Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Degradation of Pesticides Using Amine-Functionalized Cellulose Nanocrystals

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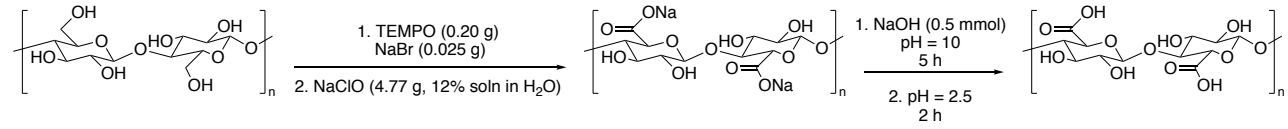
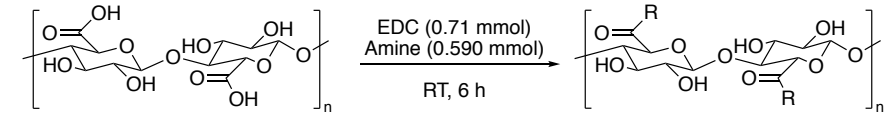
Synthetic Schemes for synthesis of PEI-CNC material:

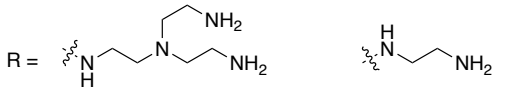


CNC-Slurry (20 g, 12.2 wt% in H_2O)

Scheme S1. TEMPO-mediated oxidation of CNC followed by ion exchange to effect the neutralization of the C-6 sodium carboxylates

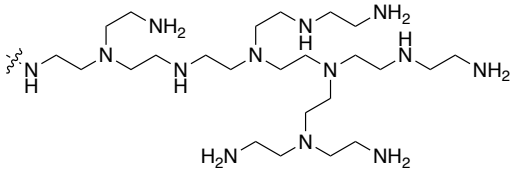


Oxidized CNC (100 mg, 1 wt% in H_2O)



Tris(2-aminoethyl)amine, TRIS

Ethylenediamine, EDA



Poly(ethylenimine), PEI

Scheme S2. Amine-functionalization of oxidized CNC.

SEM Images of CNC-PEI after Functionalization:

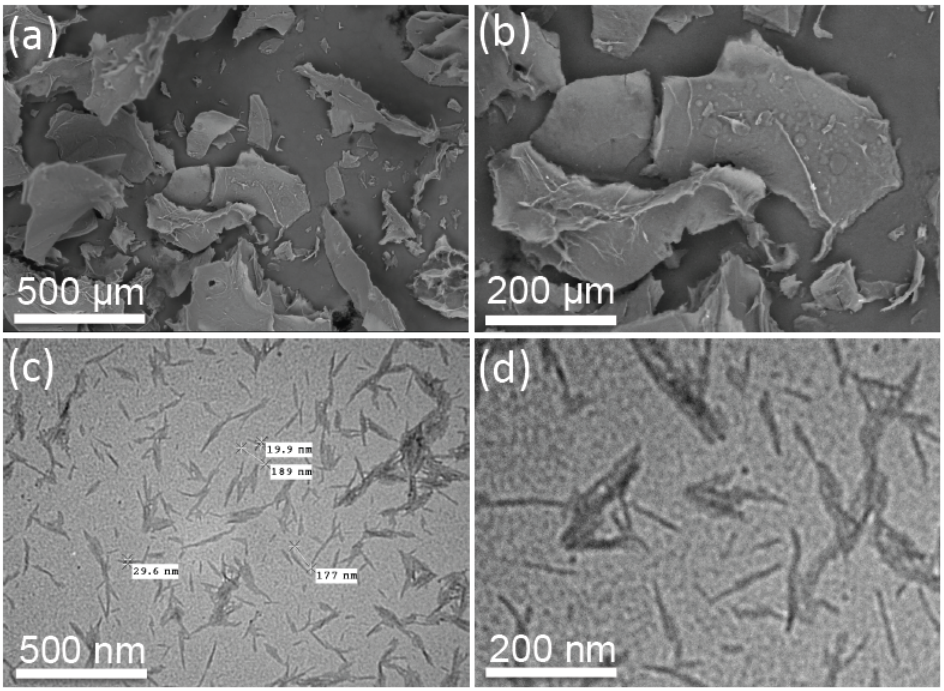


Figure S1. SEM images of CNC-PEI at different magnifications (a,b) and TEM images of CNC at different magnifications (c,d). After formulation and freeze-drying, the CNC-PEI material agglomerates into larger particles. Nevertheless, when dispersed, the nanocrystalline nature of modified material is still apparent (See: Ref. 1).

CNC-PEI Loading Experiment:

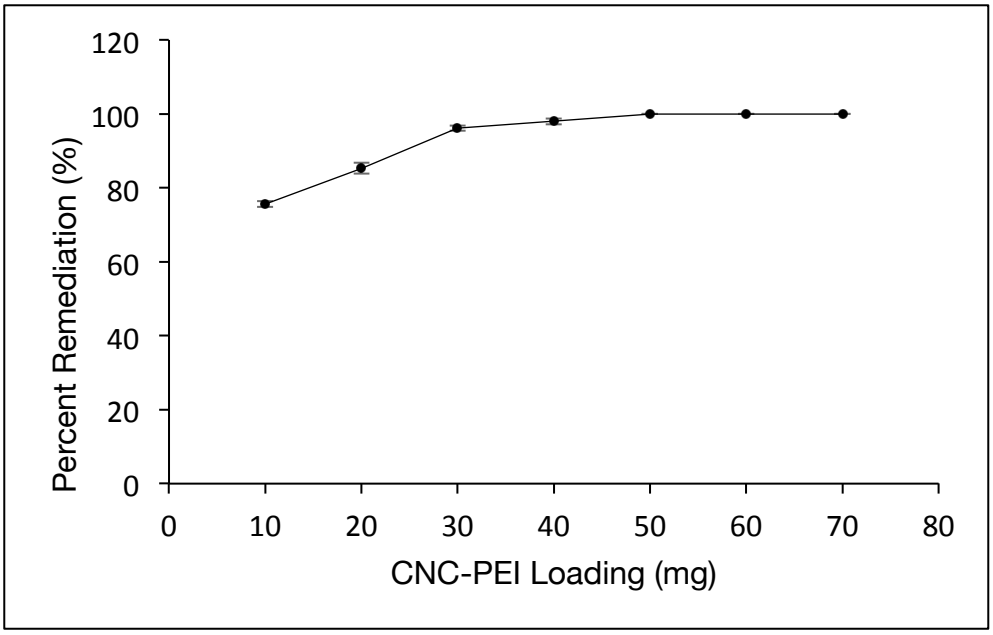


Figure S2. CNC-PEI loading experiment: Malathion pesticide samples treated with increasing amounts of CNC-PEI.

