

Supporting information

Statistical analysis

Sigma Plot Systat was used for graphs plotting in the kinetics study and statistical treatments of the experimental data for the elimination of selected pesticides by nanohybrid were represented empirically from an asymptotic analysis. The good acceptance of the outcome was shown for the triplicate and the “Microsoft Excel” program was used for the calculation of the standard deviation. The significance of experimental data was proved by comparing the results through beta coefficient (R^2) and probability values (p-values). Fit equations were used for kinetics and adsorption data.

Details of Langmuir, Freundlich, Temkin, Sip and D-R isotherms used in present study

Adsorption data through Langmuir adsorption isotherms were calculated through graph of C_e/q_e v/s C_e of the solute. Which were calculated by fitting the adsorption data into the equation:

$$\frac{C_e}{q_e} = \frac{1}{k_L X_m} + \frac{C_e}{X_m}$$

or

$$\frac{1}{q_e} = \frac{1}{C_e} \left(\frac{1}{k_L X_m} \right) + \frac{1}{X_m}$$

q_e was calculated through the equation:

$$q_e = \frac{(C_i - C_e) \times \text{Volume of solution (mL)} \times \text{Molecular weight of adsorbent}}{\text{Amount of catalyst (mg)}}$$

Freundlich Isotherm.

A typical graph of Q_e v/s C_e of the solute was a straight line.

$$Q_e = K_f + C_e^{1/n} \text{ and linear form is } \log Q_e = \log K_f + \frac{1}{n} \log C_e$$

Where C_e is the equilibrium concentration of the dye solution; Q_e is the amount of dye adsorbed per gram weight of adsorbent; K_f is the Freundlich adsorption constant (mg/g); n is adsorption intensity.

Temkin Isotherm:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e$$

Where $B=RT/b$ constant related to heat of sorption (J/mol) obtained from the Temkin plot (q_e vs $\ln C_e$); A (slope) = Temkin isotherm equilibrium binding constant (L/g); b (intercept) = Temkin isotherm constant; R = universal gas constant (8.314 J·mol⁻¹·K⁻¹) T = Temperature at 298, 308 and 318 K.

As C_e values were very low, the $\ln C_e$ values were coming out to be negative. Therefore, Temkin isotherm (Q_e v/s $\ln C_e$) was not plotted for present study.

Dubinin-Radushkevich (D-R) isotherm:

$$\ln q_e = \ln X_m - \beta \varepsilon^2$$

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right]$$

Where X_m is maximum adsorption capacity (mg/g) obtained from intercept; β (mol²/J²) is a activity coefficient constant related to sorption energy and obtained from slope; ε is Polanyi potential. D-R was plotted between $\ln q_e$ vs ε^2

Sips Isotherm

It is plotted between $1/Q_e \times 10^{-2}$ (g/mg) and $(1/C_e) \times 10^{-8}$ L/mg; where $(1/mg)$ and (mg/g) are the Sips equilibrium constant and maximum adsorption capacity values obtained from the slope and the intercept of the plot. The Sips isotherm equation is characterized by the dimensionless heterogeneity factor 'n' which can also be employed to describe the system's heterogeneity when is between 0 and 1.

$$\frac{1}{q_e} = \frac{1}{X_m K_s} \left(\frac{1}{C_e} \right)^{1/n} + \frac{1}{X_m}$$

Equation used for calculation Band Gap Energy values

The band gap energy was determined by fitting the reflectance data into the direct transition equation

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

; where A is a constant, E_g is the energy gap, ν is the frequency of incident radiation, h is Planck's constant, α is the optical absorption coefficient and exponent 2 is the number characterizing the direct transition process. Plotting $(\alpha h\nu)^2$ as a function of photon energy as shown in figure 3S, upon extrapolating the linear portion of the curve to absorption equal to zero gives the value of the band gap energy.

