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Photovoltaic driven electrochemical Remediation of Drilling Fluid Wastewater with simultaneous Hydrogen Production

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Objective of present work

The paper demonstrates the possibility of remediating ***drilling fluid wastewaters*** using the electrochemical processes:

electrocoagulation

electrooxidation

which are directly powered by a ***photovoltaic array without batteries***.

The photovoltaic electrochemical (PV-EC) system is made ***versatile to the instantaneous solar irradiation :***

by adjusting the wastewater flow rate to the current density

supplied by the PV array.

All operating parameters affecting the PV-EC process are investigated:

(pH, current density, flow rate, contact time, solar irradiation).

Drilling fluid wastewater treatment methods

Drilling fluid or ***drilling mud*** is used in the upstream petroleum industry to aid the drilling of oil.

Mud consists of a base fluid (water or oil) and various solid and liquid additives to give the mud certain desirable properties for a safe drilling performance.

The additives constitute toxic compounds, thus, mud must be appropriately treated to avoid negative environmental impacts.

Drilling fluid treatment methods:

- ***Chemically enhanced dewatering methods***
  - ***coagulation, flocculation and flotation***
- ***Electrochemical methods:***
  - ***electrocoagulation***
  - ***electrooxidation***

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Brief description of electrocoagulation

Electrocoagulation is a process consisting of creating metallic hydroxide flocks by electrodissolution of soluble anodes of **Al** or **Fe**.

The main reactions produce **Al^{3+}** ions at the sacrificial **Al** anode and hydroxide ions **OH^-** as well hydrogen gas at the cathode:

$$Al \rightarrow Al^{3+} + 3e \qquad \text{(anode)}$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad \text{(cathode)}$$

The generated Al^{3+} and OH^- ions react to form the coagulant

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$$

Additionally, a part of pollutants is removed by ***electro-flotation***, by the ***hydrogen gas bubbles*** produced at the cathode.

All phenomena, *coagulation, adsorption, flotation, anodic oxidation and cathodic reduction* occur simultaneously and synergistically leading to a rapid removal of inorganic and organic pollutants from treated wastewater.

Brief description of electrooxidation

Electrooxidation can occur:

- ☐ ***directly at the anode*** **surface and**
- ☐ ***indirectly in the bulk solution*** by the electrochemically produced strong ***intermediate oxidants***, as following:

$$H_2O \rightarrow OH^* + H^+ + e$$

$$3H_2O \rightarrow O_3 + 6H^+ + 6e$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e$$

$$2Cl^- \rightarrow Cl_2 + 2e$$

$$2OH^* \rightarrow 2H_2O_2$$

The most powerful oxidant in water is the ***free hydroxyl radical, OH**** with a very high redox potential of ***2.8 Volt*** versus normal hydrogen electrode.

Boron doped diamond electrodes (BDD) are the most suited for producing free ***OH* radicals*** and performing ***advanced oxidation processes (AOPs)*.**

Experimental

Experiments were conducted in **International Hellenic University in Kavala, Greece** with geographical data:

- ***latitude 40˚ 55΄***
- ***longitude 24˚ 22΄***
- ***altitude 138 m above the sea level***

Photovoltaic module *:*

SUNPOWER (Maxeon Cell Technology) SPR-327NE-WHT-D made from monocrystalline silicon with a surface area of 1.63 m^2 and a peak power of 327 W.

Electrochemical cell: Cylindrical glass cell of 1000 mL, solution volume 400 mL

Electrodes

electrocoagulation: ***three Al plates*** in parallel

electrooxidation: ***one central BDD as anode and two outer graphite plates as cathodes***