Agitation Experiment:

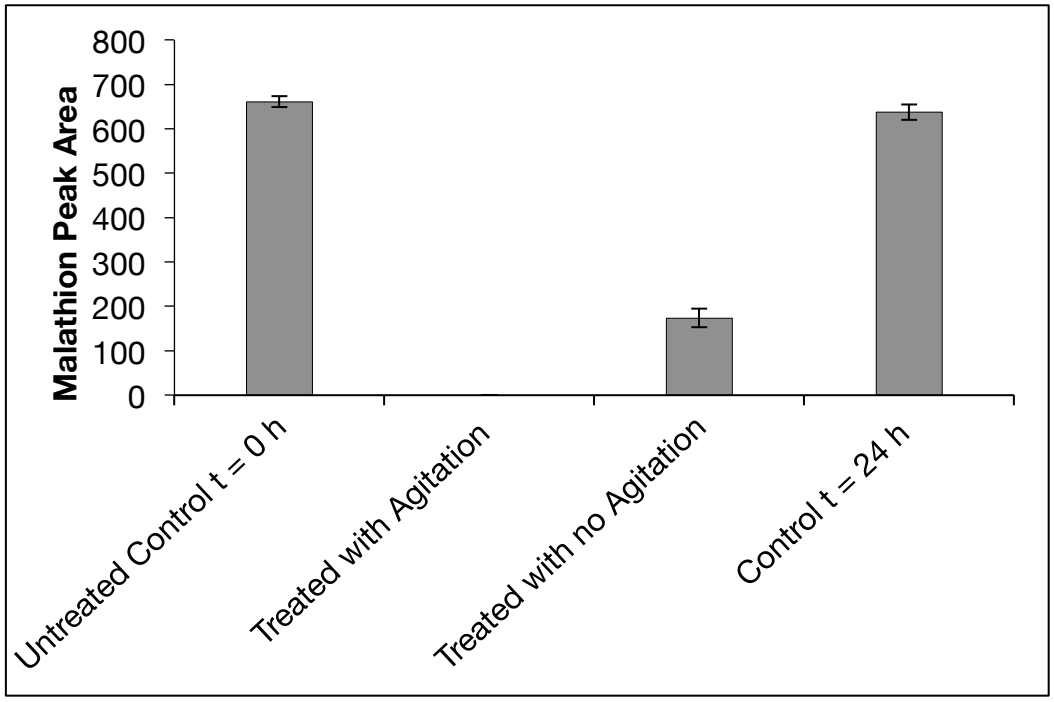
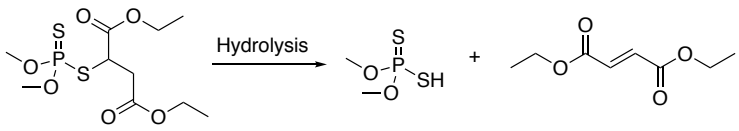


Figure S3. Agitation experiment that demonstrates the necessity of agitation of the amine-modified material and the pesticide solution.

Mass Spectrometry Analyses of Pesticide Degradation:

Malathion Degradation Studies

A 165 ppm solution of malathion was prepared in deionized water, 50 mg of CNC-PEI was added and the suspension was allowed to stir for 24 h at room temperature. Next, the solvent and any soluble compounds were filtered from the solid CNC-PEI materials and washed with deionized H_2O. The filtrate was then analyzed via GC-MS in order to identify the mass of all present compounds. The commonly observed malathion elimination by-products of diethyl fumarate and *O*,*O*-dimethyl phosphorodithioic acid (DMTP), were easily identified, with two identifiable GC peaks that displayed mass chromatograms matching those of the suggested by-products. The mass spectra of diethyl fumarate was judged in comparison to that from National Institute of Standards and Technology (NIST) library.[2] A mass spectrum for DMTP was not found in the NIST database; however, the detected ionic fragments logically align with what would be expected for this compound. Additionally, this mass spectrum corresponds to previously published GC-MS data for this malathion hydrolysis by-product.[3]



Scheme S3. Malathion hydrolysis degradation by-products products identified by GC-MS.