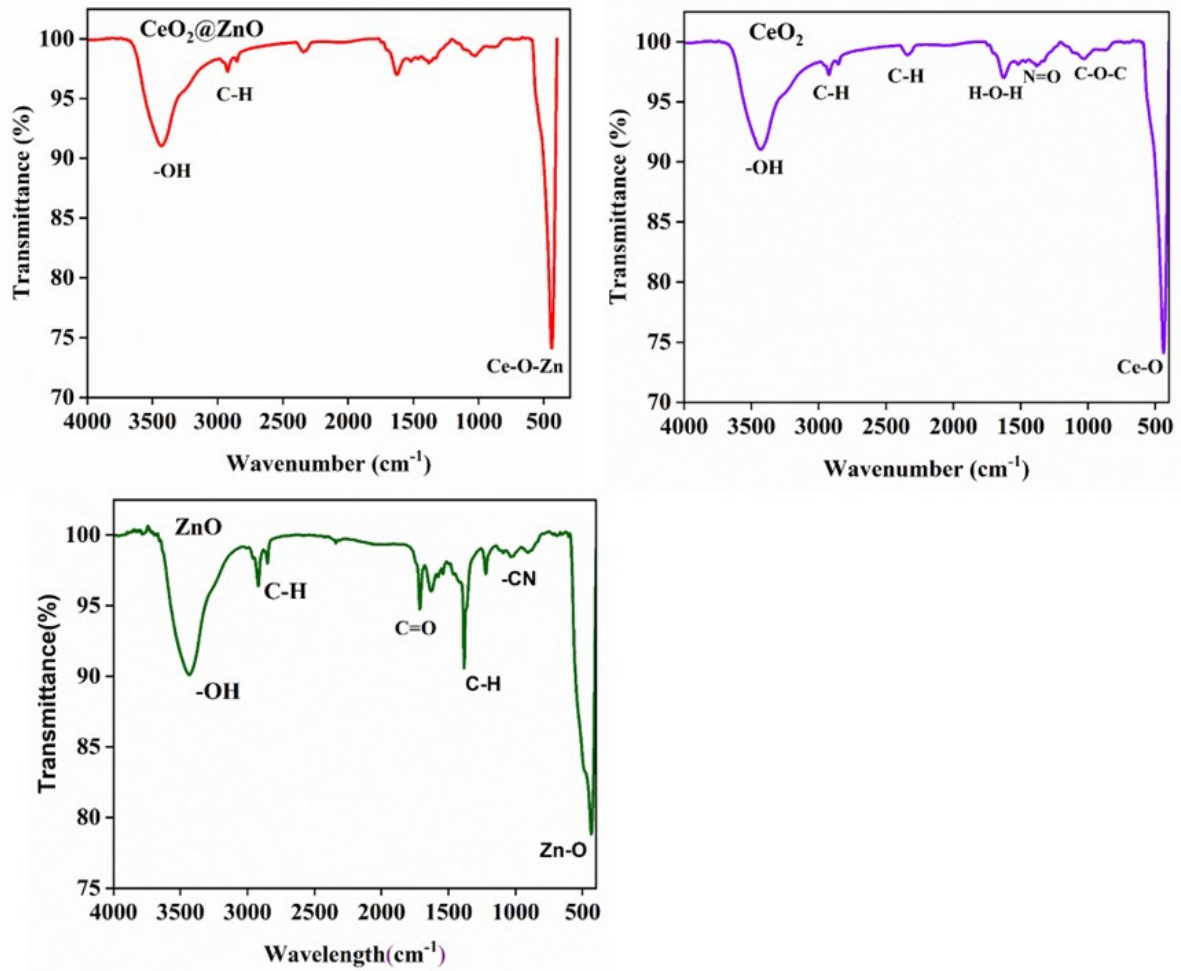


Figure 1S. FT-IR of (a) ZnO (b) CeO₂ (c) CeO₂@ZnO nanocomposite ZnO, CeO₂ and CeO₂@ZnO.

