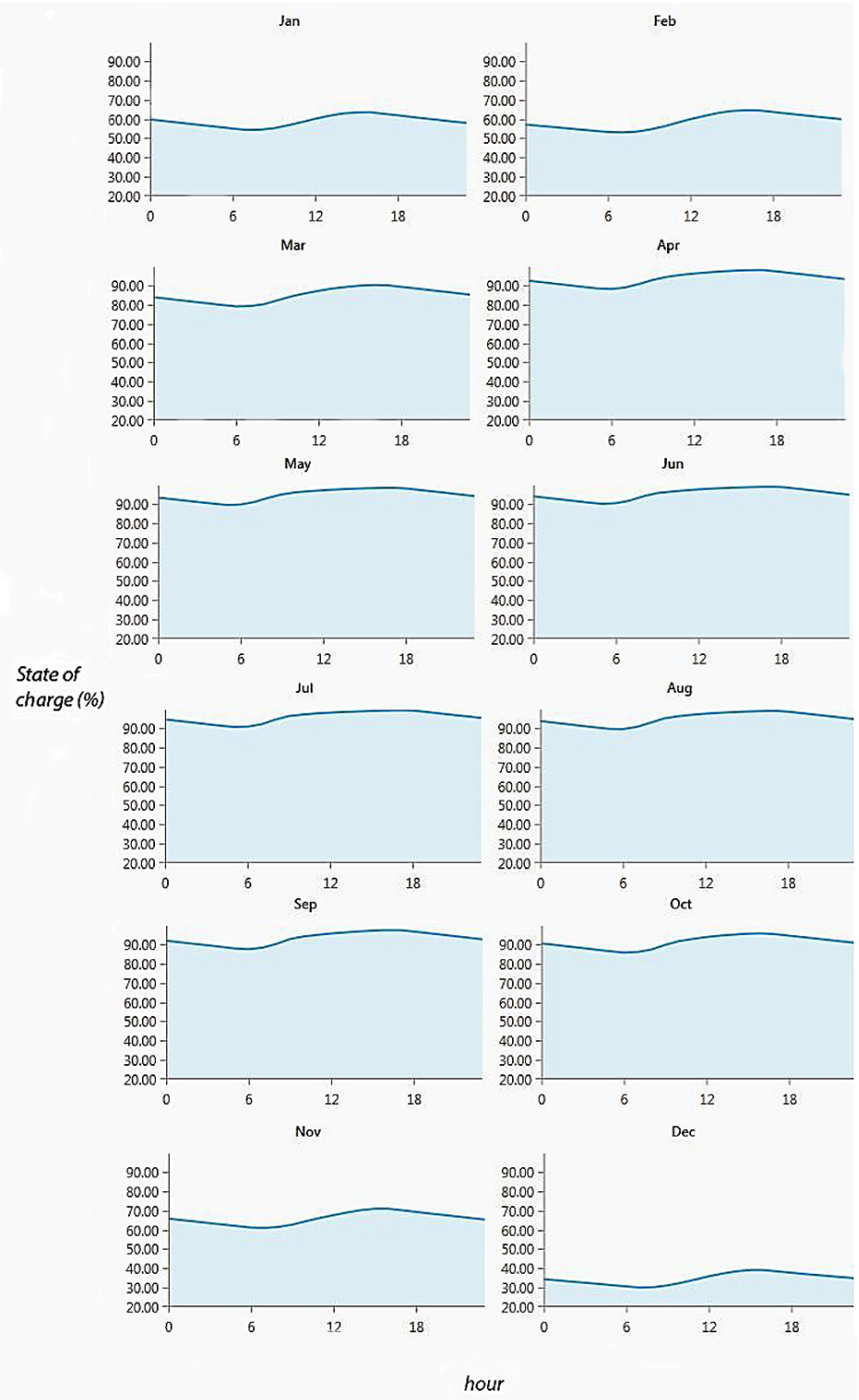

Fig. 6. State of charge of the batteries for each month.

4 Conclusion

According to this study, the electrocoagulation method, with iron and aluminum electrodes, achieved significant COD removal from actual plastic industry wastewater. Electrocoagulation and electrooxidation methods require further studies especially under field-scale conditions to fully evaluate the costs and long-term effectiveness. The necessary electricity supplied from photovoltaic panels combined with the energy storage batteries providing an autonomous system. Owing to the use of a real sample from a plastic industry, which incorporates a real difficult chemical compounds, for example ethylene, propylene, biocide and dyes, the COD values can be further enhanced using and another method.

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