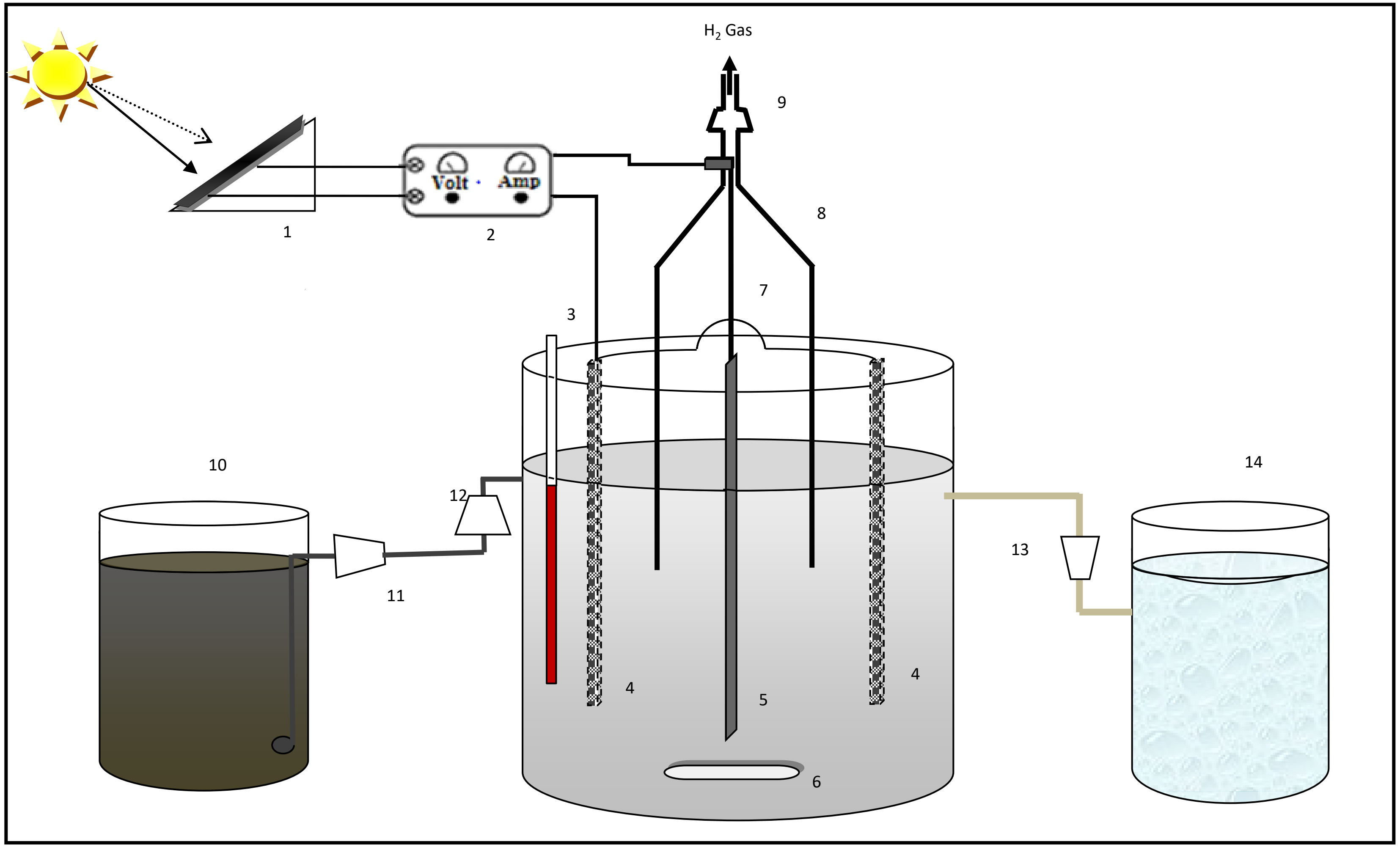
COD (Thermoreaktor TR 420 with spectrophotometer, Spectroquant Pharo 100, MERCK)

Conductometer (WTW)

pH-meter (Hanna)

Peristaltic pump

Experimental set up



1. PV Solar module, 2. Regulator, 3.Thermometer, 4. Anodes, 5.Cathode, 6. Magnetic stirrer,
7. Conducting wire, 8. Separator, 9. Hydrogen gas flow meter, 10. Wastewater deposit,
11. Peristaltic pump, 12. Flow meter, 13. Filter, 14. Treated pure water

Drilling Fluid wastewater sample
before and after the electrochemical treatment

Effect of pH on the efficiency of electrocoagulation and electrooxidation

Electrocoagulation:

pH 5-10: optimal solution pH region

COD removal percent : >60 %

pH < 3: very low COD removal percent: < 20 %

pH >11: COD removal markedly decreases.

Electrooxidation:

pH 6-8: very high COD reduction >95 %.

This pH dependence is related to the stability of the produced hydroxyl radicals OH^* :

In acidic pH:

$$H^+ + OH^* \longrightarrow H_2O^+ \text{ (protonated radical)}$$

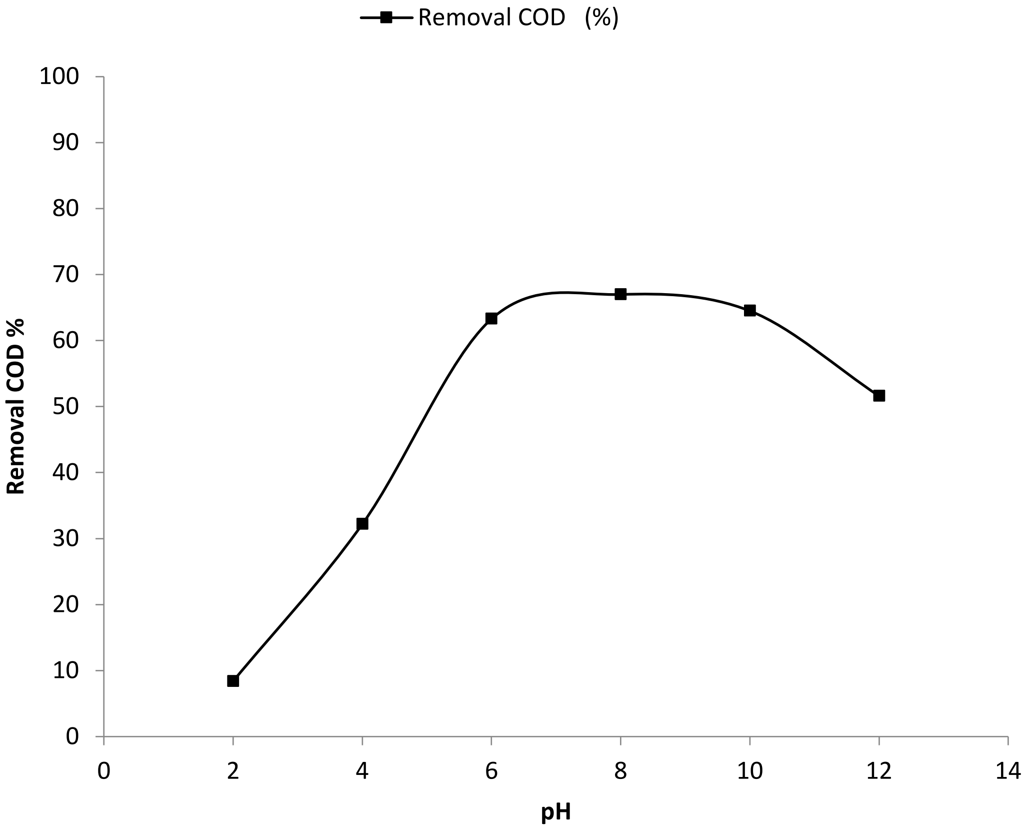
$$H_2O^+ + H_2O \longrightarrow H_2O^+ \cdot H_2O$$

In alkaline pH:

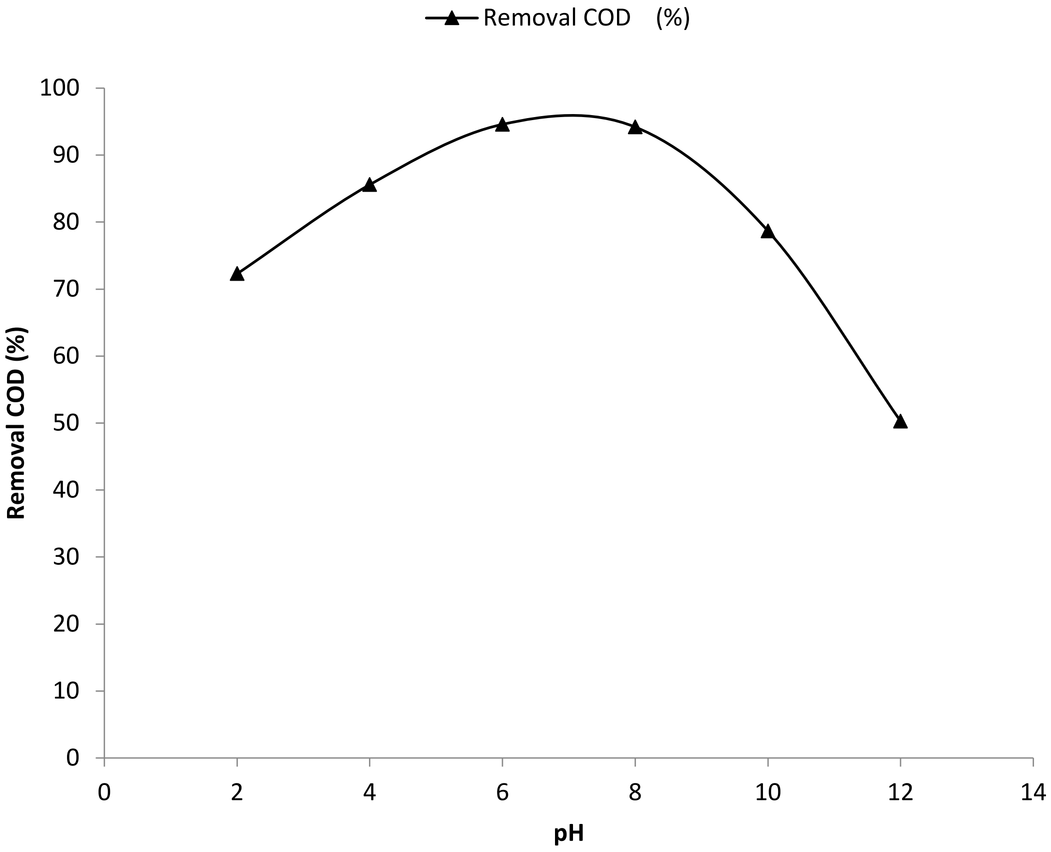
$$OH^* + OH^- \rightleftarrows \cdot O^- + H_2O$$

COD removal versus initial pH

Electrocoagulation:



Electrooxidation



Effect of applied current density

Electrocoagulation:

Increased current density ***accelerates proportionally*** the COD removal efficiency.