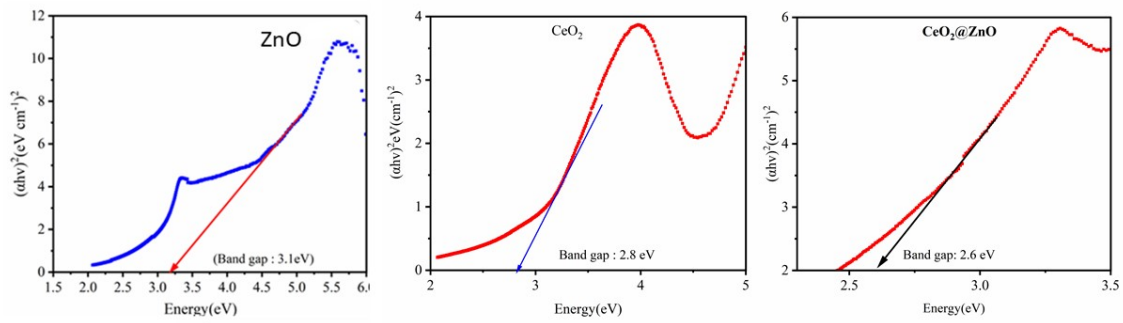


Figure 2S. Band gap of (a) ZnO (b) CeO₂ (c) CeO₂@ZnO nanocomposite

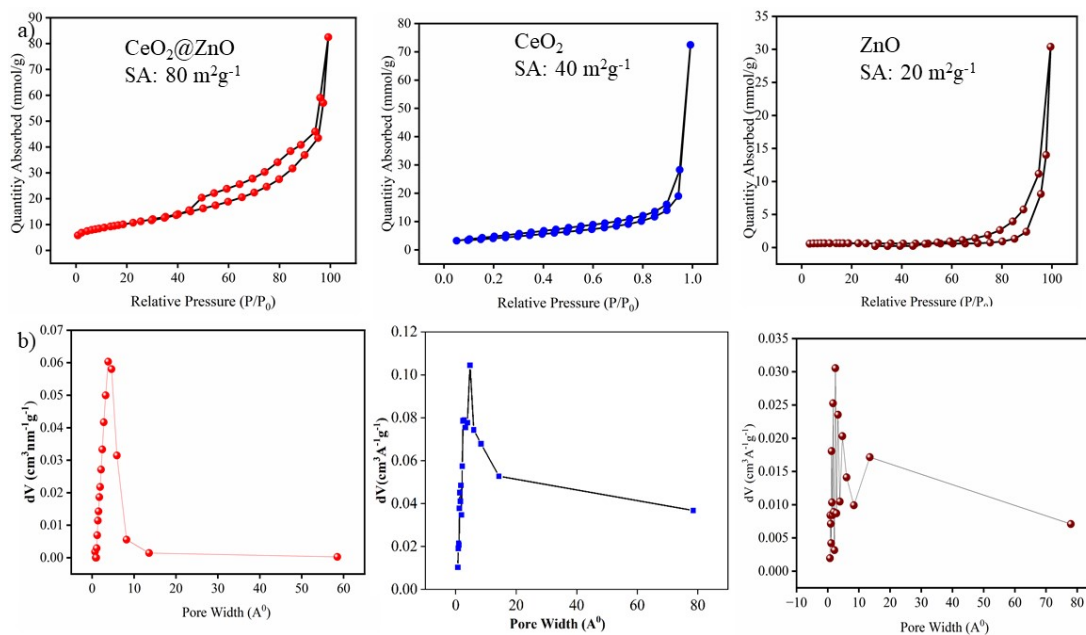


Figure 3S. (a) N_2 adsorption/desorption isotherms and (b) pore size distribution curves of $CeO_2@ZnO$ nanocomposite, CeO_2 and ZnO nanoparticle

