Supplementary information.

Electrochemical Green PC/IL@GCE Sensor for Trace-level Detection of Hazardous Triclopyr Herbicides in Serum and Fruits

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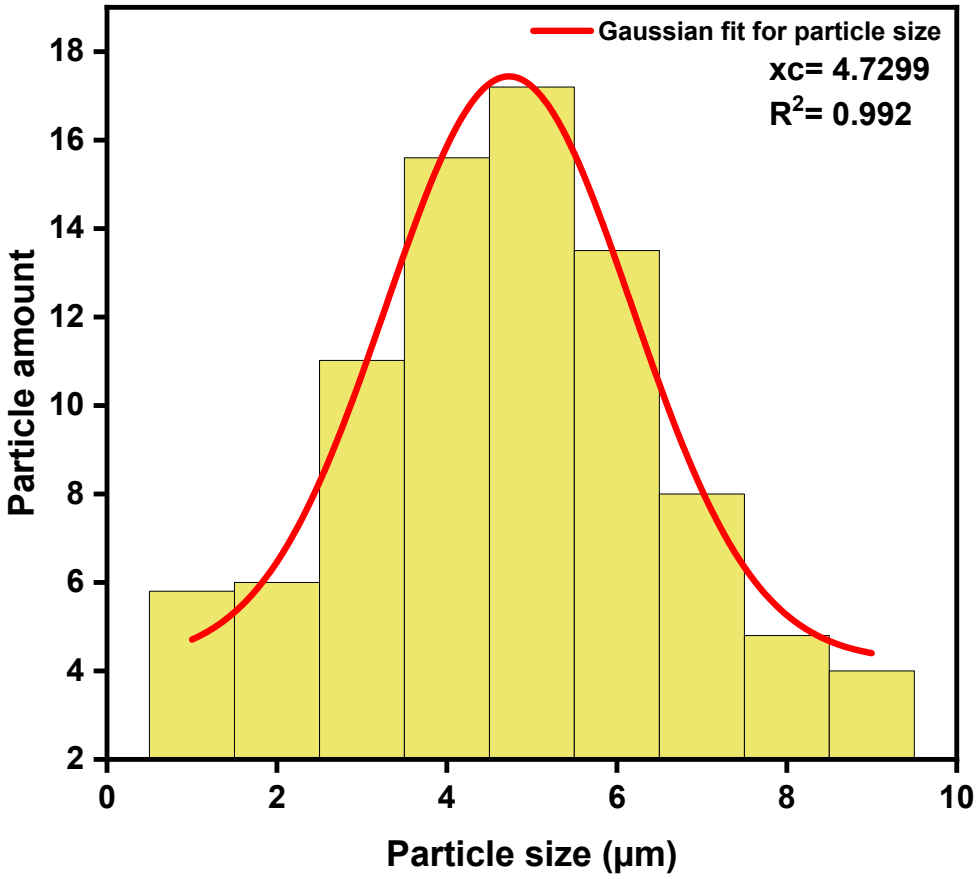
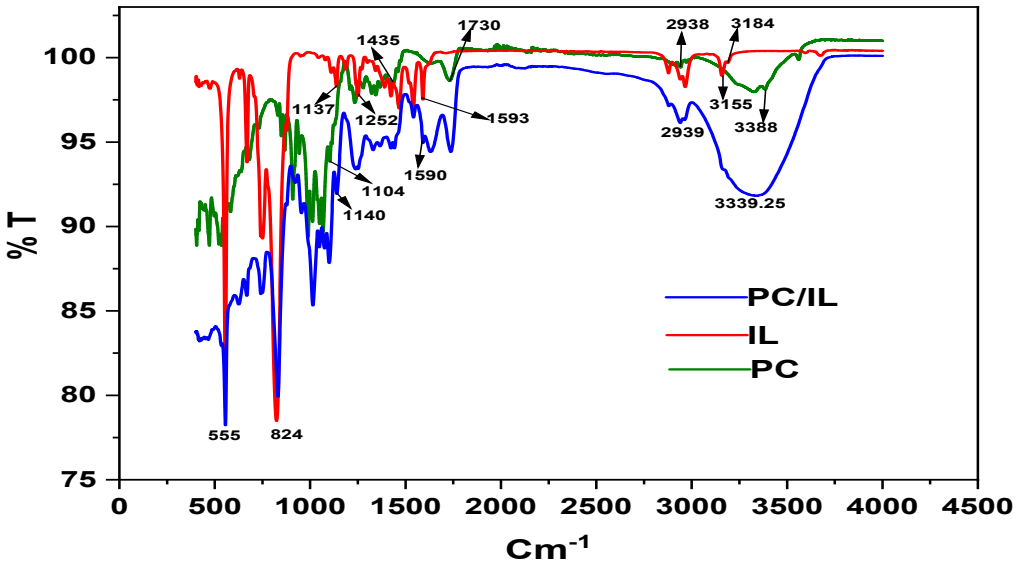
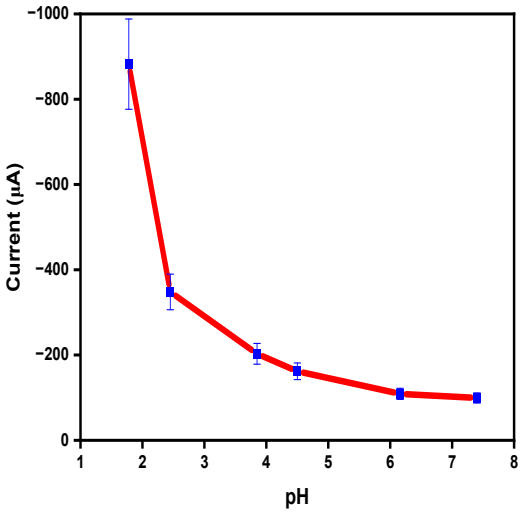