Electrooxidation:

Increased current density ***accelerates more than proportionally*** the COD removal efficiency.

This is indicated by the ***much shorter needed electrolysis times*** than the proportional:

current densities: 30, 60 and 90 mA/cm^2,

electrolysis times: 120, 50 and 20 minutes,

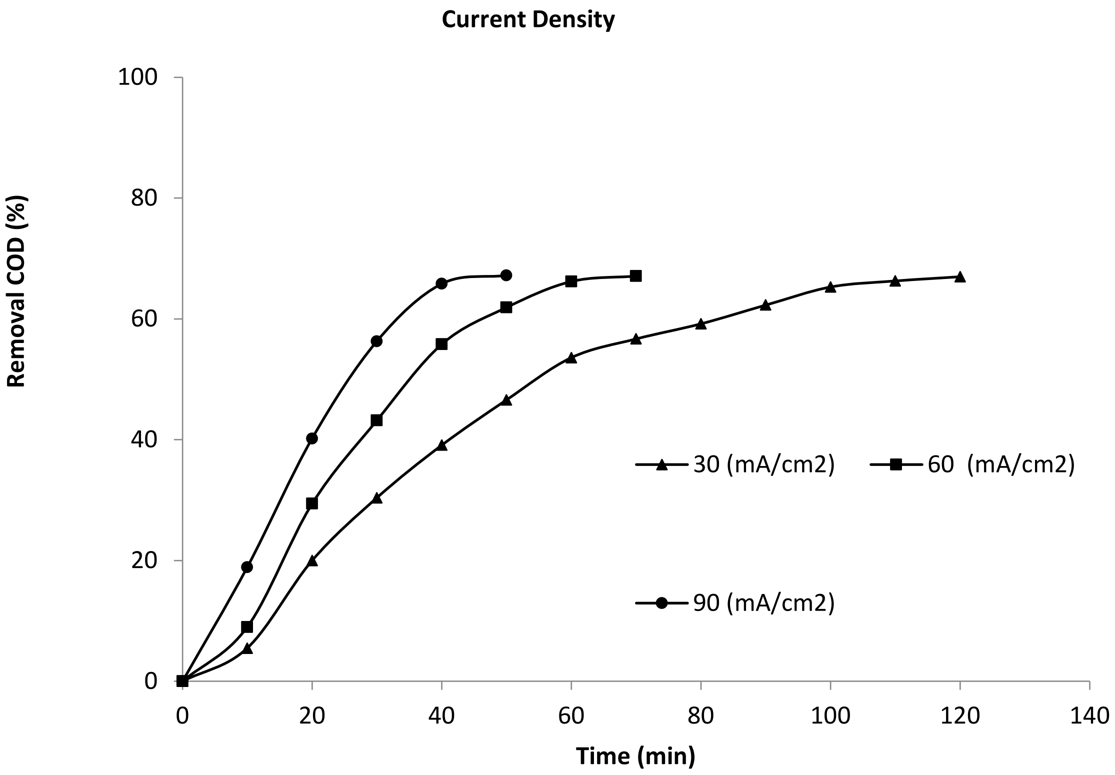
electrical energy consumptions 29.92, 23.87 and 18.47 kWh/m^3

Less electrical energy is consumed at higher than at lower current densities due to:

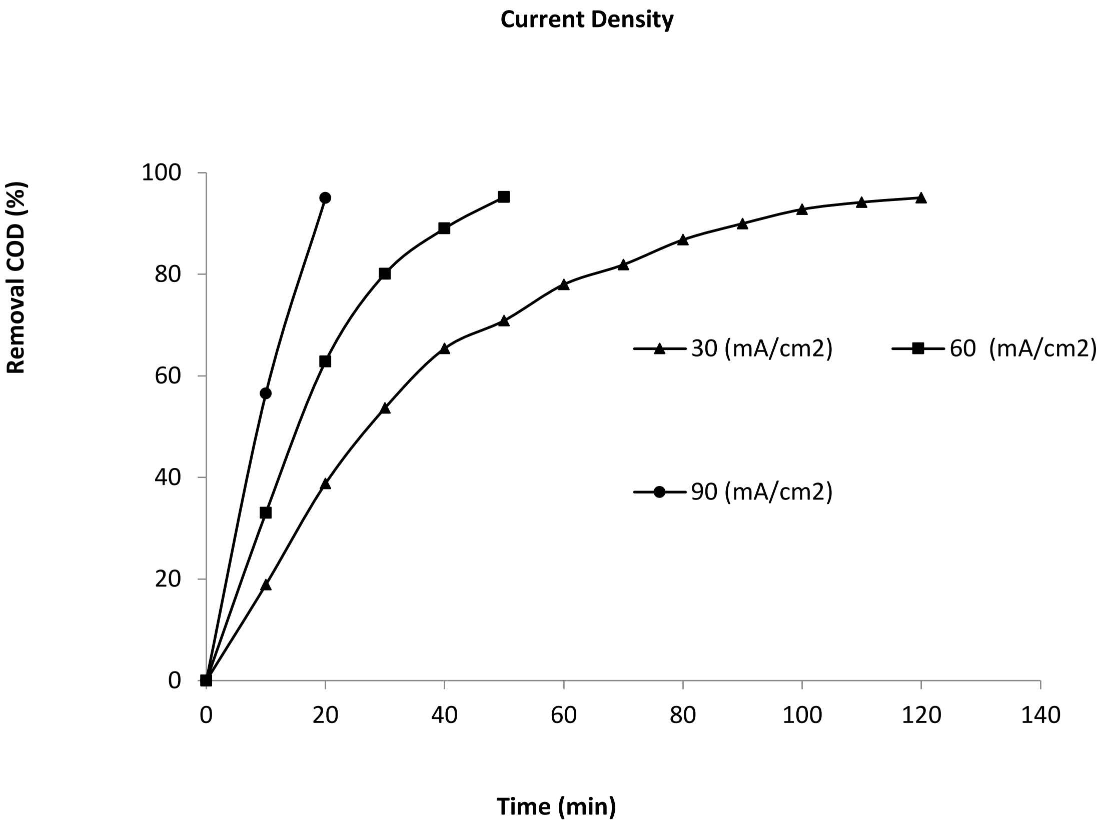
substantially higher production of OH* radicals and shorter electrolysis time.

COD removal percentage versus time at various current densities

Electrocoagulation



Electrooxidation



Effect of temperature

Electrocoagulation:

The COD removal depends only slightly on temperature changes.

Slight increase of COD removal is initially observed with increasing temperature ***until 30 ^{0}C****, due to better particle mobility.*

Slight decrease of COD removal is observed at higher temperatures, due to formation of larger hydrogen bubbles associated with reduced flocculation time.

Electrooxidation:

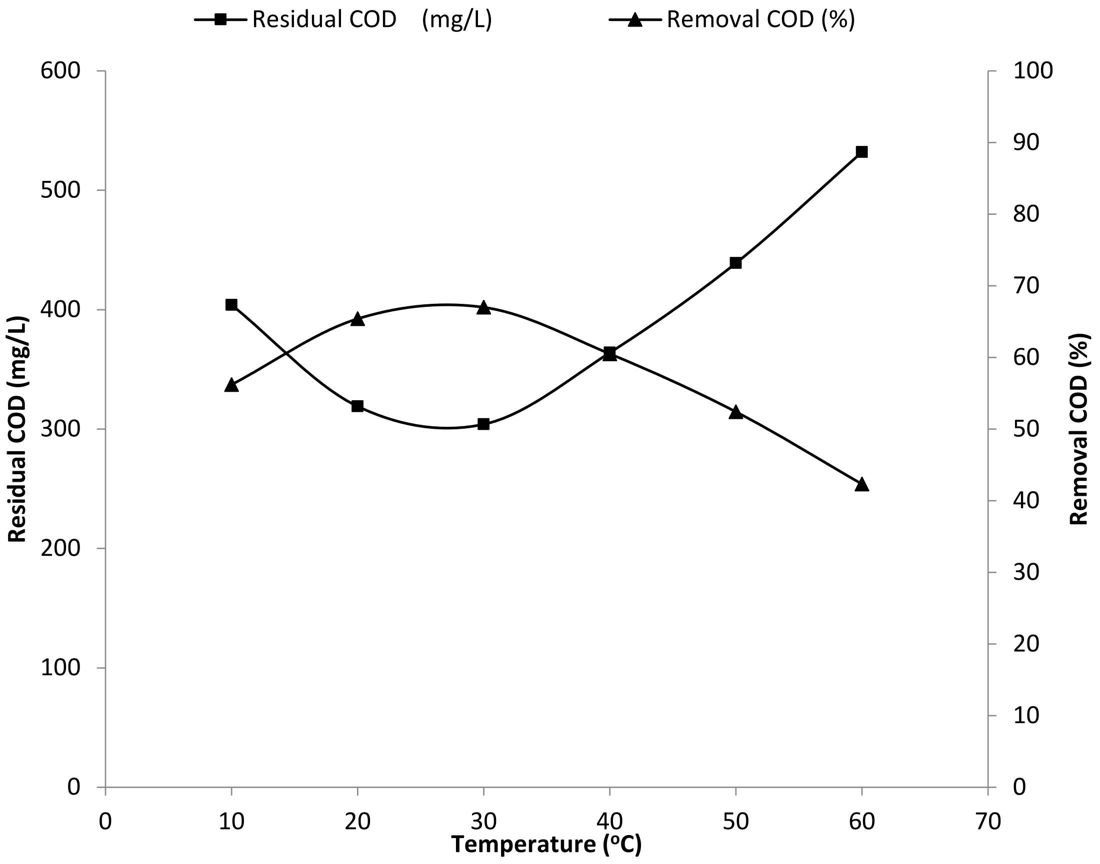
The electrooxidation treatment of the drilling fluid sample was investigated at three different temperatures of 25, 40 and 60 ^{0}C.