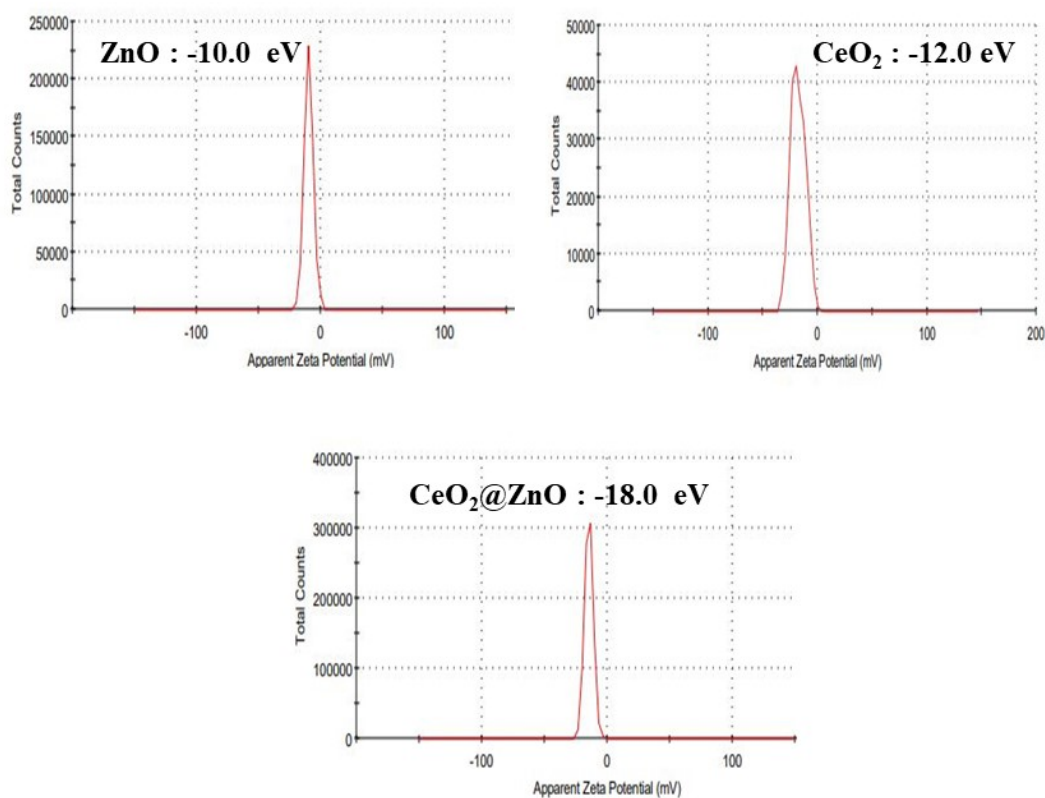


Figure 4S. Zeta potential of (a) ZnO (b) CeO_2 (c) $CeO_2@ZnO$ nanocomposite

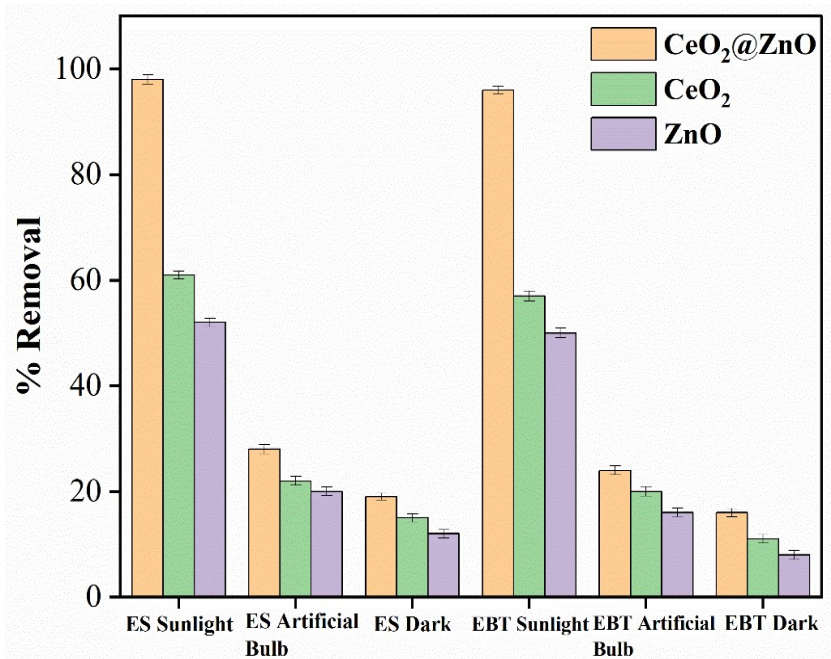


Figure 5S. Removal of ES and EBT under natural sunlight, bulb and dark

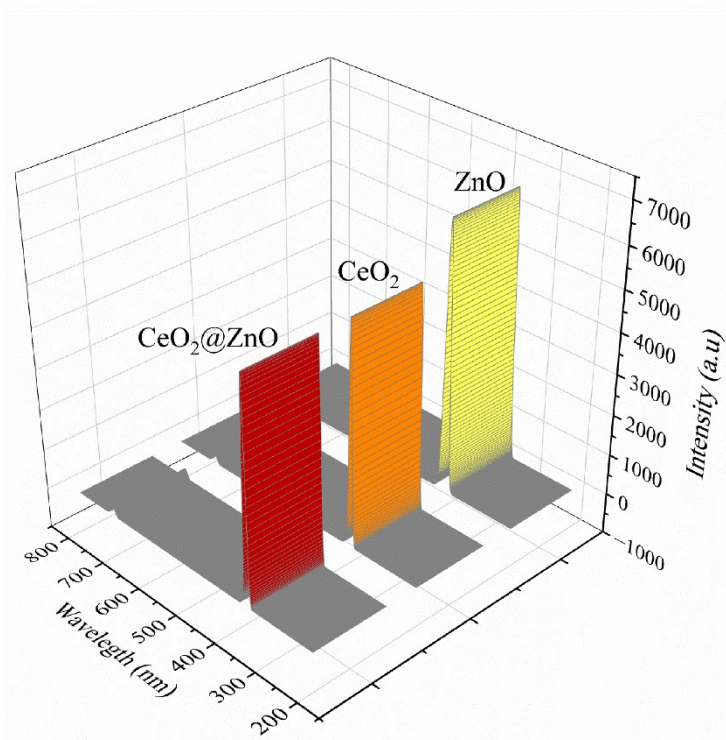


Figure 6S. photoluminescence (PL) of CeO₂@ZnO nanocomposite and native nanoparticle CeO₂ as well as ZnO nanoparticle