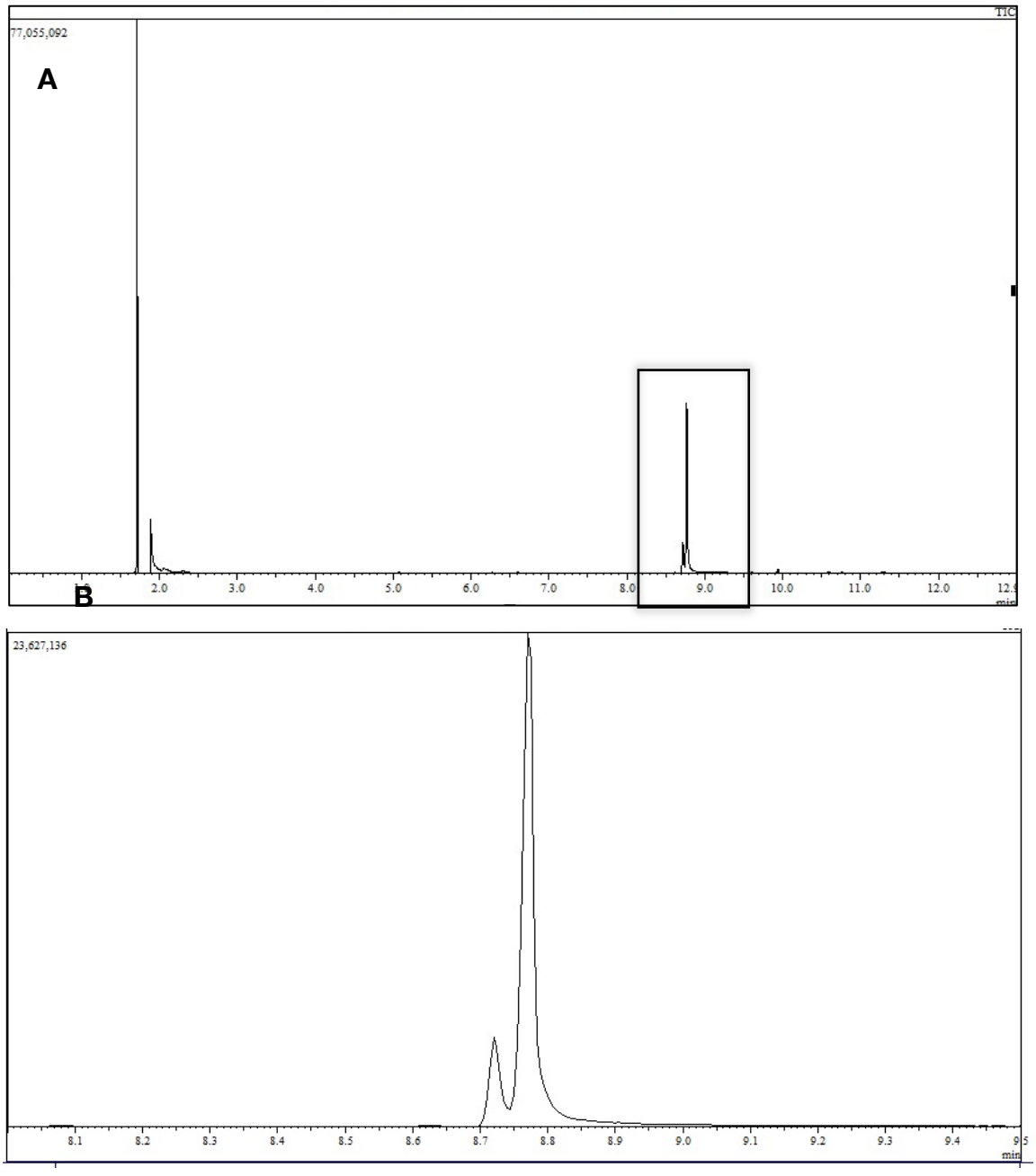


Figure S4. GC trace of malathion solution following 24 h treatment with CNC-PEI. A) Full GC analysis chromatogram B) Zoomed in to highlight peaks at RT = 8.70 and 8.75 min. Note: Peaks seen before RT = 3 min can be attributed to solvent oversaturation and impurities.

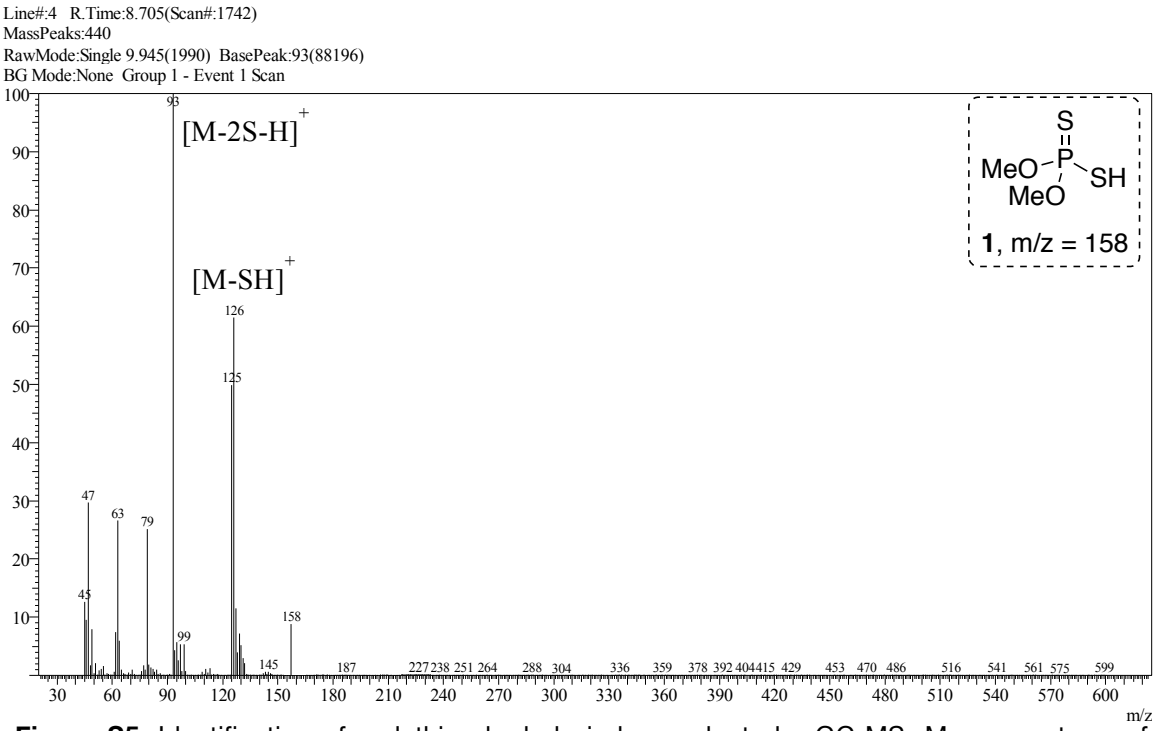


Figure S5. Identification of malathion hydrolysis by-products by GC-MS. Mass spectrum of *O*,*O*-dimethyl phosphorodithioic acid (DMTP) (m/z=158), RT = 8.70 min.