Remediation is accelerated with increased temperature showing a

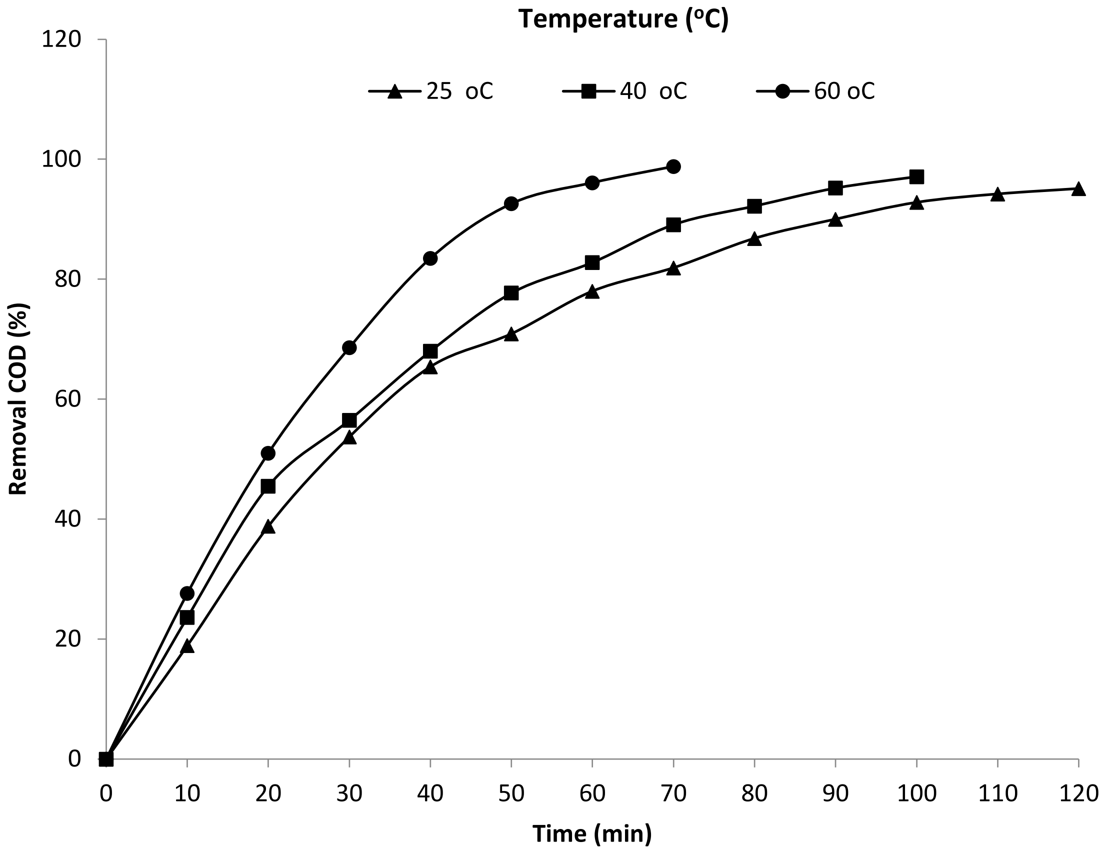
COD reduction of >95 %

COD removal percentage versus temperature

Electrocoagulation



Electrooxidation



Continuously operated process

The ***electrooxidation process*** reaches higher COD removal efficiency ***(>95%)*** and was selected for continuous operation.

The PV-EC system becomes ***versatile to instantaneous solar irradiation*** **by keeping constant the** ***ratio current density/flow rate*** i.e. when the current density changes, also the flow rate must proportionally change to maintain this ratio constant.