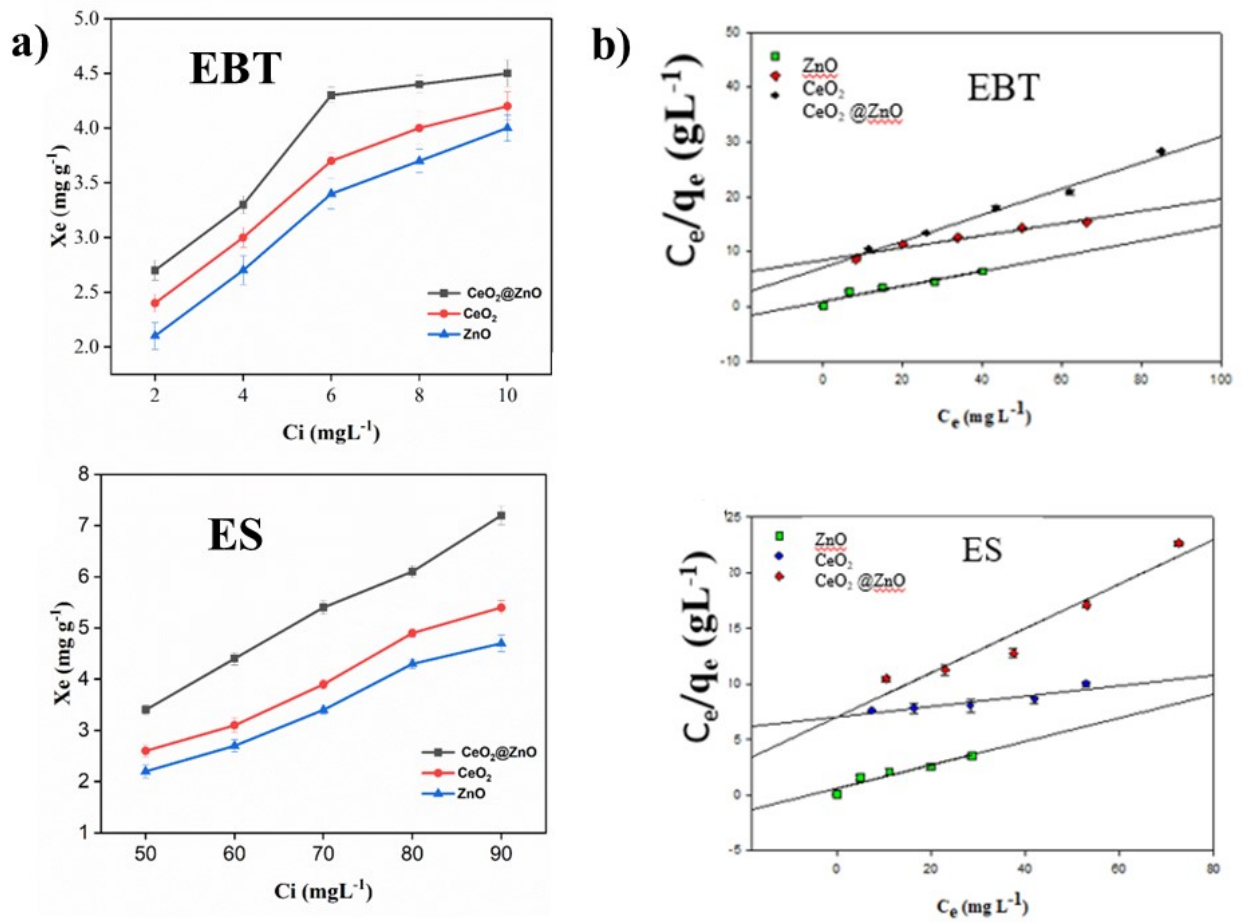


Figure 7S. (a) Adsorption and (b) Langmuir isotherms of EBT and ES adsorption upon the synthesized nanomaterials. Errors were estimated by taking triplicates of the sample.