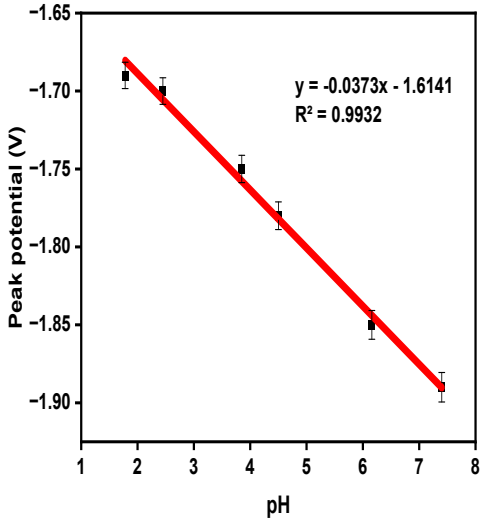
SI 1: Histogram of particle size analyser with gaussian curve showing maximum particle size of PC/IL.



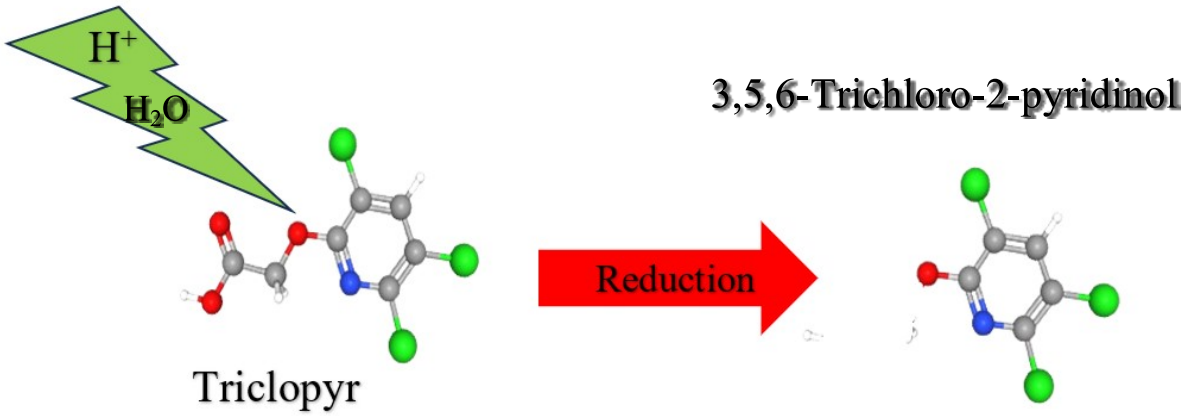
SI 2: FTIR spectra of PC, IL and PC/IL



(a)

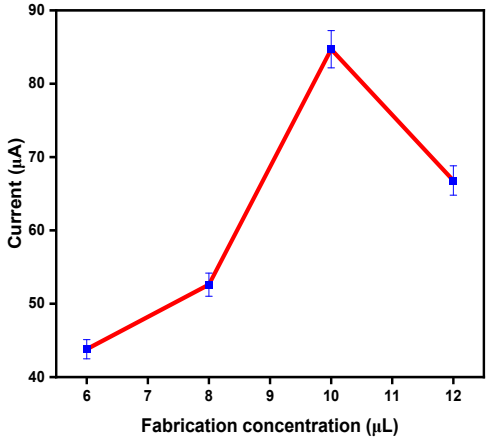


(b)

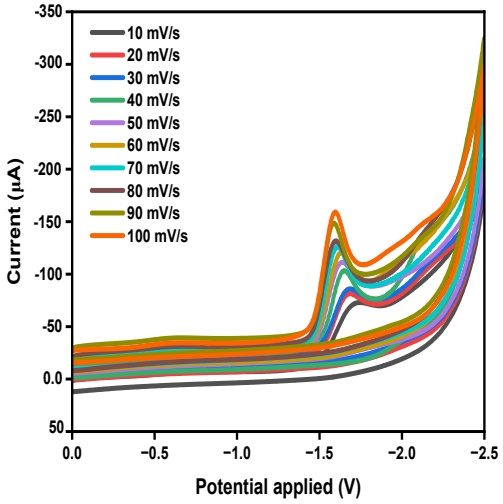


(c)

