Cheese whey wastewater treatment by combined Electrocoagulation-Electrooxidation

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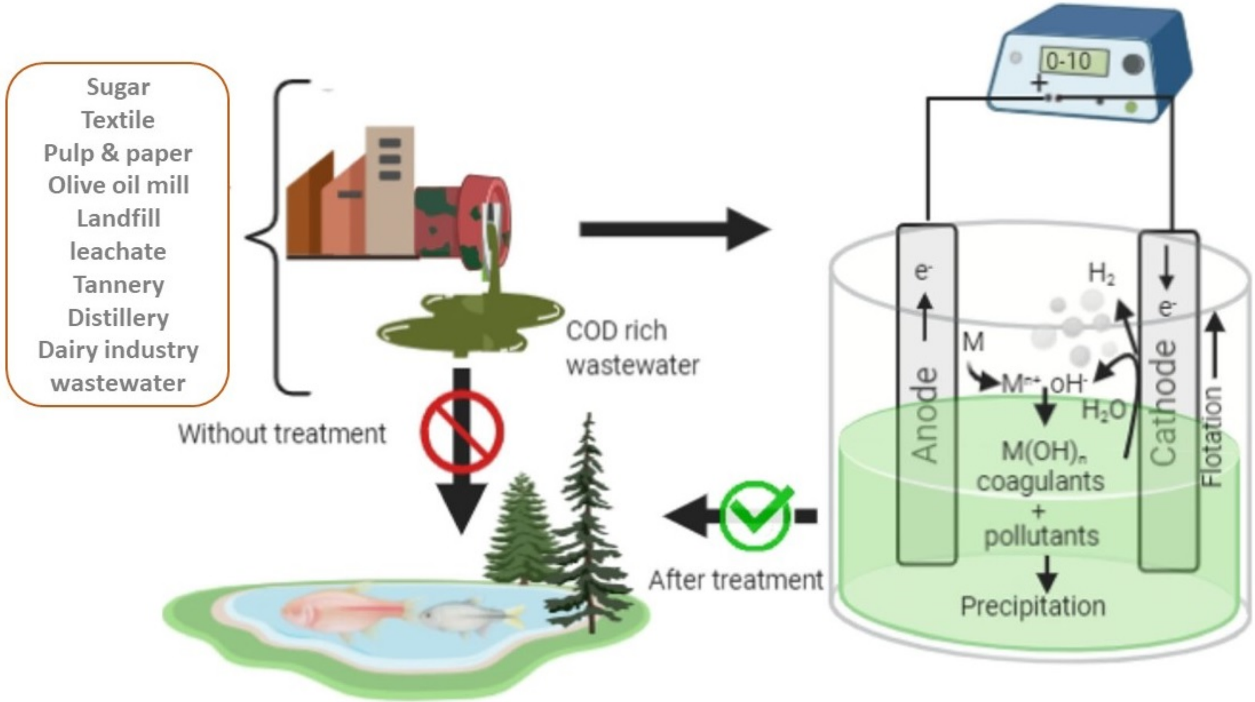
Goat cheese whey wastewater

- Whey as a waste is characterized by high COD.
- It is a polluting by-product, which needs to be treated to protect the environment.
- In Europe, their direct discharges to surface waters are not permitted under the relevant European Directives 91/2717/EEC and 97/771/EEC, respectively.
- Electrochemical processes such as electrocoagulation (EC) and electrooxidation (EO) have been reported to be the most effective for COD removal.



Mousazadeh, M. **(2021)** A critical review of state-of-the-art electrocoagulation technique applied to COD-rich industrial wastewaters. Environmental Science and Pollution Research 2021 28:32, 28(32), 43143–43172. https://doi.org/10.1007/S11356-021-14631-W

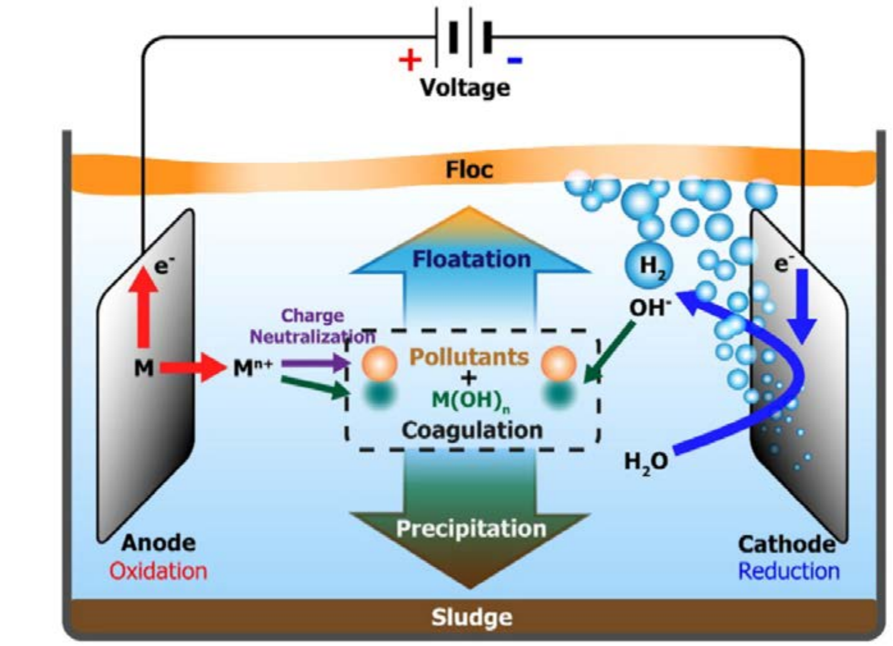
Electrocoagulation (EC)

- Mainly Fe and Al electrodes are used, which are immersed in wastewater.

- Its effectiveness is due to the formation of insoluble metal hydroxides $M(OH)_3$ through redox reactions, which act as coagulants and are capable of destabilizing organic matter.

$$M \rightarrow M^{n+} + ne^-$$

$$nH_2O + ne^- \rightarrow nOH^- + (n/2)H_{2(g)}$$



Magnisali, E., Yan, Q., & Vayenas, D. V. **(2022)** https://doi.org/10.1002/JCTB.6880

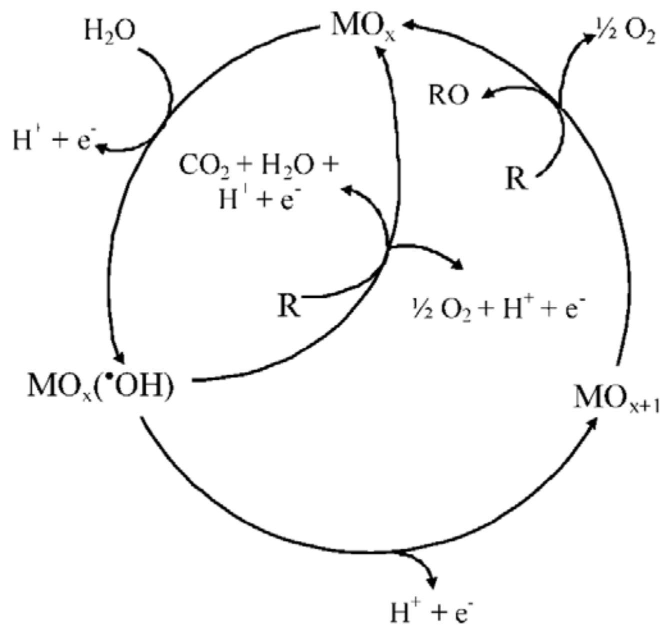
Electrochemical wastewater treatment

- The organic charge is destroyed due to the hydroxyl radicals (·OH) formed on the anode surface by the oxidation of water.