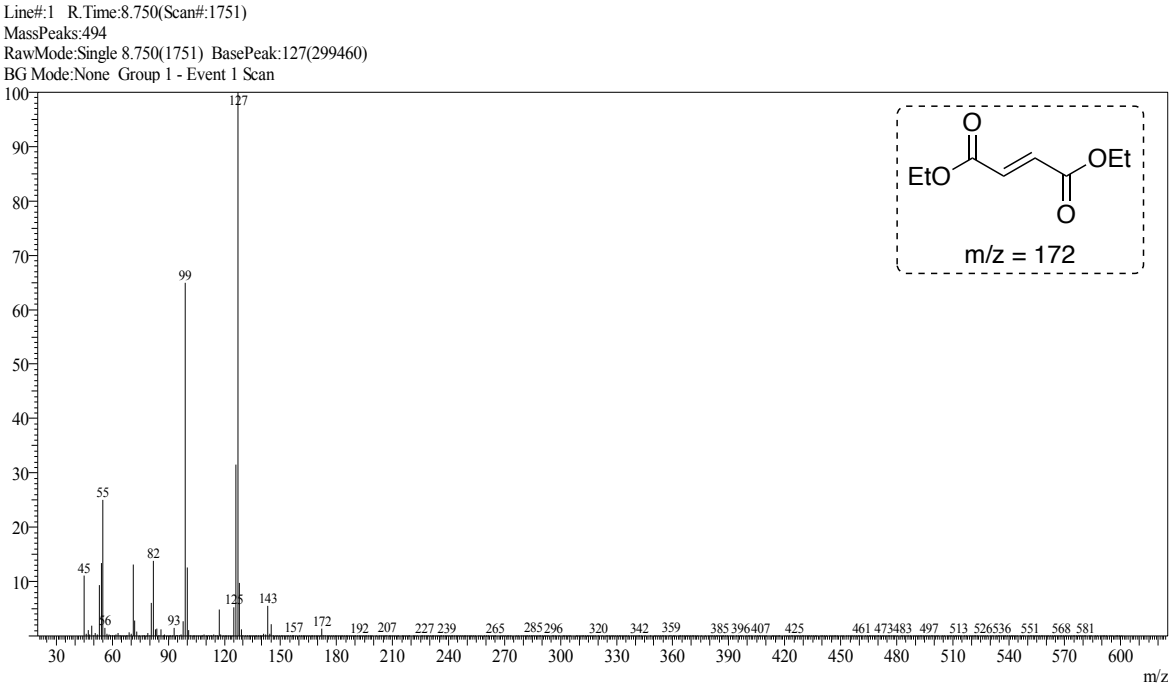
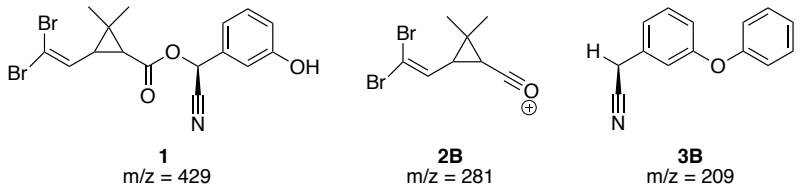


Figure S6. Identification of malathion hydrolysis by-products by GC-MS. Mass spectrum of diethyl fumarate (m/z=172), RT = 8.75 min.

Deltamethrin Degradation Studies

Following the same procedure described above, a 165 ppm solution of deltamethrin was prepared in deionized water, 50 mg of CNC-PEI was added and the suspension was allowed to stir for 24 h at room temperature. Next, the water and any soluble compounds were filtered from the solid CNC-PEI materials, and the collected nanocrystals were washed with deionized H_2O. The aqueous filtrates were then analyzed via GC-MS in order to identify the mass of all detectable by-products of deltamethrin degradation. Upon GC-MS analysis, three lower molecular weight by-products were identified.



1 m/z = 429 **2B** m/z = 281 **3B** m/z = 209

Figure S7. Detectable lower molecular weight degradation by-products of deltamethrin.

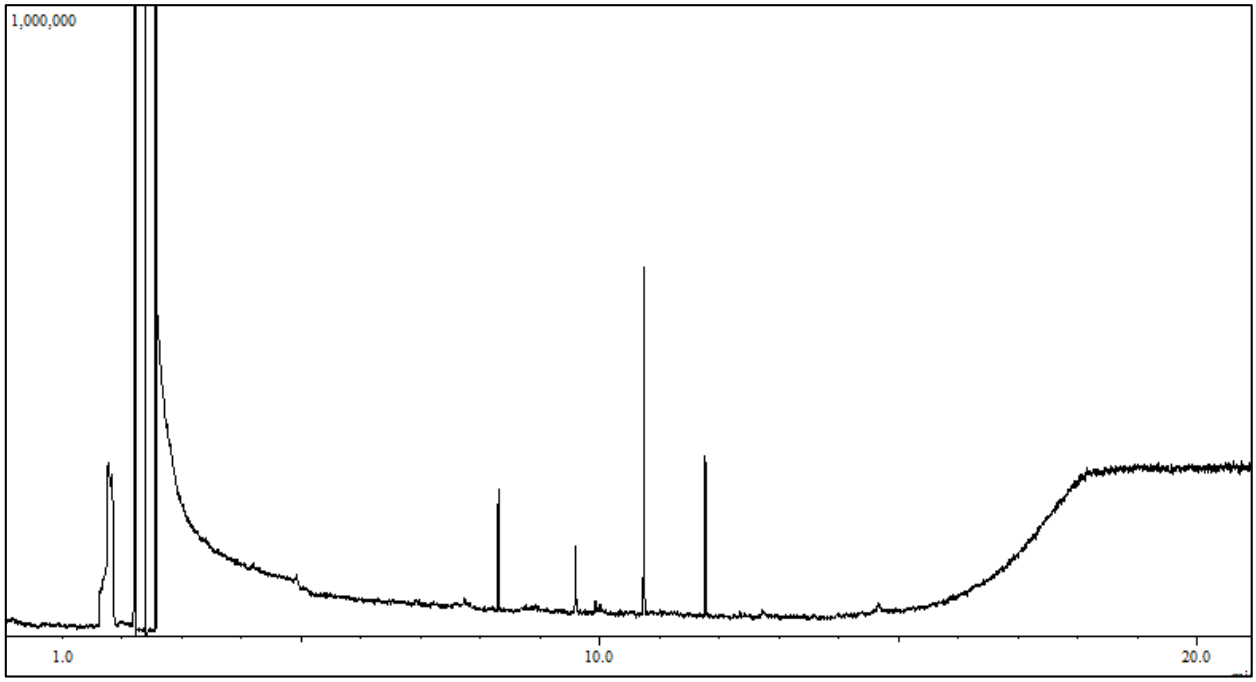


Figure S8. GC trace of deltamethrin solution following 24 h treatment with CNC-PEI. GC analysis chromatogram. Peaks attributed to degradation by-products were found at RT = 8.3, 9.6, 10.73, and 11.77 min.