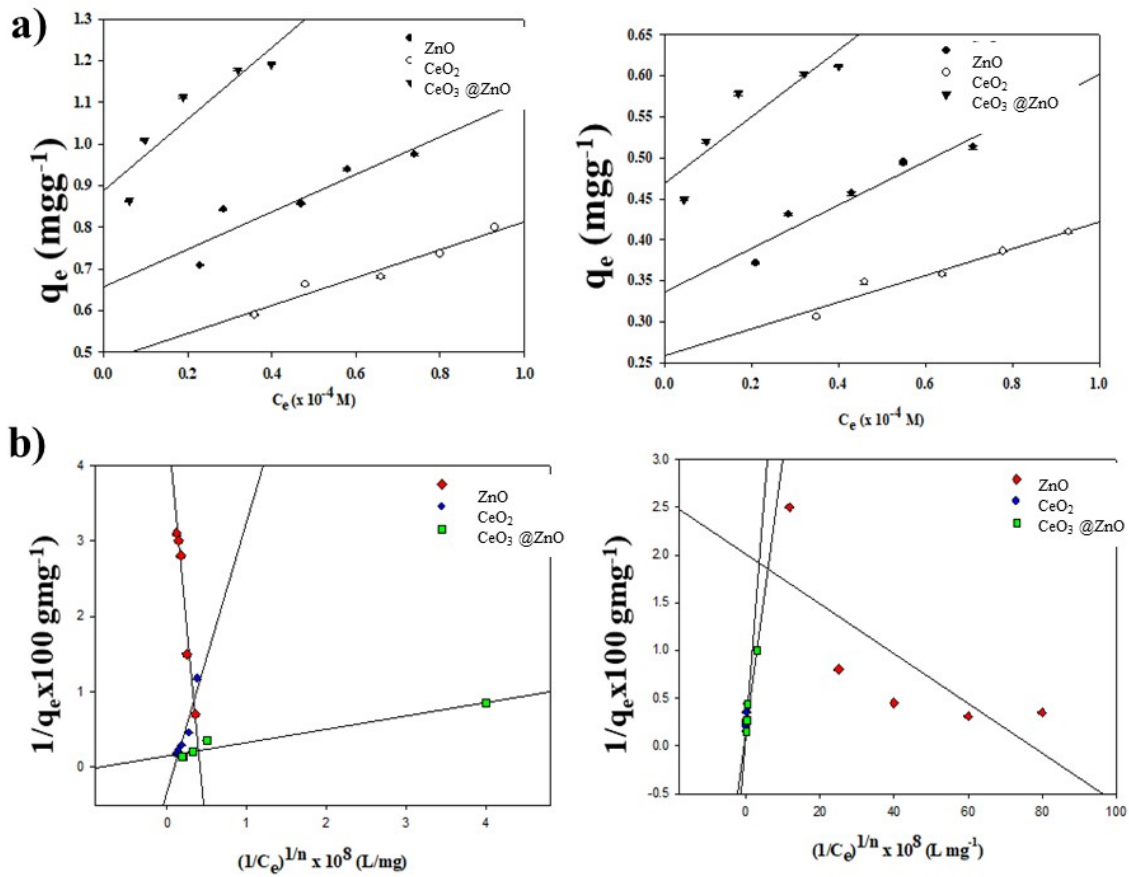
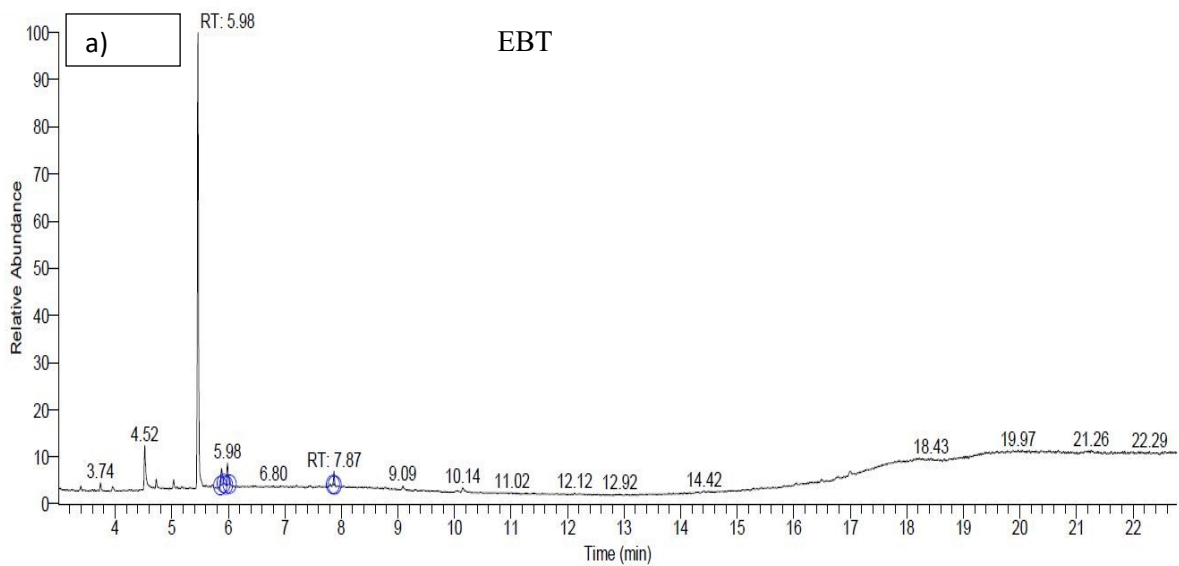