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^-$$

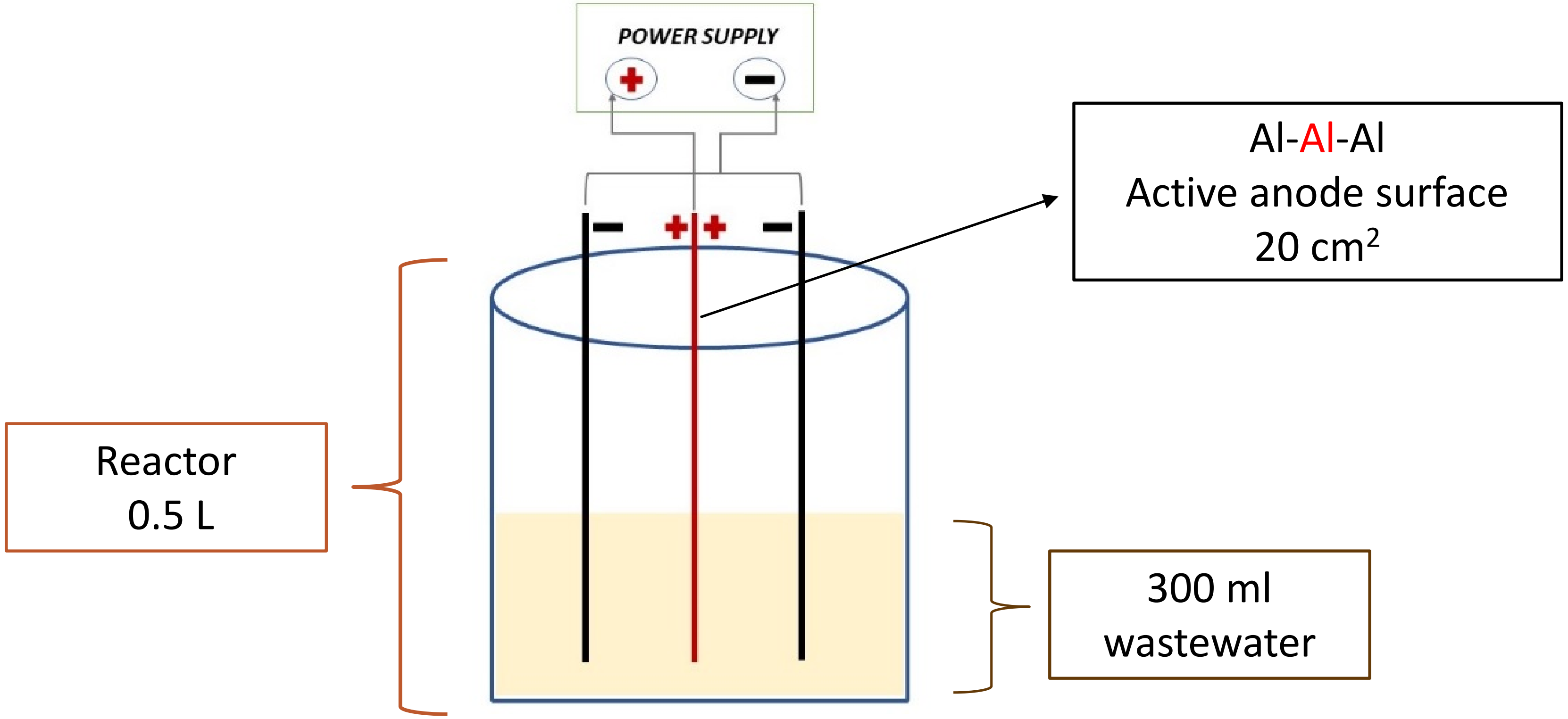
- The use of Boron-doped diamond (BDD) electrode, is able to completely and non-selectively mineralize organic pollutants (R) with high efficiency.

$$BDD(\cdot OH) + R \rightarrow BDD + nCO_2 + nH_2O + H^+ + e^-$$

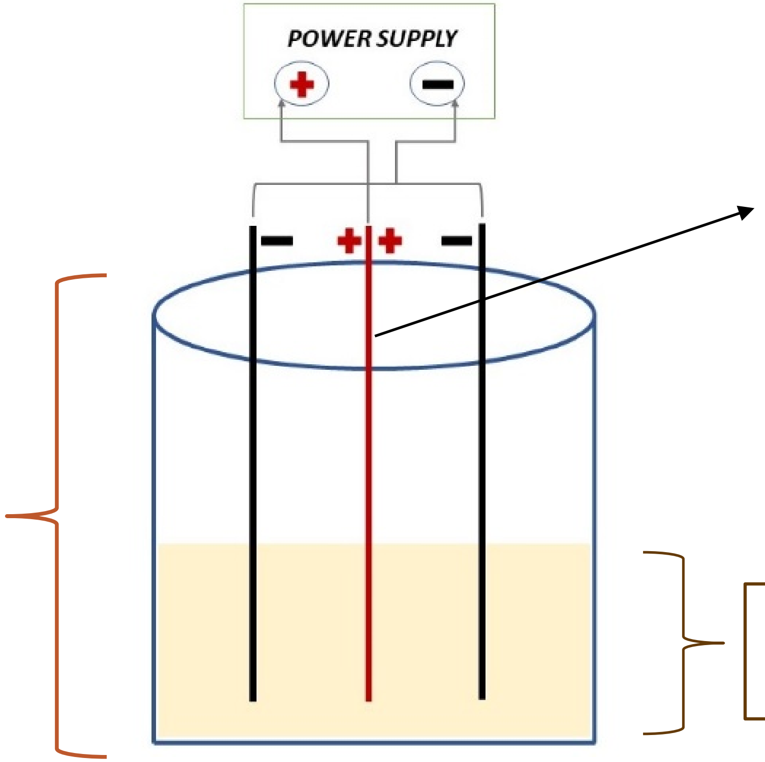


Panizza, M., & Cerisola, G. **(2009)** https://doi.org/10.1021/CR9001319

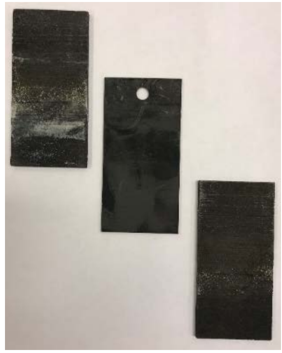
Experimental layout of the EC process



Experimental layout of the EO process



graphite-BDD-graphite
Active anode surface
20 cm^2



Reactor
0.4 L

300 ml
wastewater

Optimization of EC and EO operating parameters

The main parameters that affect the efficiency of EC and EO treatment were studied:

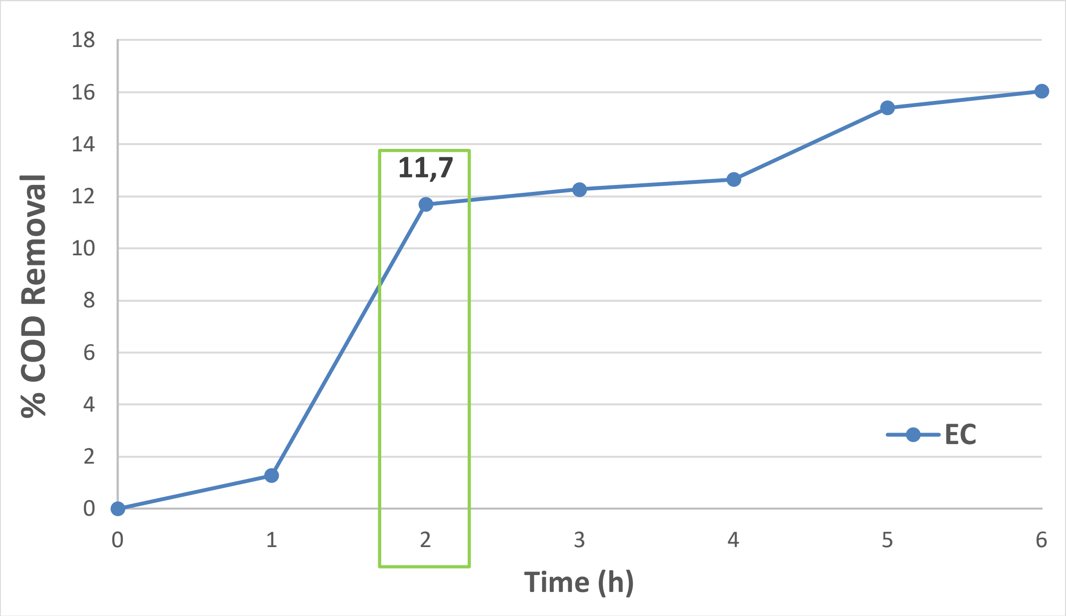
1) Operating time (h)
2) Agitation rate (rpm)
3) pH
4) Current density (mA/cm^2)

The purpose was to find the optimal operating conditions for the highest efficient removal of COD from cheese whey wastewater

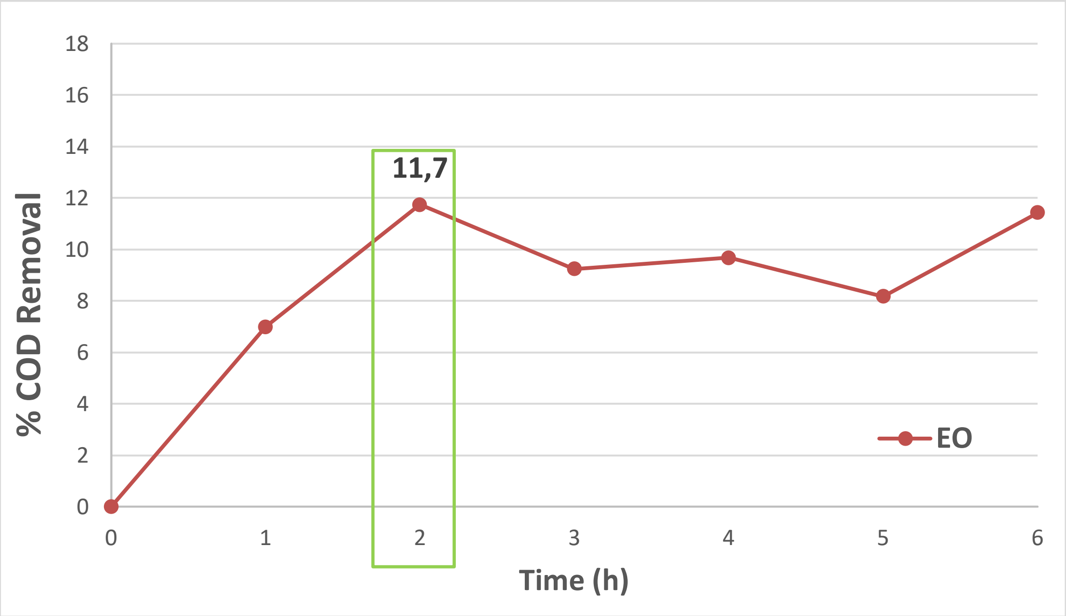
$$\% \; Removal = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100$$

➢ Operating time (h)

Electrocoagulation (EC)

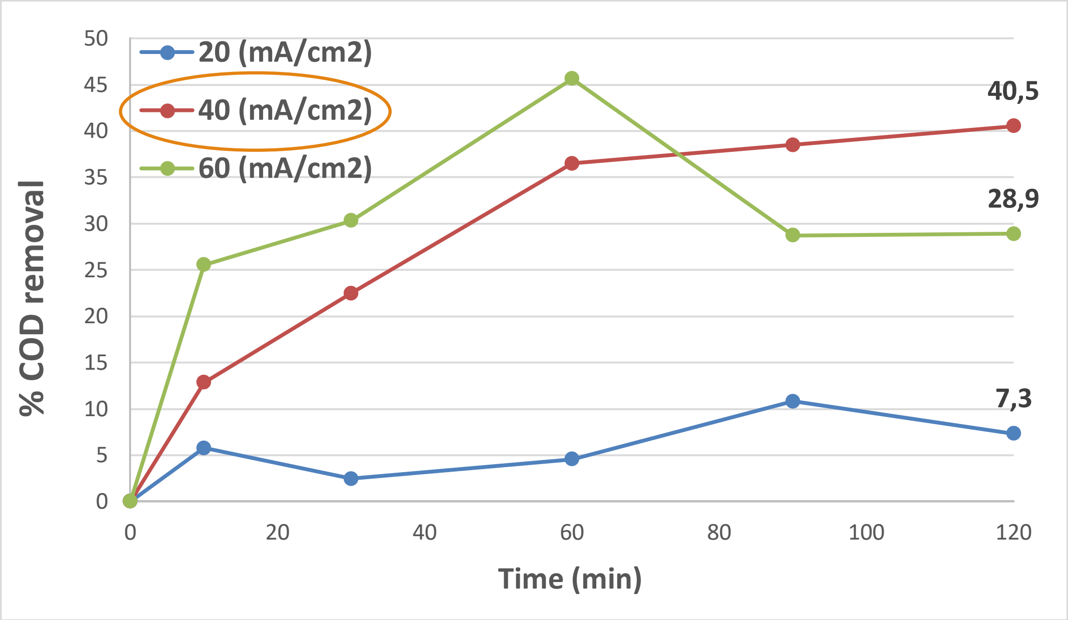


Electrooxidation (EO)

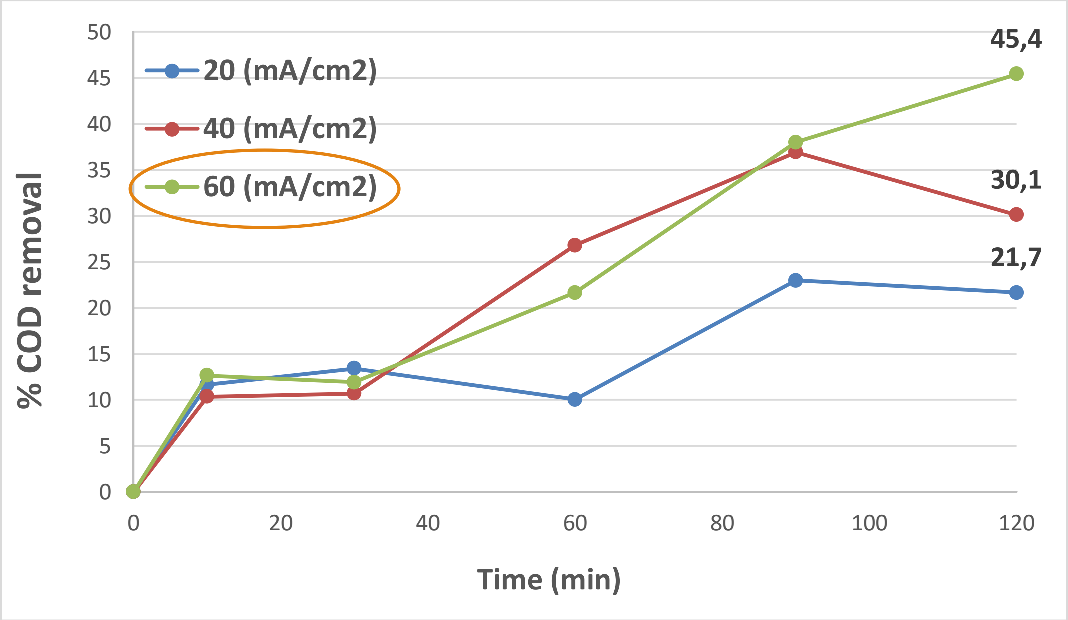


Current density (mA/cm^2)