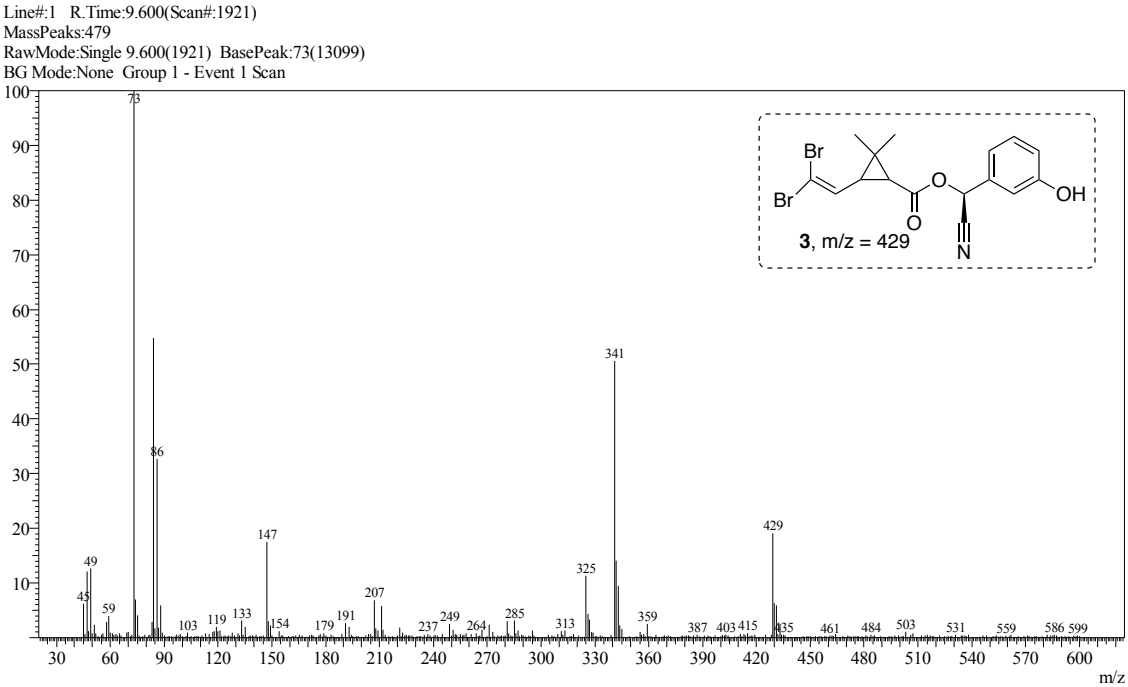


Figure S9. Identification of deltamethrin by-product by GC-MS. Mass spectrum of suggested compound **3** (m/z=429), RT = 9.6 min.

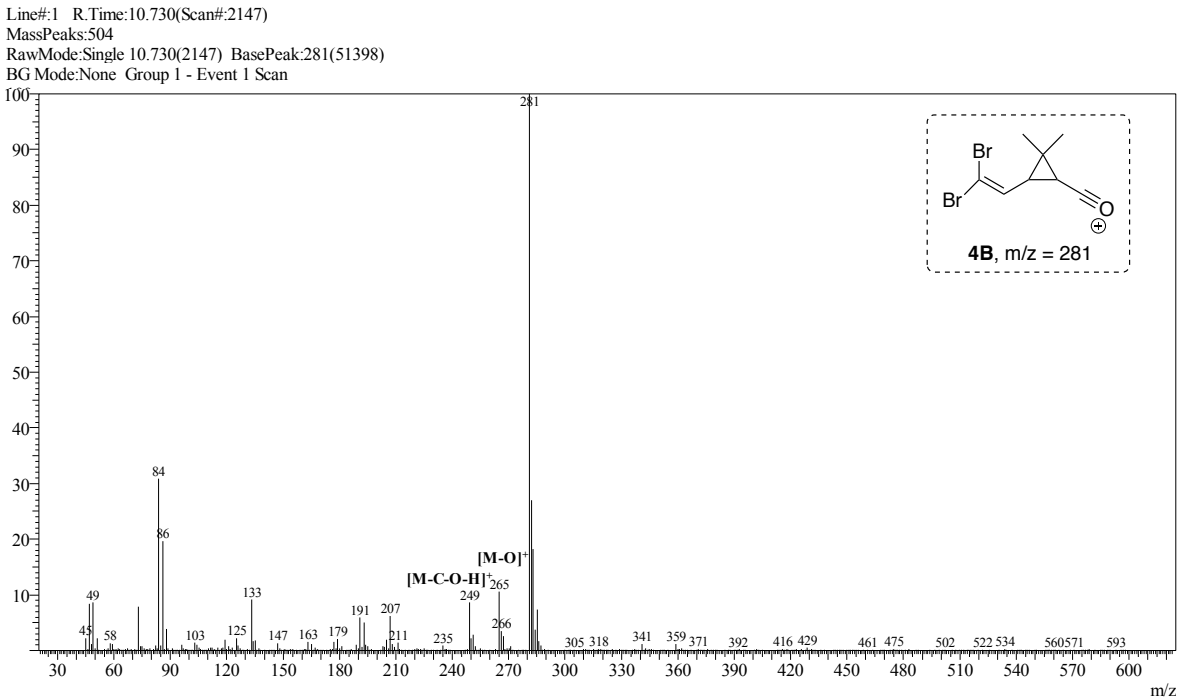


Figure S10. Identification of deltamethrin degradation by-products by GC-MS. Mass spectrum of **4B** (m/z=281) the acylium ion of deltamethrinic acid (**4A**), RT = 10.73 min.