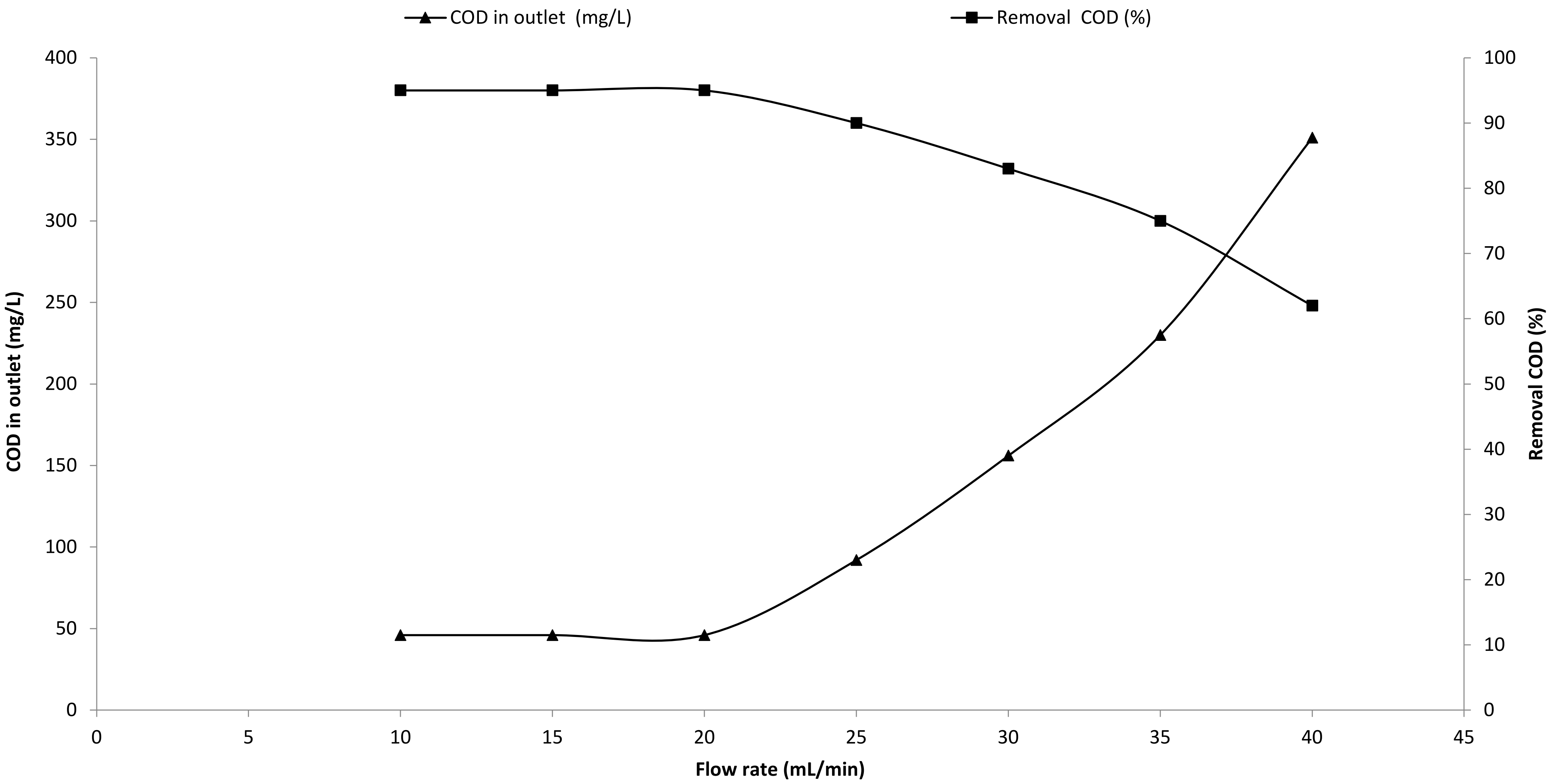
By increasing the current density, the cell voltage and flow rate increase proportionally, while the residence time decreases.

The removal percentage of COD is not affected and remains high >95 % in all experiments.

Advantages for not using batteries:

- ✓ ***lower installation costs***
- ✓ ***higher electrical energy utilization***
- ✓ ***avoidance of environmental problems regarding battery disposal***

Continuous electrooxidation - Effect of flow rate



Solar irradiation and I-V curve of photovoltaic module

The solar irradiation intensity depends on the occasional ***meteorological/geographical conditions*** and influences the photovoltaic output current and the performance of the electrochemical process.