Figure 8S. (a) Freundlich (b) Sips model for targeted ES and EBT adsorption. Triplicate experiments (n=3) were evaluated for estimation of error bar.



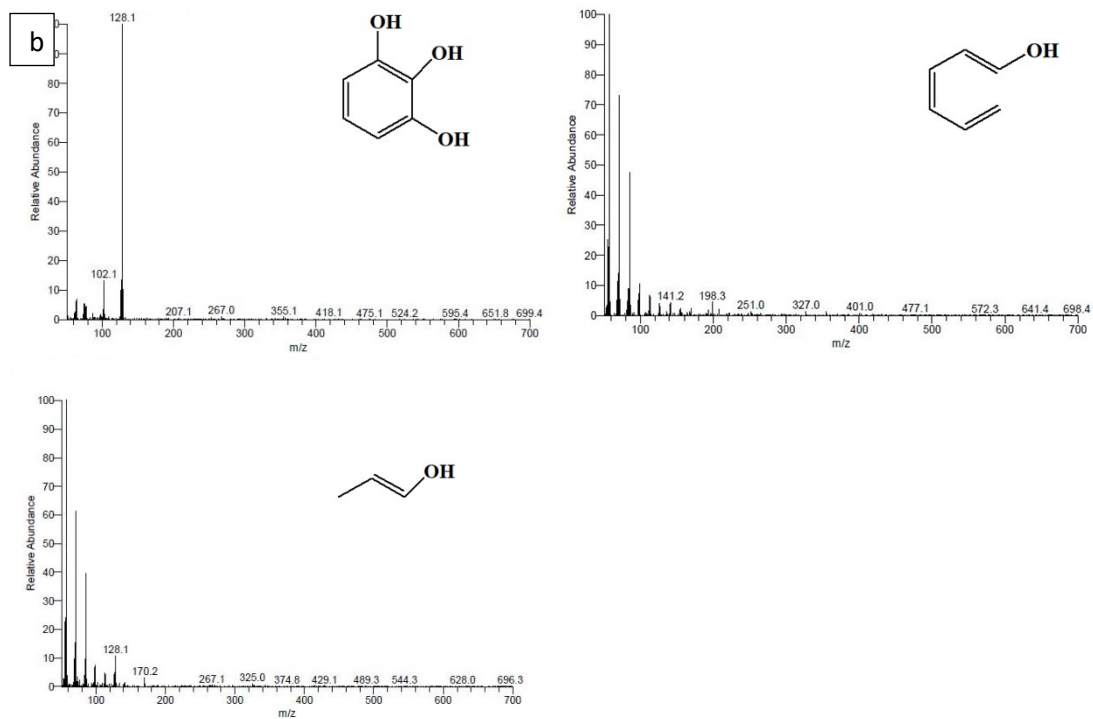
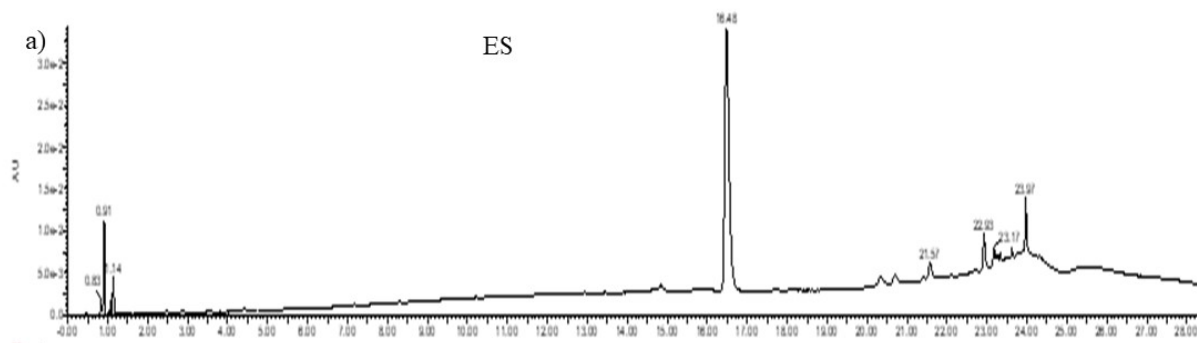


Figure 9S. (a) TIC and (b) mass spectra of EBT dye.