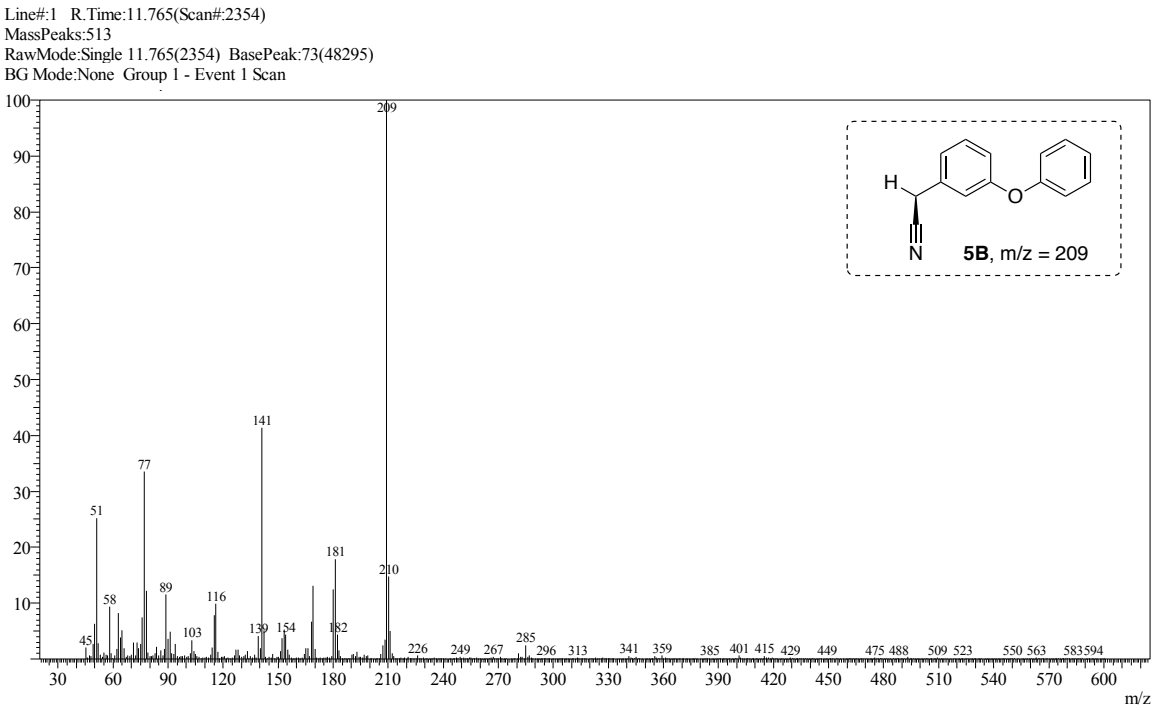


Figure S11. Identification of deltamethrin degradation by-products by GC-MS. Mass spectrum of 3-phenoxyphenyl-acetonitrile (m/z=209), RT = 11.765 min.[4]

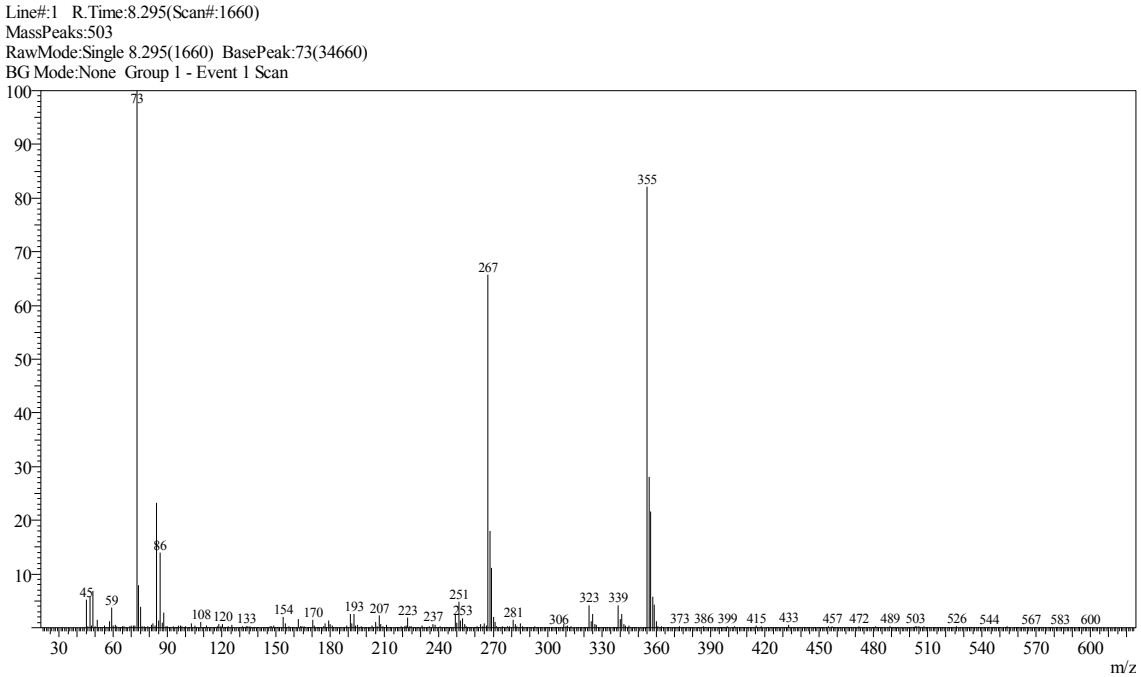


Figure S12. Identification of deltamethrin degradation by-products by GC-MS. Mass spectrum of unidentified compound (m/z=355), RT = 8.3 min.

IR and TGA analyses of recycled PEI-CNC Material:

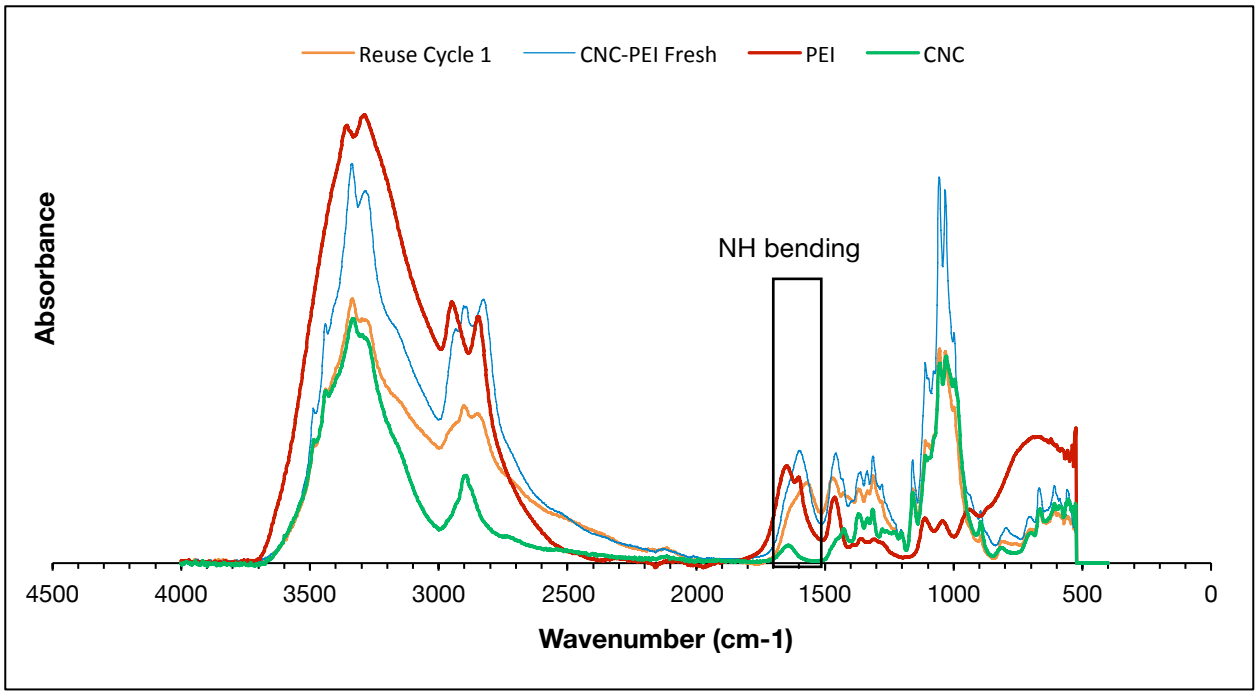


Figure S13. Infrared spectra of reused CNC-PEI. CNC-PEI after Reuse Cycle 1 (orange line), Fresh CNC-PEI (blue line), PEI (red line) and unmodified CNC (green line). The diagnostic NH bending following successful PEI-functionalization is still present in the CNC-PEI after reuse cycle 1.