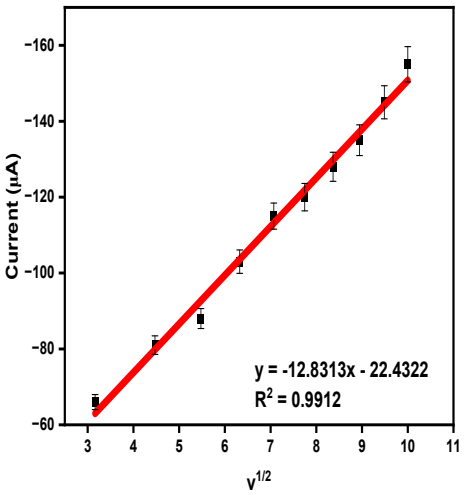
SI 3: (a) Effect of pH (BR 1.78 to 7.5) on peak current toward reduction of TCP; (b) correlation between peak potential (Ep) and pH (c) mechanism of triclopyr reduction.



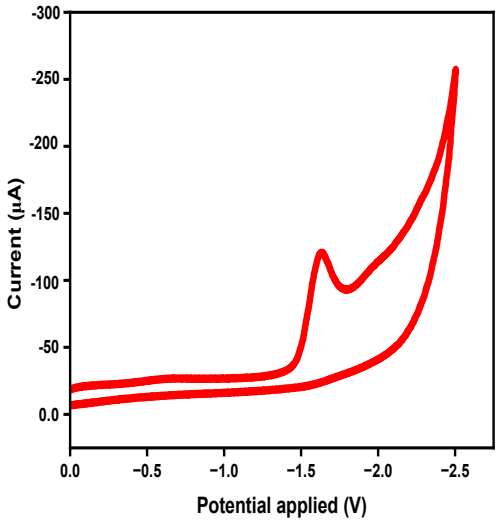
SI 4: Effect of different loadings of PC/IL composite towards the reduction of TCP.



(a)

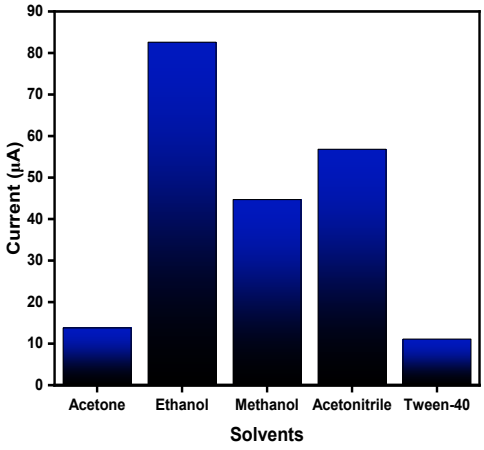


(b)

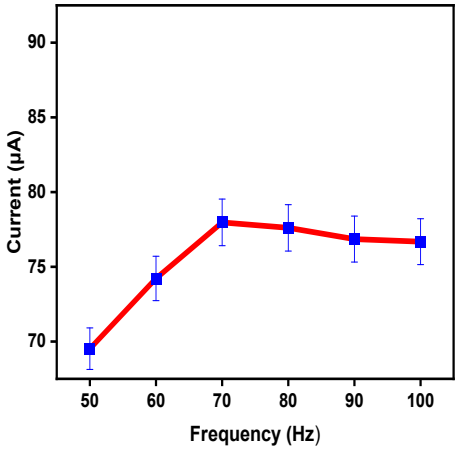


(c)

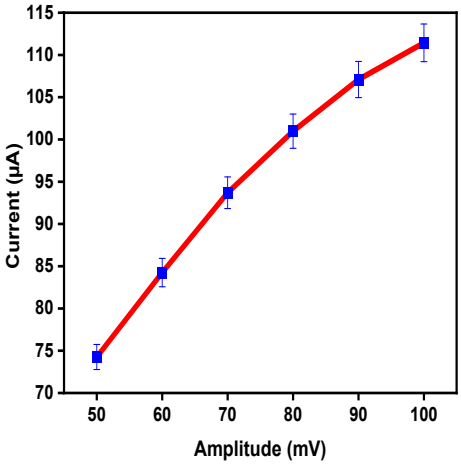
SI 5: Plots of (a) different scan rates (b) $\upsilon^{1/2}$ vs. current (c) CV showing redox behaviour of TCP


Current (μA)
Acetone
Ethanol
Methanol
Acetonitrile
Tween-40
Solvents

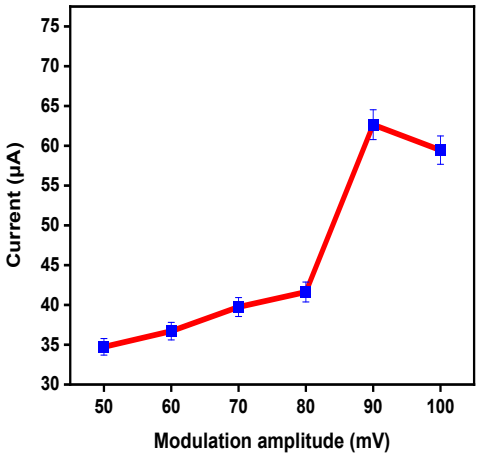
(a)


Current (μA)
Frequency (Hz)