Electrocoagulation (EC)



Electrooxidation (EO)



The current determines the release rate of

Al → Al^{3+} + **3e^-**

↑ mA/cm^2 ➔ ↑ e^- ➔ $Al(OH)_3$

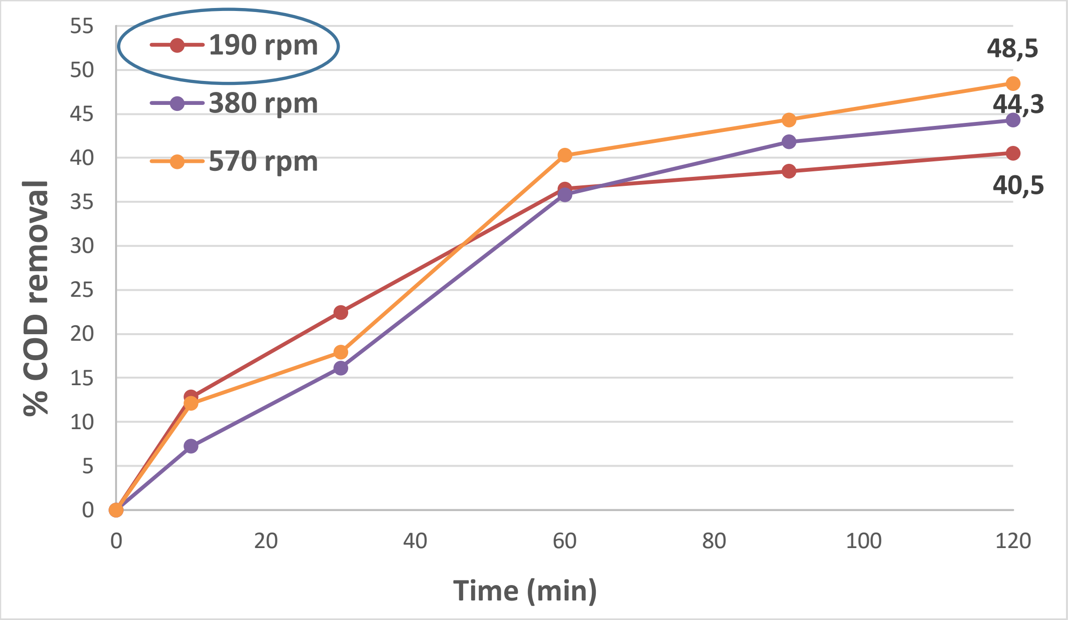
The current determines the formation of

BDD + H_2O → BDD**(·OH)** + H^+ + e^-

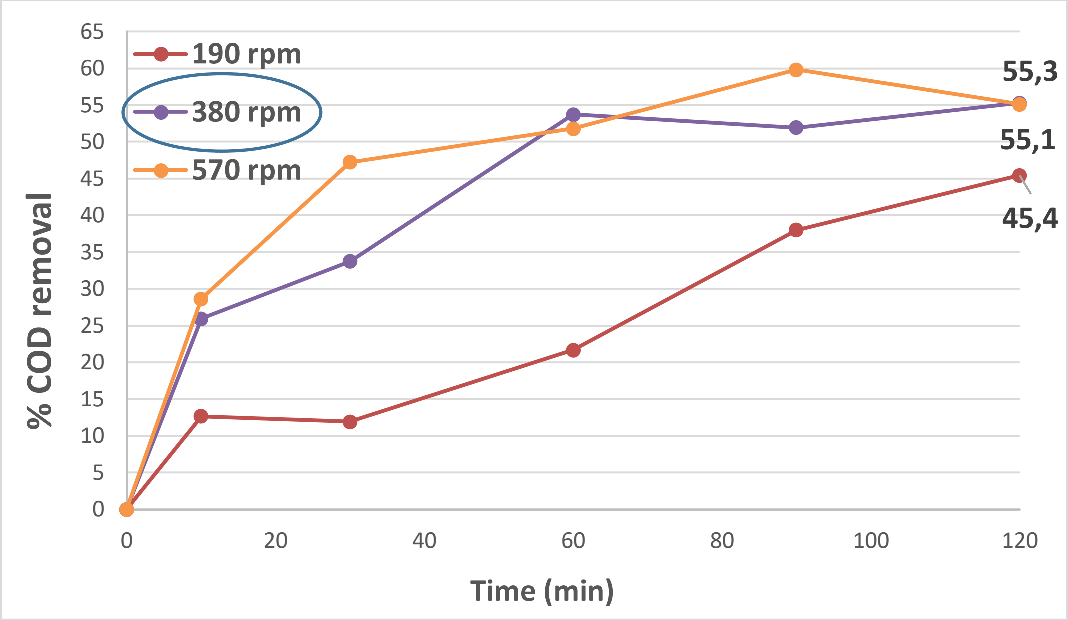
↑ mA/cm^2 ➔ ↑(·OH)

Agitation rate (rpm)

Electrocoagulation (EC)



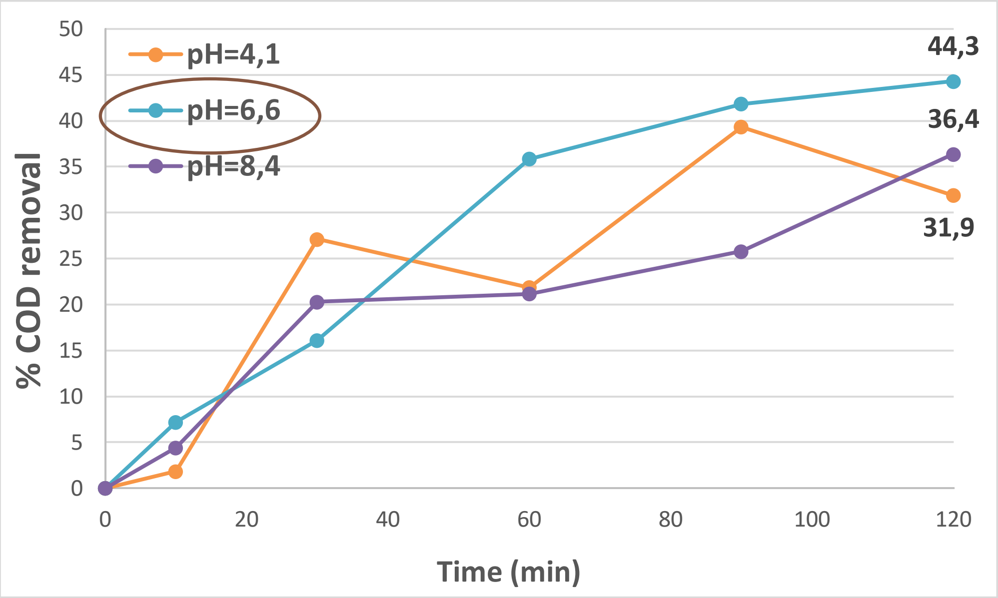
Electrooxidation (EO)