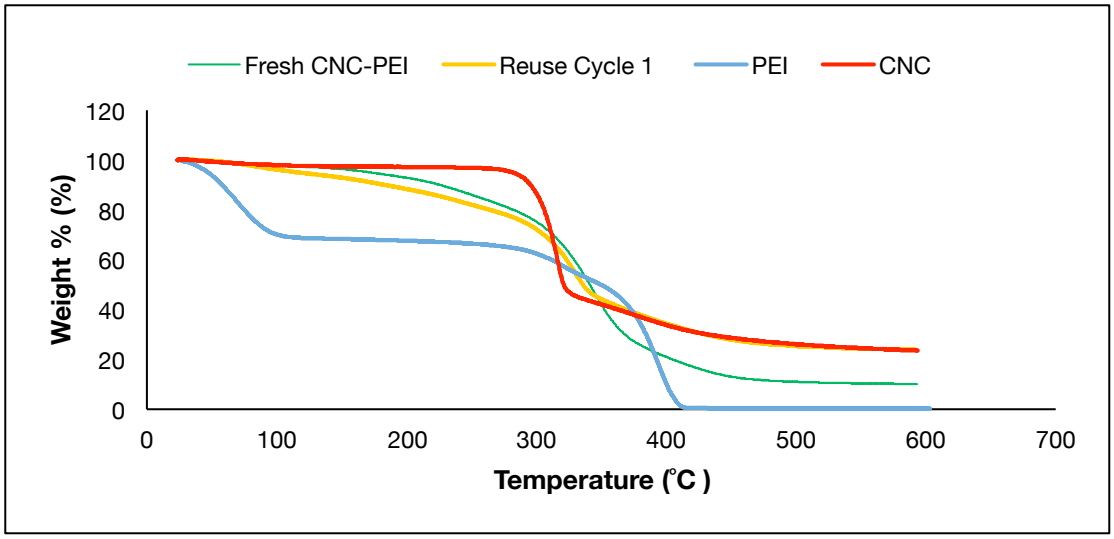


Figure S14. TGA analysis of fresh CNC-PEI (green line), CNC-PEI after reuse cycle 1 (yellow line), PEI (blue line) and unmodified CNC (red line).

SEM analysis of Recycled CNC-PEI.

SEM analysis was conducted on samples of CNC-PEI before (panels A and B) and after recycling. As is evident from the images, morphological differences before and after washing were not evident.

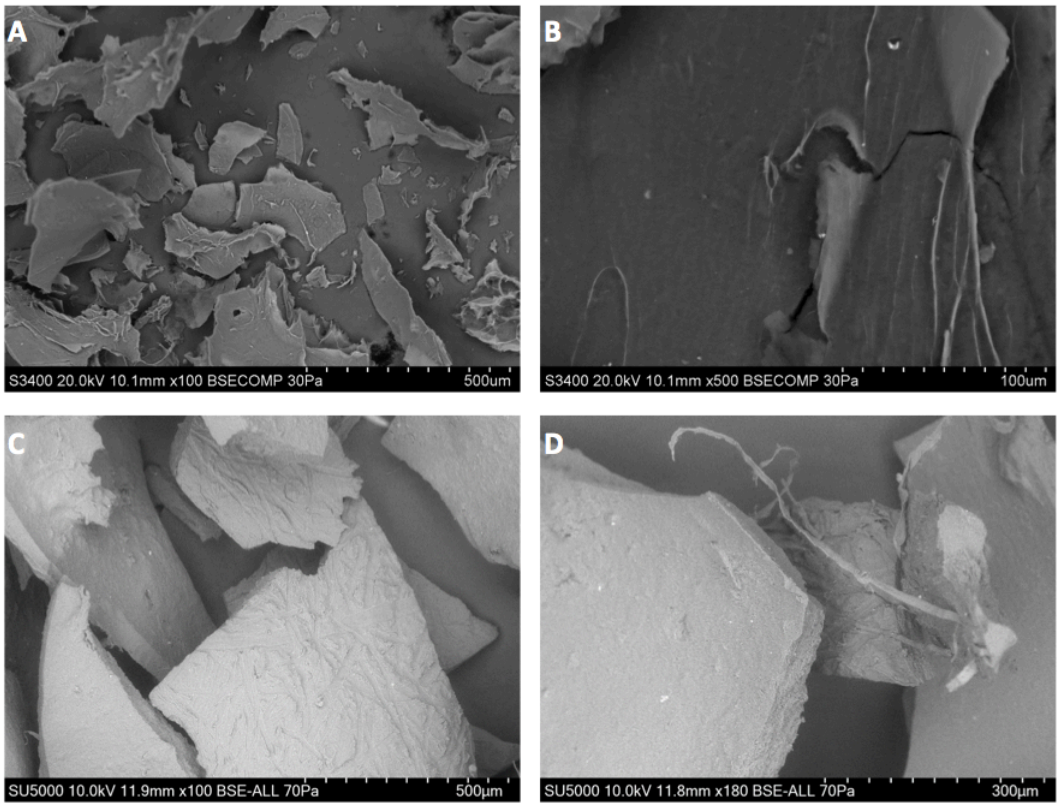
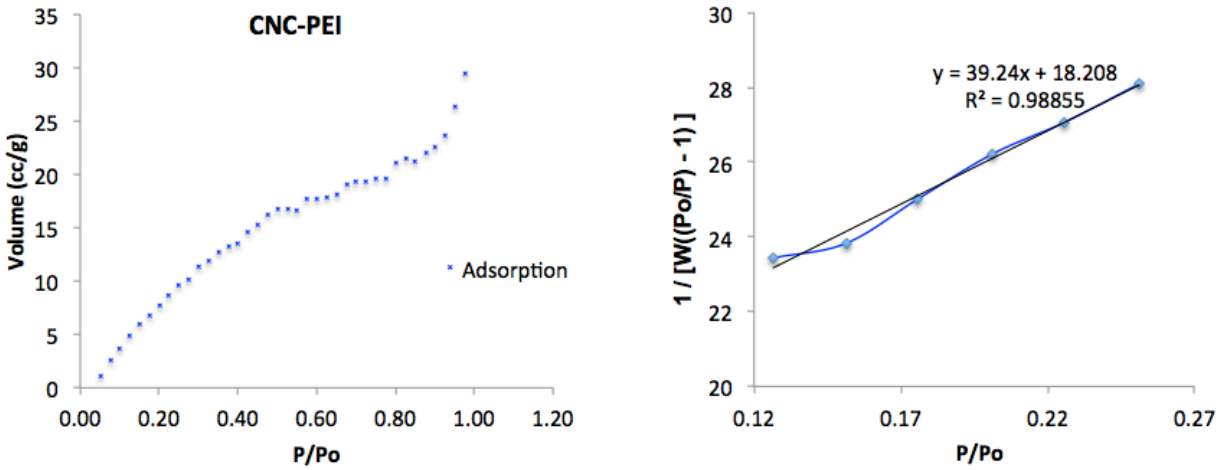