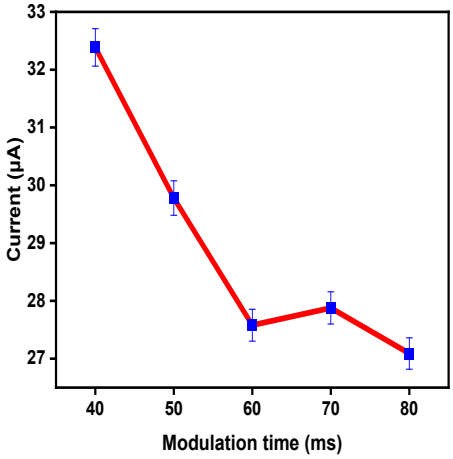
(b)


Current (μA)
Amplitude (mV)

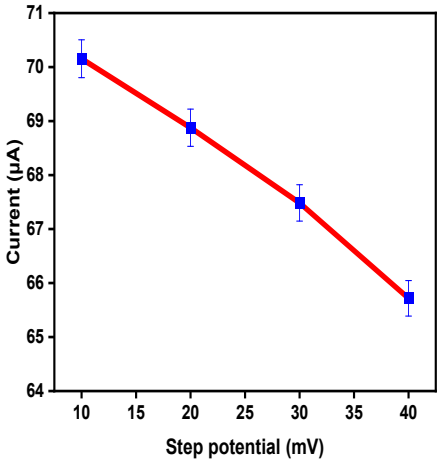
(c)


Current (μA)
Modulation amplitude (mV)

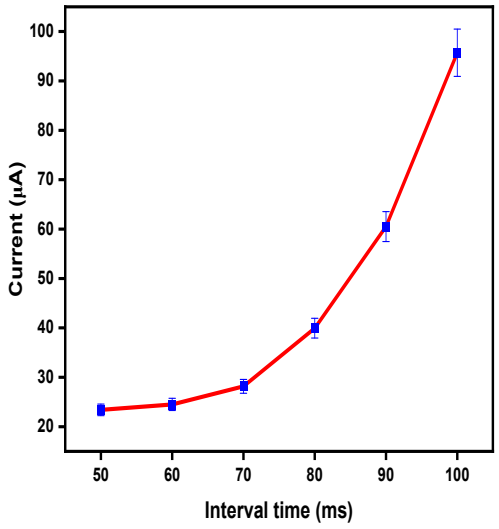
(d)


Current (μA)
Modulation time (ms)

(e)

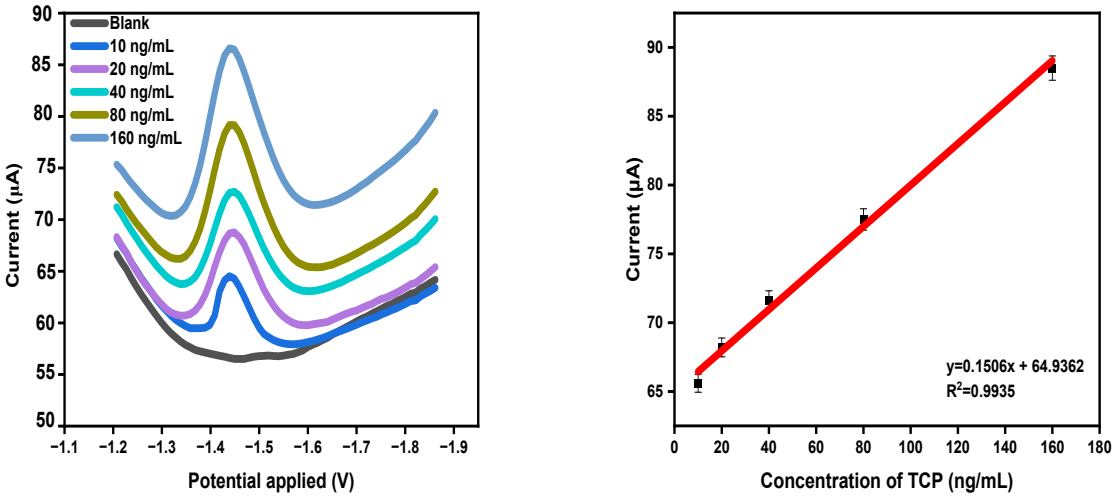

Current (μA)
Step potential (mV)

(f)