Parameter (n=3)	% Reducing weight of Al-Al-Al		
Agitation rate (rpm)	190 rpm	380 rpm	570 rpm
	0.5 %	0.7 %	1.1 %

➢ pH

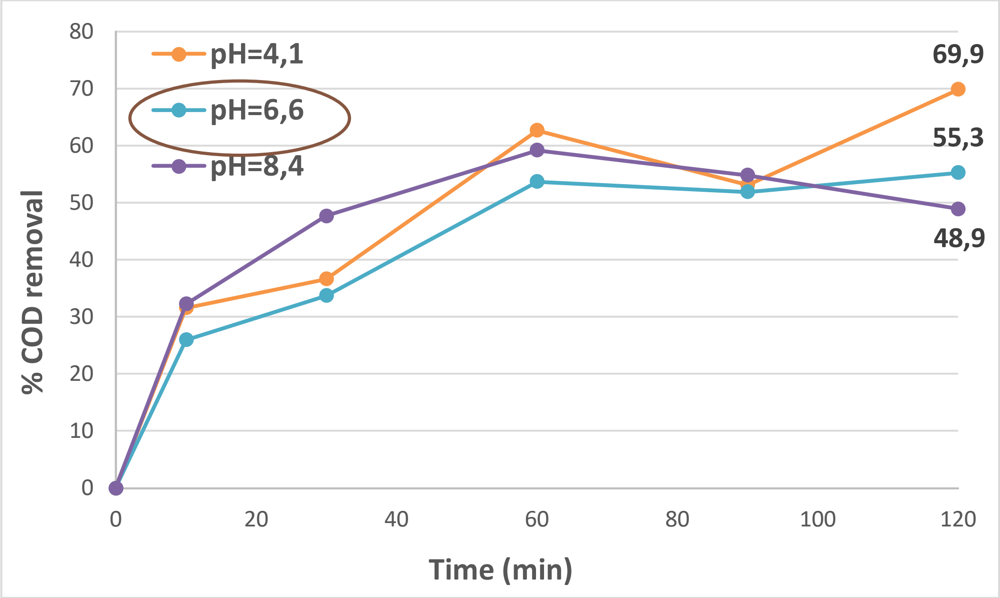
Electrocoagulation (EC)



According to Yilmaz Nayir and Kara et al. (2017)

- **pH=4.1** → $Al(OH)^{2+}$, $Al(OH)_2^{+}$
- **pH=6.6** → $Al(OH)_3$
- **pH=8.4** → $Al(OH)_4^{-}$

Electrooxidation (EO)



According to Stergiopoulos et al. (2021)

- **pH=4.1** → H^+ → ↓(·OH)
- **pH=8.4** → OH^- → ↓(·OH)

H^+ + (·OH) → (·H_2O)

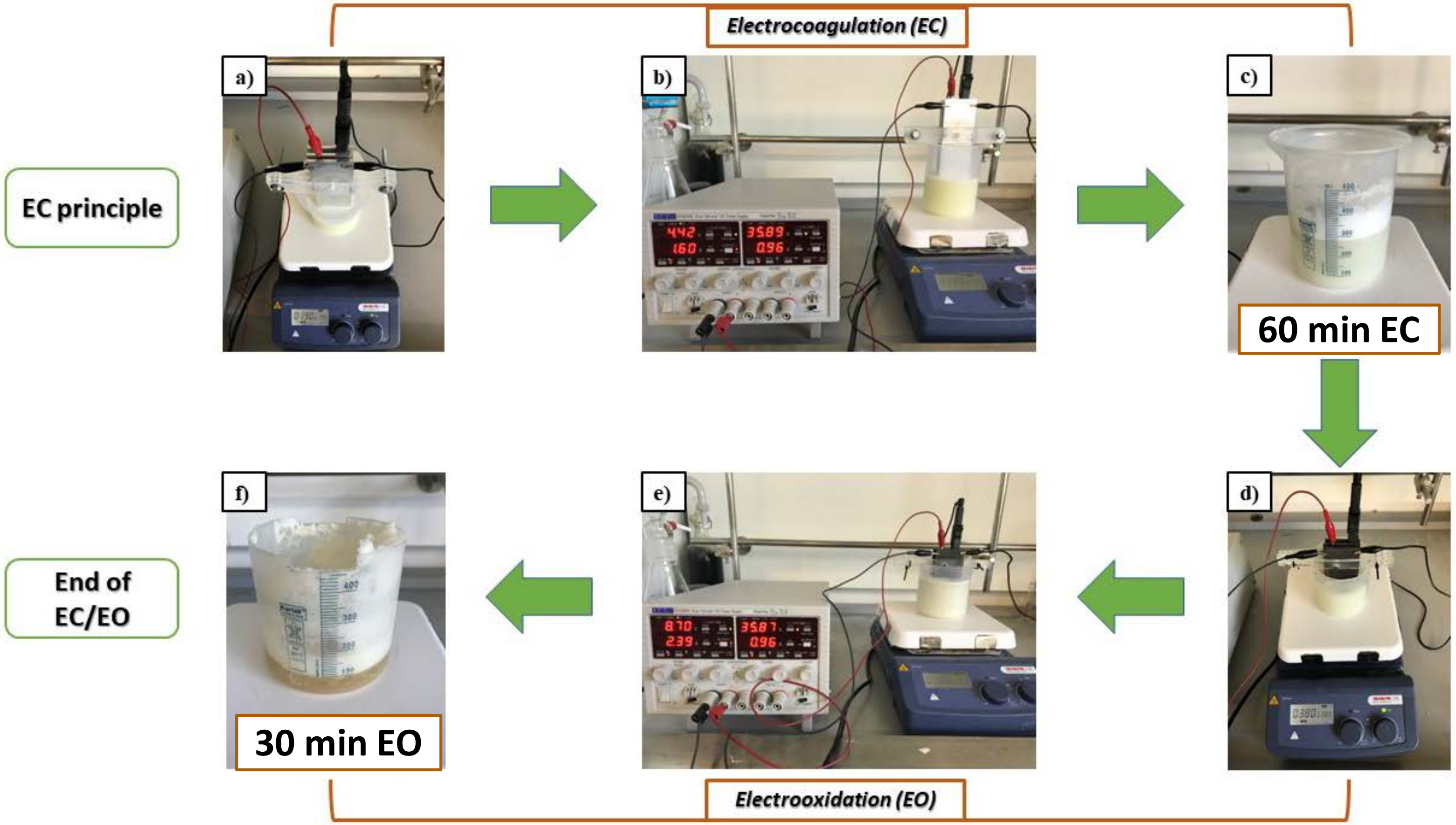
(·H_2O) + H_2O → (·H_2O) x H_2O

OH^- + (·OH) → $O\cdot^-$ + H_2O

Yılmaz Nayır, T., & Kara, S. **(2017)** Container washing wastewater treatment by combined electrocoagulation–electrooxidation. Seperation Science and Technology, 53(10), 1592–1603. https://doi.org/10.1080/01496395.2017.1411365

Stergiopoloulos D. **(2021)** Application of electrochemical technologies for the removal of organic and inorganic pollutants from aqueous waste. Doctoral thesis. Aristotle University of Thessaloniki.