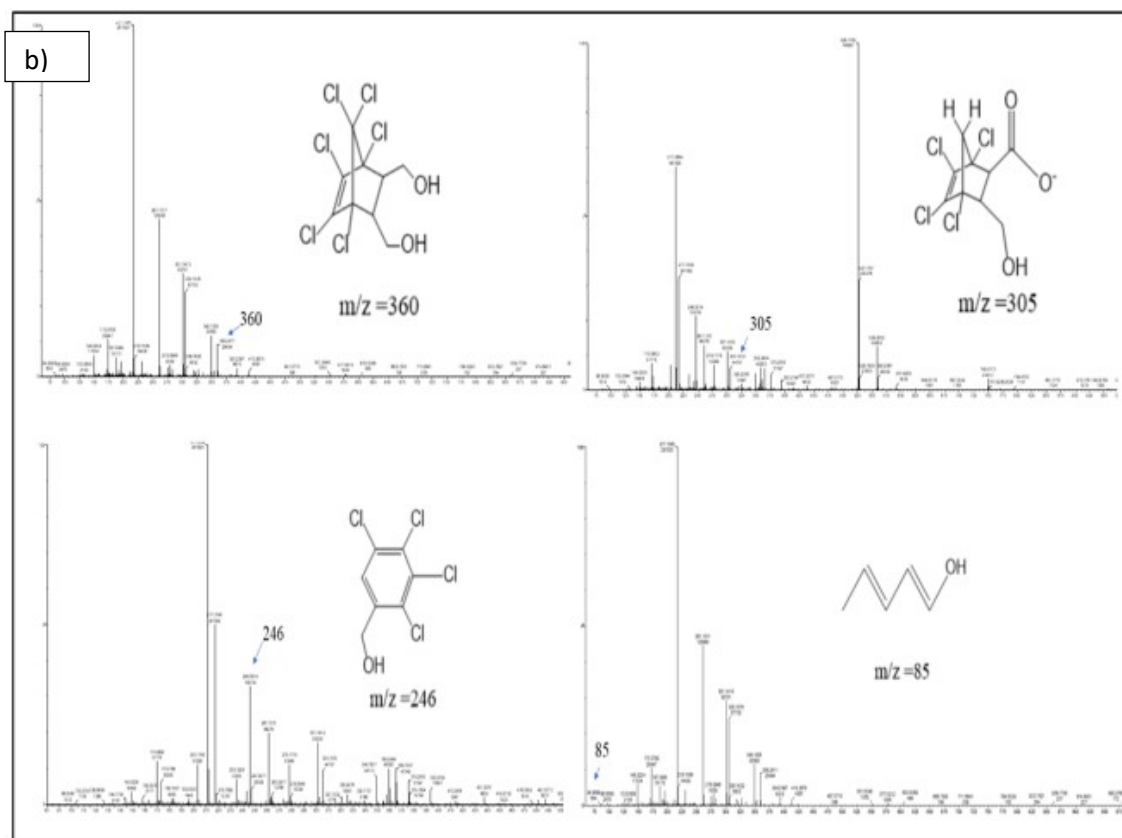


Figure 10S. (a) TIC and (b) mass spectra of ES pesticide

Table 1S. Comparison of different isotherms on the basis of R^2 and p values for EBT and ES adsorption

	Langmuir				Sips			
	EBT		ES		EBT		ES	
Catalyst	R^2	p	R^2	p	R^2	p	R^2	p
CeO₂@ZnO	0.99	0.005	0.98	0.012	0.86	0.034	0.85	0.026
CeO₂	0.98	0.004	0.96	0.015	0.85	0.025	0.88	0.035
ZnO	0.99	0.008	0.99	0.017	0.87	0.022	0.89	0.031

Freundlich	
EBT	ES

Catalyst	R²	<i>p</i>	R²	<i>p</i>
CeO₂@ZnO	0.82	0.031	0.83	0.032
CeO₂	0.83	0.022	0.85	0.003
ZnO	0.88	0.037	0.85	0.002