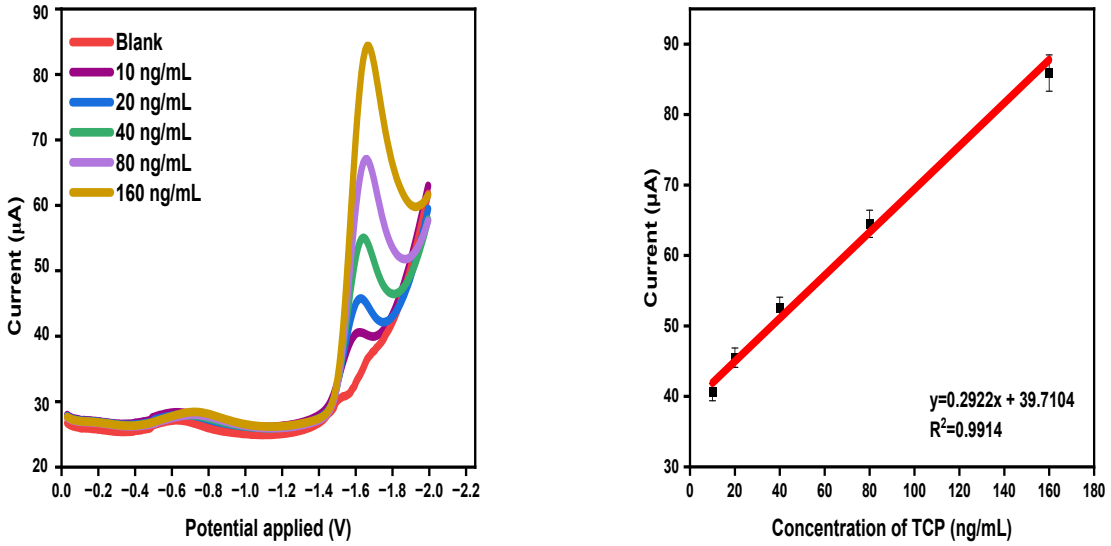


(g)

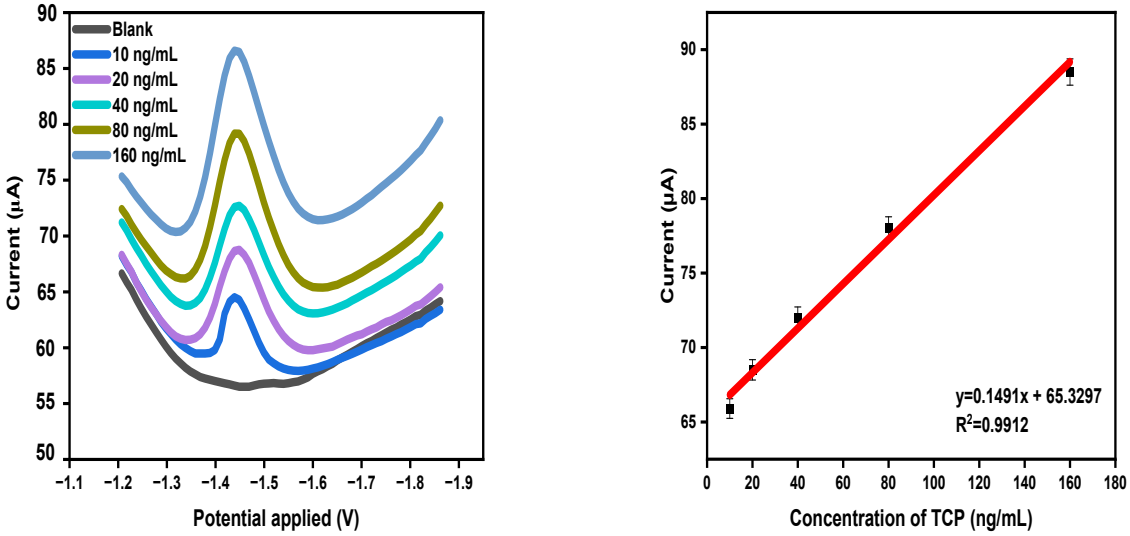
SI 6: (a) Effect of solvents on peak current (b) Effect of frequency on peak current (c) Effect of amplitude on peak current (d) Effect of modulation amplitude on peak current (e) Effect of modulation time on peak current (f) Effect of step potential on peak current (g) Effect of interval on peak current toward reduction of TCP.



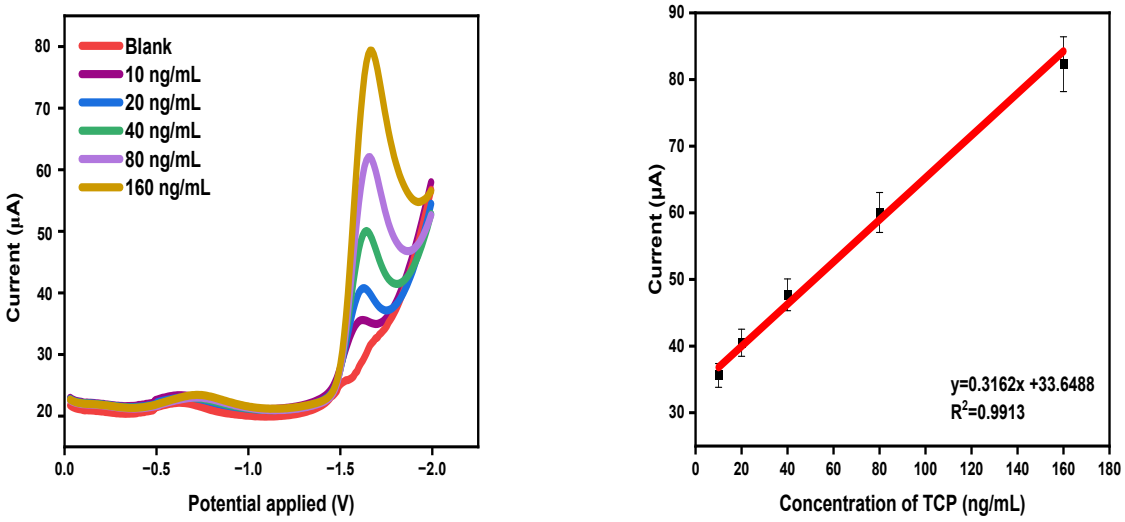
(a)