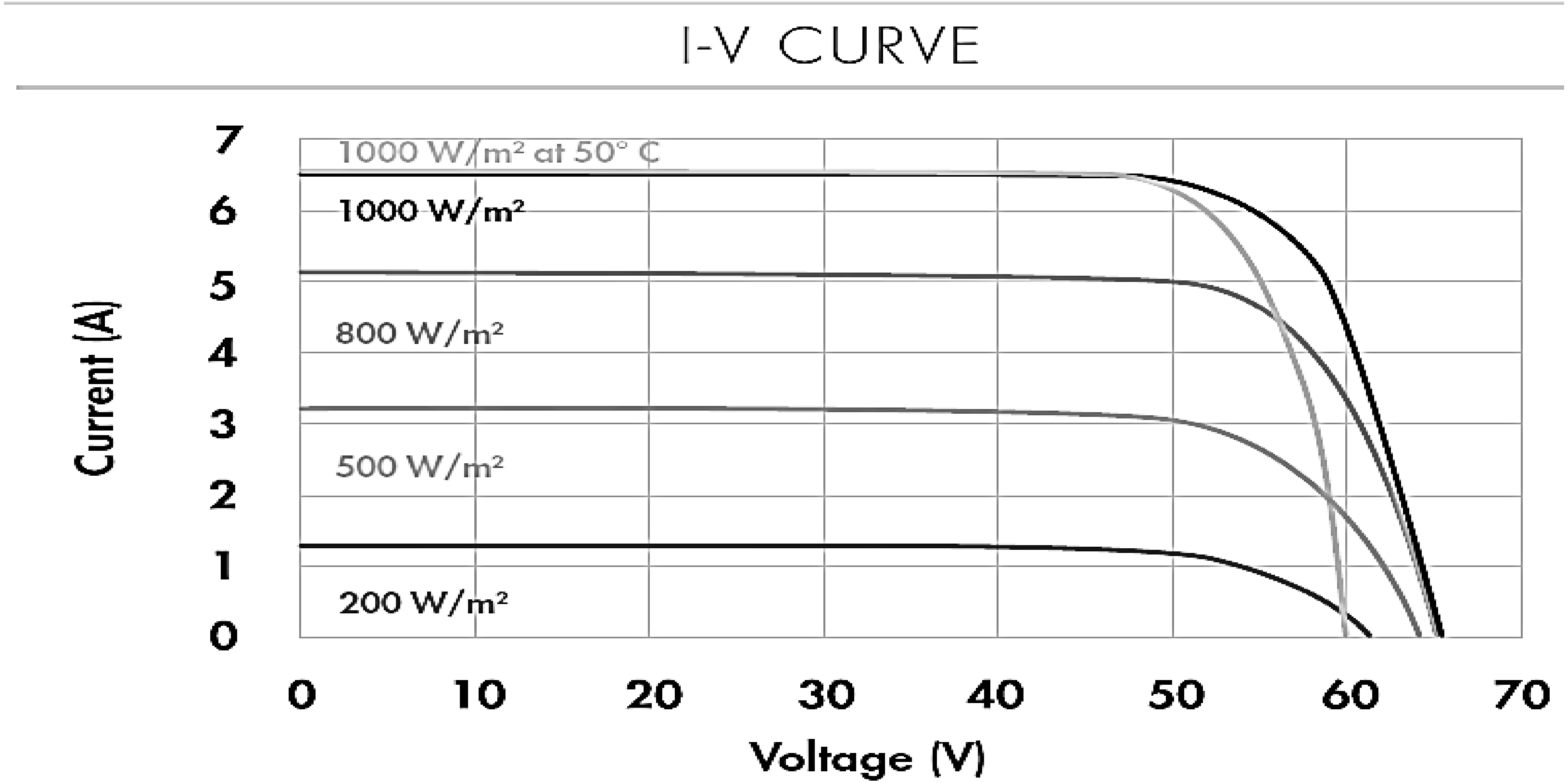
The flow rate of the treated wastewater can be used as the ***control parameter***.

For solar irradiation of 1000 w/m^2 and temperature of 25^o C the most important characteristics of the current-voltage curve of the photovoltaic module are :

i. ***the short circuit current I_{sc} (6.46 A),*** *which is the maximum current at zero voltage depending mainly on solar irradiation.*

ii. ***the open circuit voltage (64.9 V),*** *which is the maximum voltage in absence of load depending mainly on temperature.*

I-V curve of photovoltaic module



Eletrolytic hydrogen production

The electrochemical treatment of aqueous organic waste can be coupled with hydrogen production.

The energy harvesting via the produced hydrogen gas is calculated from equation:

$$E_{H2} = m_{H2} \times 122\ kJ/g_{H2}$$

(***m*** is the mass of produced hydrogen and

122 kJ the specific heat per g of hydrogen).

During the continuous electrooxidation treatment of the drilling fluid wastewater at the **flow rate 20 mL min^{-1}** and **current density 90 mA cm^2** about **1.5 m^3 H_2/m^3** of treated wastewater can be produced.

In this way, the utilization of photovoltaic solar energy aims at a double useful objective:

✓***environmental cleanup***

✓***energy harvesting***

Conclusions

- It is possible to effectively remediate drilling fluid wastewater
  ***by directly connecting the electrochemical reactor to the photovoltaic generator without batteries*.**
- The PV-EC system is made versatile to instantaneous solar irradiation by adjusting the wastewater flow rate and
  keeping constant the ratio current density/flow rate.
- The COD removal percentage for various wastewater flow rates **20-40 mL/min**
  remained high ***(>95 %)***
- The proposed PV-EC process is a safe and efficient method for purification applications of drilling fluid wastewater and particularly
  ***in isolated places with lack of electric grid*.**

Thank you for your attention!