Combined of EC/EO processes



Optimal operating conditions:

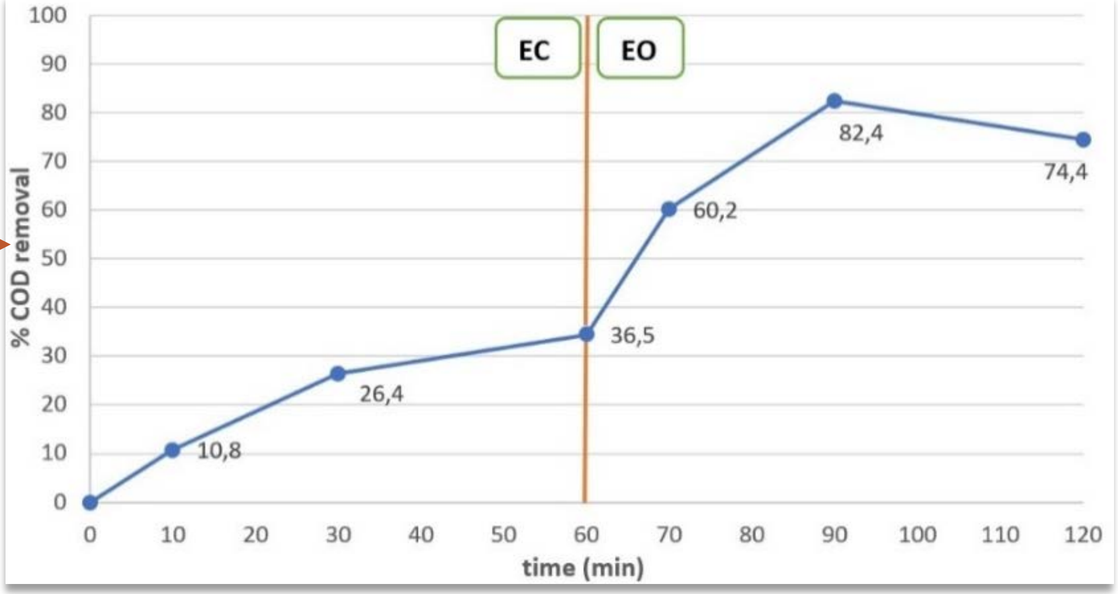
EC

- 40 mA/cm^2
- 190 rpm
- without pH adjustment

EO

- 60 mA/cm^2
- 380 rpm
- without pH adjustment

	EC followed by EO				
Efficiency %	Removal	Removal	Increase	Removal	Increase
Time (min)	60 min EC	90 min EC/EO		120 min EC/EO	
COD	36.5	82.4		74.4	
TN	25.2	38.3		45.8	
Cl^-	17.5		32.5		19.2
NO_3^-	31.0		20.8		31.4
PO_4^{-3}	11.7	12.7		14.5	
TPCs	56.5		74.2		86.4
Opti. Dens.	9.3	16.9		33.4	



Type of wastewater	Electrochemical system	Electrode anode/cathode	Current density (mA/cm^2)	Time (min)	pH	COD removal (%) *	References
Cheese whey wastewater	EC	Fe/Fe	60	20	5	86.4	Tezcan Un et al. **(2014)**
Artificial dairy wastewater	EC	Al/Al	-	30	7.1	61.0	Tchamango et al. **(2010)**
Dairy wastewater	EC	6xAl	31.5	60	7.2	98.8	Bazrafshan et al. **(2013)**
Dairy wastewater	EC	8xFe	5	15	7	58	Valente et al. **(2012)**
Cheese whey wastewater	EC/EO	Al/Fe	25	120	5	82	Yılmaz Nayır & Kara et al. **(2017)**
		BDD/Fe	25	300		89	
Dairy wastewater	EC/EO	Al/Al	60	6	6.6	40	Chakchouk et al. **(2017)**
		Ti/Ti	140	75		70	

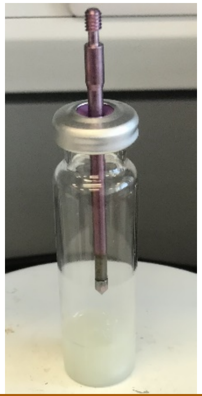
* The % removal efficiency of COD is calculated based on its initial concentration, so the comparative results also depend on the initial content of wastewater in COD.

HiSorb TD-GC/MS sample analysis

The developed HiSorb TD-GC/MS method was used to analyze the VOCs of cheese whey wastewater before and after the optimal electrochemical processes (EC, EO and EC/EO).

$$Semi - quantified = \frac{A_c}{A_{IS}} \times C_{IS}\ (mg\ L^{-1})$$

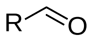
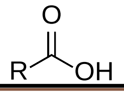
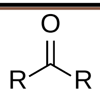
$$Compound\ category\ (\%) = \frac{\sum_{category} \frac{A_C}{A_{IS}}}{\sum_{total\ VOCs} \frac{A_C}{A_{IS}}} x\ 100$$