Blank
10 ng/mL
20 ng/mL
40 ng/mL
80 ng/mL
160 ng/mL
Current (µA)
Potential applied (V)
y=0.2922x + 39.7104
R2=0.9914
Concentration of TCP (ng/mL)

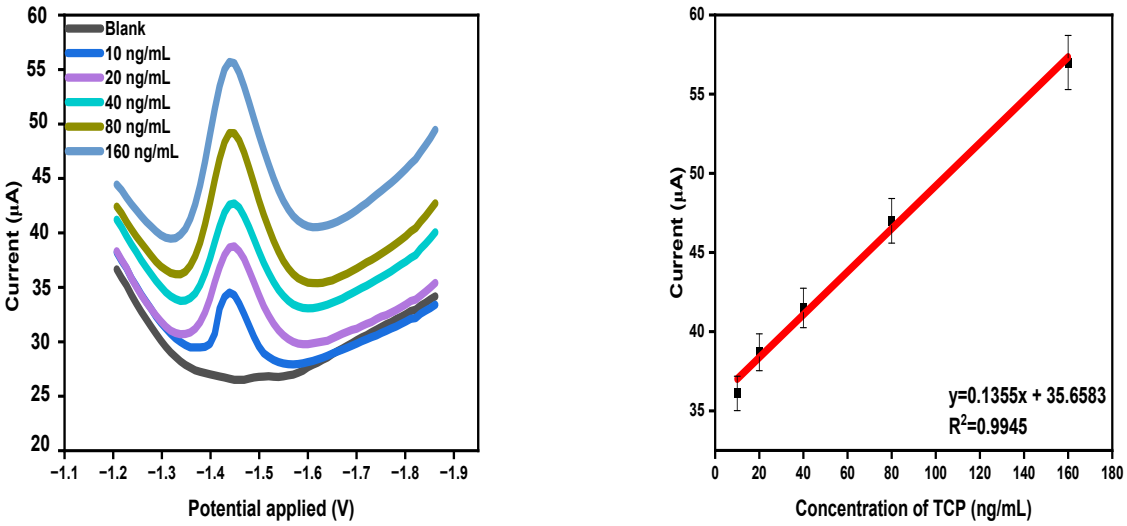
(b)


Blank
10 ng/mL
20 ng/mL
40 ng/mL
80 ng/mL
160 ng/mL
Current (µA)
Potential applied (V)
y=0.1491x + 65.3297
R2=0.9912
Concentration of TCP (ng/mL)

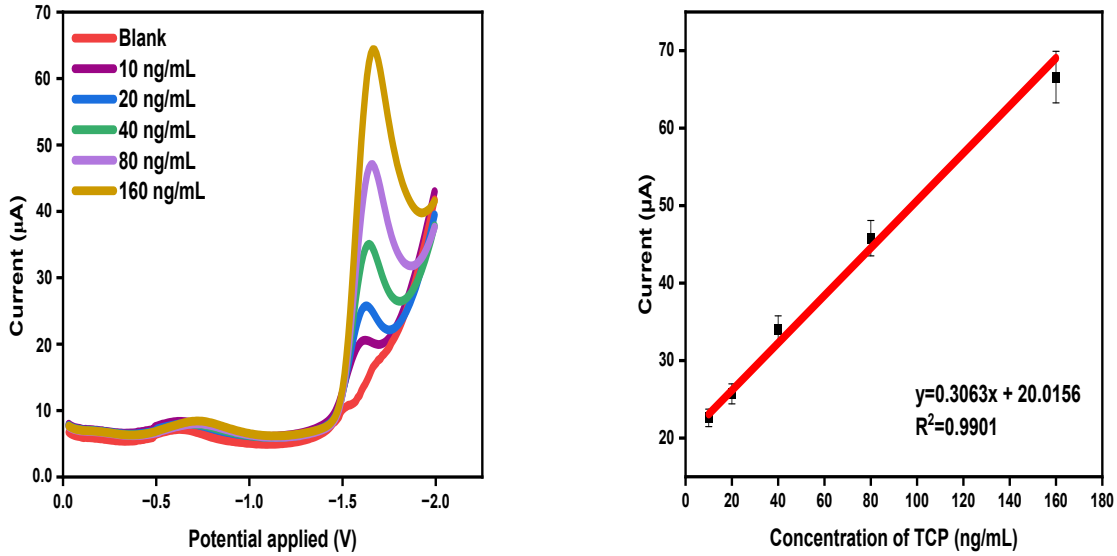
(c)


Blank
10 ng/mL
20 ng/mL
40 ng/mL
80 ng/mL
160 ng/mL
Current (µA)
Potential applied (V)
y=0.3162x +33.6488
R2=0.9913
Concentration of TCP (ng/mL)