Figure S15. SEM Comparison of Pre- and Post-recyclced CNC-PEI. **A.** and **B.** are SEM images before recycling. **C.** and **D.** are SEM images after the first recycle experiment (*i.e.* after treatement with malathion and washing 5-6 times is according to the protocol outlined above).

BET Analysis of PEI-CNC material.

BET analysis was conducted on the PEI-CNC material, and the surface area was calculated to be 60.625 m^2/g.



BET Summary	
	CNC-PEI
Slope	39.24 g^{-1}
Intercept	18.208 g^{-1}
Correlation coefficient, r	0.994277
C constant	3.155
Surface Area	60.625 m^2/g

Figure S16. BET analysis of CNC-PEI material.

Calibration Curve for Malathion Analysis

A calibration curve over the concentration range of 0.1 mM (33 ppm) to 1.5 mM (496 ppm) was generated. Remediation of malathion was successfully conducted at the low and high ranges of this calibration curve.

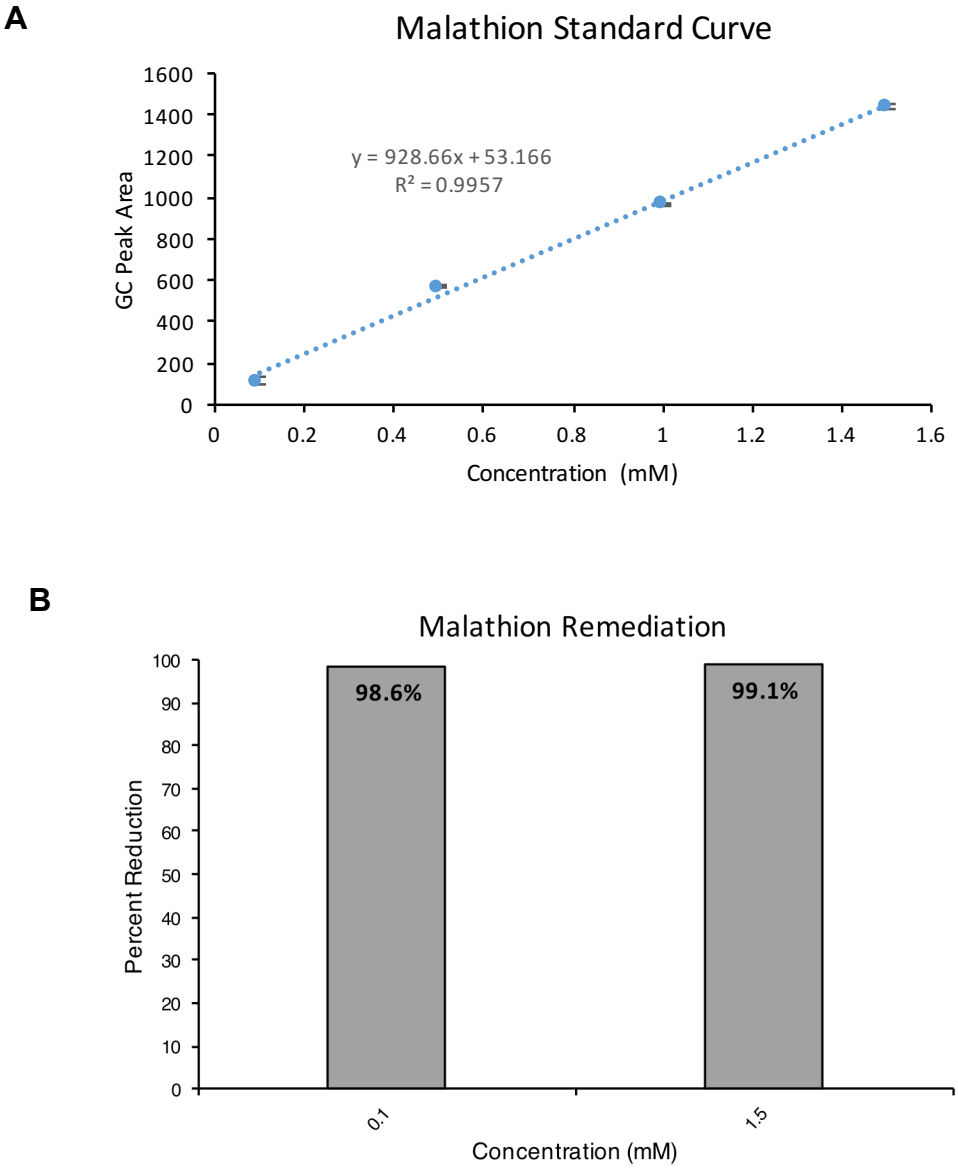


Figure S17. A. Calibration curve for Malathion over the concentration range of 0.1 mM (33 ppm) to 1.5 mM (496 ppm). **B.** Successful Malathion remediation at 0.1 and 1.4 mM concentrations of malathion.

References

[1] Guerra, F. D.; Campbell, M. L.; Attia, M. F.; Whitehead, D. C.; Alexis, F. *ChemistrySelect* **2018**, *3*, 5485-5501.

[2] https://webbook.nist.gov/cgi/cbook.cgi?ID=C623916&Mask=200#Mass-Spec Spec (accessed Jan. 10, 2019)

[3] Zhao, X.; Hwang, H. M. *Arch. Environ. Contam. Toxicol.* **2009**, *56*, 646-653.

[4] NIST Chemistry Web Book. https://webbook.nist.gov/cgi/cbook.cgi?Name=3-Phenoxyphenylacetonitrile+&Units=SI&cMS=on#Mass-Spec (accessed March. 15, 2019).