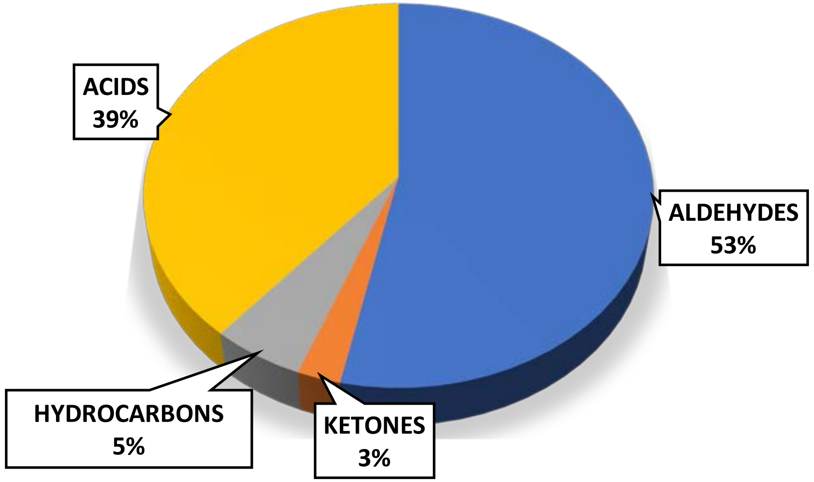
HS-HiSorb

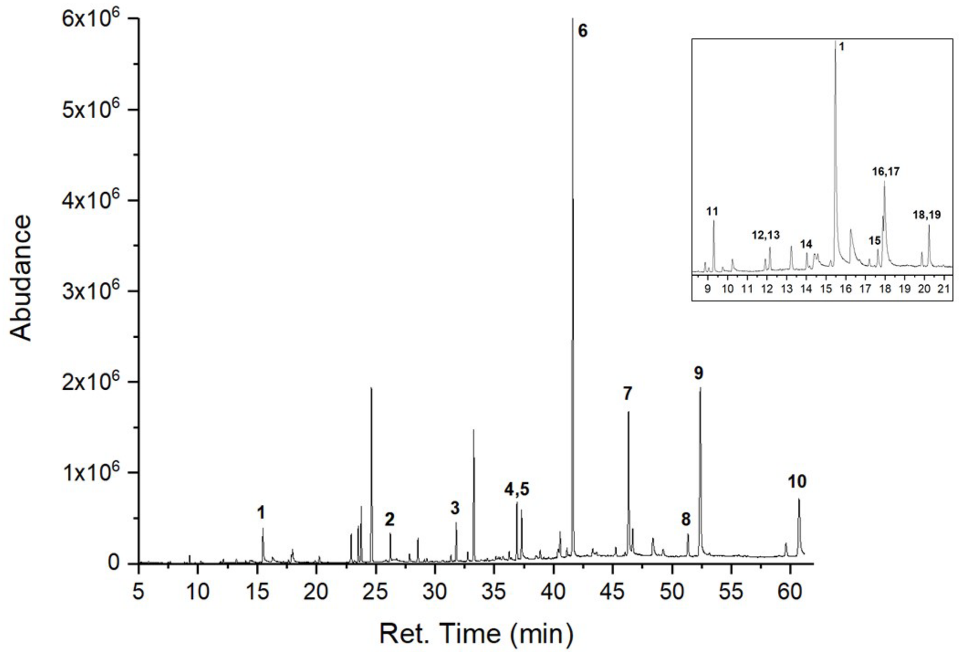
TD-GC/MS

❑ *VOCs of raw cheese whey wastewater (n=9)*

Categories of VOCs	Number of emitted VOCs	Structure	Σ mg L^{-1} (±CL)
Aldehydes	14		1.379 (±0.955)
Acids	9		1.003 (±0.522)
Ketones	7		0.067 (±0.036)
Hydrocarbons	9	R–R R=R R≡R	0.137 (±0.102)
Others	2		0.002 (±0.001)
Total VOCs	**41**		**2.588 (±1.616)**

Raw





No	VOCs	No	VOCs
1	1,3-Cyclopentadiene, 1-methyl	11	Acetone
2	Hexanal	12	1-Hexene
3	Heptanal	13	n-Hexane
4	Octanal	14	Butanal
5	Hexanoic acid	15	1-Heptene
6	Nonanal	16	Heptane
7	Octanoic acid	17	Acetic acid
8	Nonanoic acid	18	2-Pentanone
9	2-Undecenal	19	Pentanal
10	n-Decanoic acid		

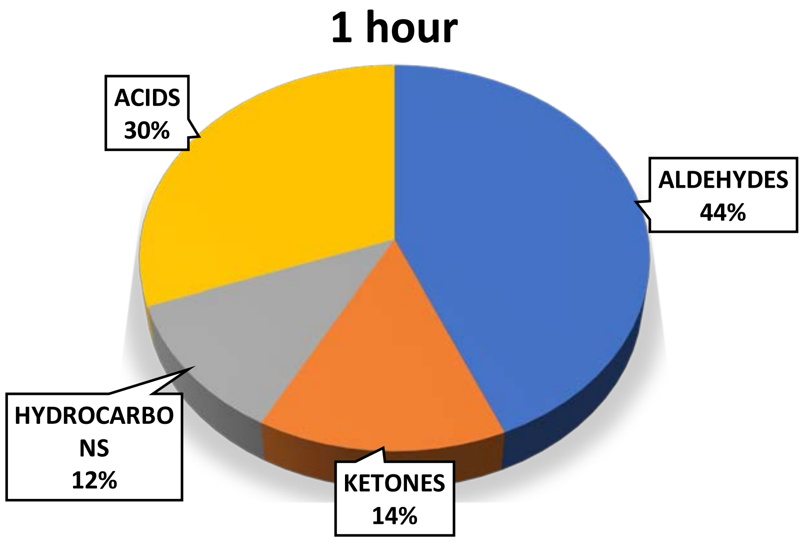
❑ *VOCs of EC-treated (2 h) cheese whey wastewater (n=3)*

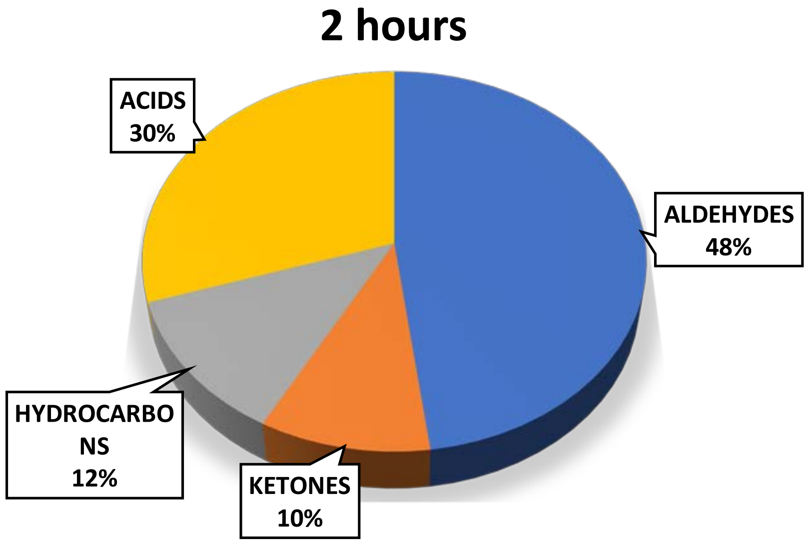
Categories of VOCs	Optimized EC process	
	Σ mg L^{-1} (±CL)	[b]Efficiency (↓ ή ↑)
Aldehydes	0.293 (±0.144)	↓ 78.8 %
Acids	0.183 (±0.115)	↓ 81.8 %
Ketones	0.062 (±0.036)	↓ 7.5 %
C-H	0.074 (±0.057)	↓ 46.0 %
Others	[a]S/N	
Total VOCs	0.612 (±0.352)	↓ 76.4 %

[a] Low signal to noise ratio (S/N≤3)

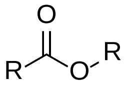
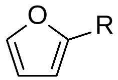
$$^{b}\%\ \text{Efficiency}\ (\downarrow) = \frac{C_{RAW} - C_{EC-treated}}{C_{RAW}} \times 100$$

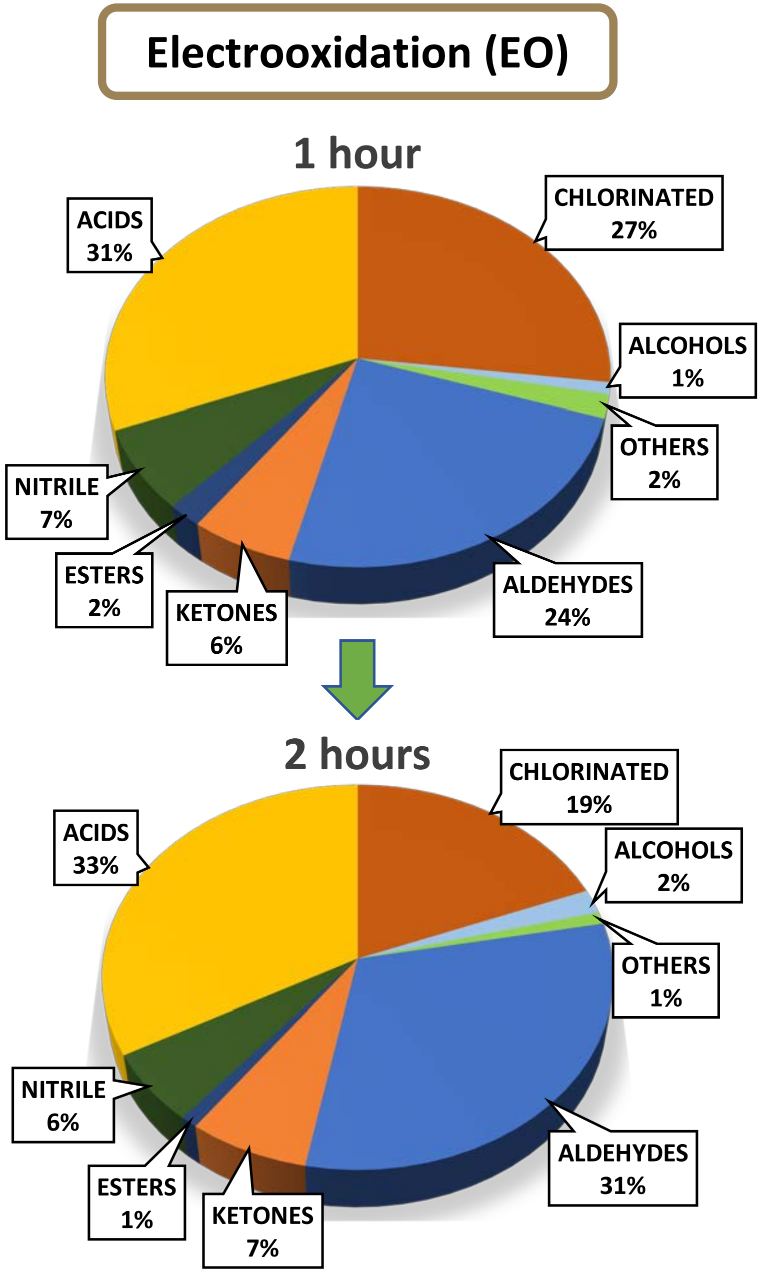
Electrocoagulation (EC)