(d)

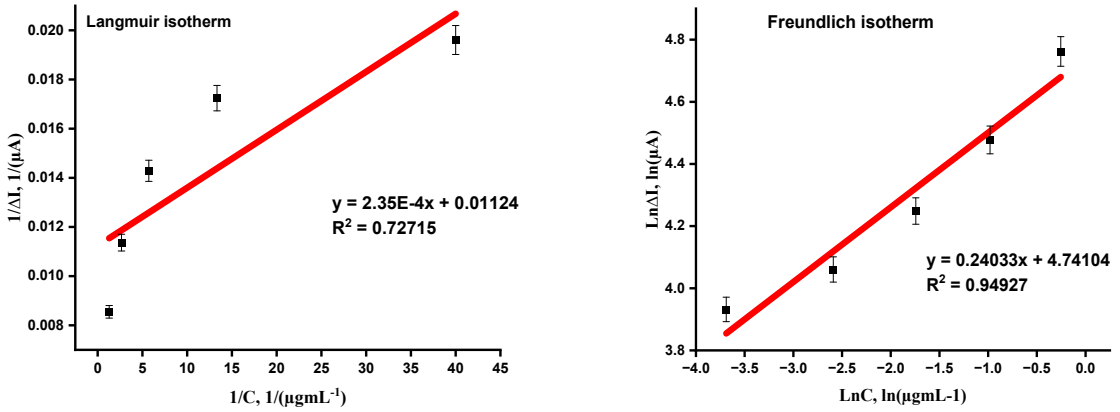

Blank
10 ng/mL
20 ng/mL
40 ng/mL
80 ng/mL
160 ng/mL
Current (µA)
Potential applied (V)
y=0.1355x + 35.6583
R2=0.9945
Concentration of TCP (ng/mL)

(e)

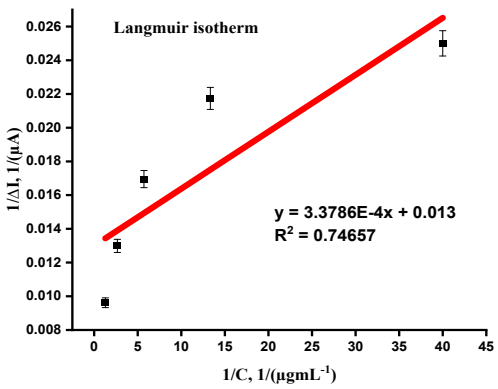


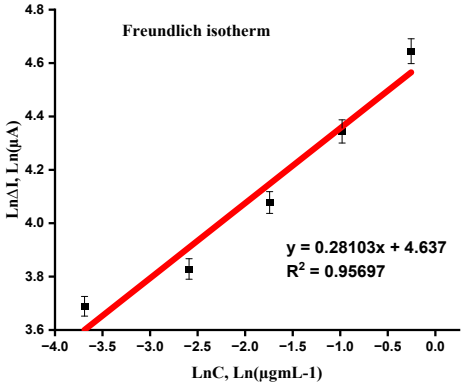
(f)

SI 7: Calibration curve for concentrations from 10 ng/mL-160 ng/mL: tomato sample (a) SWV (b) DPV, apple sample (c) SWV (d) DPV, Human serum sample (e) SWV (f) DPV.



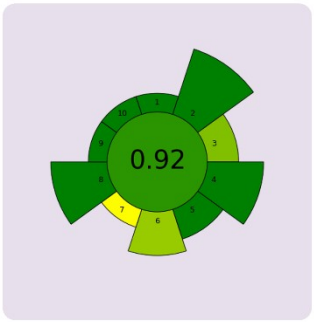
(A) (B)





(C) (D)

SI 8: Mathematical models for sensing interaction: DPV-(A) Langmuir isotherm (B) Freundlich isotherm; SWV- (C) Langmuir isotherm (D) Freundlich isotherm.



SI 9: Greenness percentage metric

#	Criterion		Score	Weight
1.	Sample preparation placement:	In-line/In situ	1.00	1
2.	Hazardous materials:	0 [g or mL]	1.00	5
3.	Sustainability, renewability, and reusability of materials:	> 75% of reagents and materials are sustainable or renewable	0.75	2
4.	Waste:	0 [g or mL]	1.00	4
5.	Size economy of the sample	Mass or volume of the sample: 0.001 [g or mL]	1.00	2
6.	Sample throughput:	20 [samples/h]	0.71	3
7.	Integration and automation	Sample prep. steps: 2 steps or fewer, Semi-automated systems	0.50	1
8.	Energy consumption:	10 [W]	1.00	4
9.	Post-sample preparation configuration for analysis:	Simple, readily available detection: smartphones, desktop scanners, paper strips, etc.	1.00	1
10.	Operator's safety:	Not set	1.00	1

SI 10: GAC principles used to evaluate the greenness of process.

ST 1: FTIR peak frequencies with their corresponding functional groups.