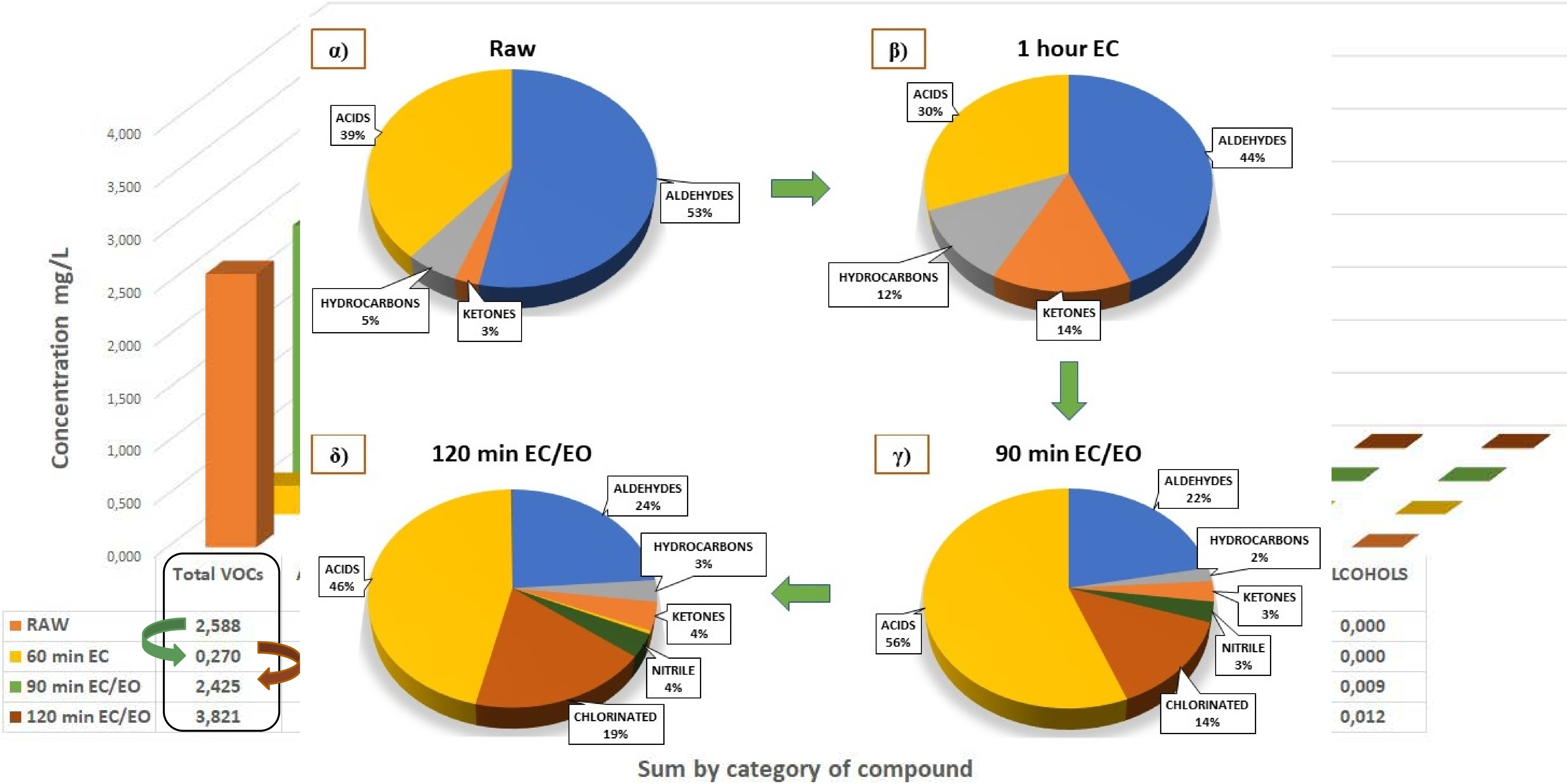


❑ *VOCs of EO-treated (2 h) cheese whey wastewater (n=3)*

Categories of VOCs	Optimized EO process	
	Σ mg L^{-1} (±CL)	Efficiency (↓ ή ↑)
Aldehydes	1.074 (±0.253)	↓ 22.1%
Acids	1.155 (±0.281)	↑ 13.2 %
Ketones	0.236 (±0.050)	↑ 71.6 %
C-H	0.010 (±0.003)	↓ 92.7 %
Alcohols R–OH	0.062 (±0.019)	
Esters 	0.042 (±0.007)	
Nitriles R—≡N	0.212 (±0.012)	
Chlorinated R–Cl	0.659 (±0.150)	
Furans 	0.021 (±0.005)	
Total VOCs	3.471 (±0.816)	↑ 25.4 %



❑ VOCs of EC/EO treated cheese whey wastewater (n=3)



Conclusions

1) Implementation and optimization of EC and EO operating parameters

EC	**40 mA/cm²**	**190 rpm**	**pH = 6.6**	**t= 120 min**	**40.5 % ↓ COD**
EO	**60 mA/cm²**	**380 rpm**	**pH = 6.6**	**t= 120 min**	**55.3 % ↓ COD**
EC/EO	**40/60 mA/cm²**	**190/380 rpm**	**pH = 6.6**	**60/30 min**	**82.4 % ↓ COD**

2) EC showed good efficiency in reducing all metered parameters, including VOCs

3) EO failed to reduce TPCs, PO_4^{-3}, NO_3^- and Cl^-

4) The HiSorb TD-GC / MS method identified and semi-quantified (Total VOCs):

	Raw	EC	EO	EC/EO
identification	41 VOCs	26 VOCs	52 VOCs	55 VOCs
Semi-quantification	2.588 mg L^{-1}	0.612 mg L^{-1}	3.471 mg L^{-1}	2.425 mg L^{-1}

In conclusion

EC appeared to be a favorable process for the reduction of VOCs emitted, while conjugated EC/EO as more effective for the reduction of cheese whey wastewater COD

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Thank you!