Frequency	**Vibrational functional group**	**Reference**
3388 cm^{-1}	-OH stretching of carboxylic acid due to inter and intramolecular hydrogen bonding	[1]
2938 cm^{-1}	stretching and bending of C-H, CH_2 and CH_3	[2]
1730 cm^{-1}	C=O stretching	[1]
1435 cm^{-1}	stretching of C-H methyl group	[3]

1104 cm^{-1}	C-O bond of alcohols, esters	[4]
1140 cm^{-1}	C-O bond of carboxylic acid	[4]
3184 and 3155 cm^{-1}	C-H stretching of the aromatic	[5]
1252 and 1137 cm^{-1}	C-N stretching in aromatic and aliphatic amines	[5]

ST 2: Sensor reproducibility data for TCP at PC/IL@GCE sensor.

	Sensor reproducibility			**Sensor repeatability**	
	Sensor 1	**Sensor 2**	**Sensor 3**	**Intraday**	**Interday**
3 Replicates	81.073	81.073	80.573	81.073	80.073
	81.099	80.795	80.156	81.099	80.095
	80.156	79.299	79.425	80.156	79.299
Mean current	80.776[a]	80.389[a]	80.051[a]	80.776[a]	79.822 [a]
SD	0.537	0.954	0.581	0.537	0.453
%RSD	0.664	1.187	0.725	0.664	0.568
Average	80.405[b]	0.691(SD)	0.859(% RSD)		

a Mean of three replicates.
b Mean of three sensors.

ST 3: Interference analysis for TCP in presence of different interferents at PC/IL@GCE sensor using DPV.

Interferent	**Concentration (ng/mL)**	**Recovery (%)**	**RSD %**
L-Tryptophan	80	98.75	1.50
Tartaric Acid	80	98.84	0.12
L-Aspartic Acid	80	99.96	0.87
Citric Acid	80	99.21	0.45
KCl	80	97.80	0.92

NaCl	80	100.16	1.03
$MgSO_4$	80	99.45	0.58

ST 4: Selectivity analysis for TCP in presence of similar structure compounds at PC/IL@GCE sensor using DPV.

Interferent	**Concentration (ng/mL)**	**Recovery (%)**	**RSD %**
Alachlor	80	98.54	0.44
Urea	80	100.58	0.70
Sodium azide	80	101.25	0.37

ST 5: Recovery studies of TCP in human serum, tomato and apple.

Samples	**Sample concentration (ng/mL)**	**Spiked concentration (ng/mL)**	**Concentration found in SWV(ng/mL)**	**Concentration found in DPV(ng/mL)**	**% Recovery in SWV±RSD**	**% Recovery in DPV±RSD**
Human serum	20	60	80.84	79.59	100.36 ±**1.51**	99.64±**0.83**
	40	40	80.85	80.83	100.06±**1.36**	101.92±**1.00**
Tomato	20	60	80.32	79.31	100.27±**0.42**	99.44±**0.90**
	40	40	80.99	79.75	100.87±**1.23**	99.44±**0.26**
Apple	20	60	80.86	80.43	100.85±**1.04**	100.14±**0.95**
	40	40	81.31	78.70	101.40±**1.51**	99.02±**1.72**

**Each value is the mean of three repetitions.*

ST 6: The parameters calculated from Langmuir, Freundlich isotherms.

	Langmuir			**Freundlich**	
	DPV	**SWV**		**DPV**	**SWV**
K_D	0.04902	0.0625	ΔI_{max}, µA	4.762174	4.644391
ΔI_{max}, µA	0.019608	0.025	1/n	0.24033	0.28103
R^2	0.72715	0.74657	R^2	0.94927	0.95697

References:

[1] T. Mada, R. Duraisamy, F. Guesh, Optimization and characterization of pectin extracted from banana and papaya mixed peels using response surface methodology, Food Sci Nutr 10 (2022). https://doi.org/10.1002/fsn3.2754.

[2] B. Rezaei, H. Khosropour, A.A. Ensafi, A modified electrode using carboxylated multiwalled carbon nanotubes and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ionic liquid for a simultaneous hazardous textile dye sensor, Analytical Methods 9 (2017). https://doi.org/10.1039/c6ay01884j.

[3] J. yi Huang, J. song Liao, J. ru Qi, W. xin Jiang, X. quan Yang, Structural and physicochemical properties of pectin-rich dietary fiber prepared from citrus peel, Food Hydrocoll 110 (2021). https://doi.org/10.1016/j.foodhyd.2020.106140.
[4] N. Wathoni, C. Yuan Shan, W. Yi Shan, T. Rostinawati, R.B. Indradi, R. Pratiwi, M. Muchtaridi, Characterization and antioxidant activity of pectin from Indonesian mangosteen (Garcinia mangostana L.) rind, Heliyon 5 (2019). https://doi.org/10.1016/j.heliyon.2019.e02299.
[5] S.R. Pilli, T. Banerjee, K. Mohanty, 1-Butyl-2,3-dimethylimidazolium hexafluorophosphate as a green solvent for the extraction of endosulfan from aqueous solution using supported liquid membrane, Chemical Engineering Journal 257 (2014). https://doi.org/10.1016/j.cej.2014.07.019.