Supplementary Material (ESI) for ***RSC Adv***

Preponderant Adsorption for Chlorpyrifos over Atrazine by Wheat Straw-Derived Biochar: Experimental and Theoretical Studies

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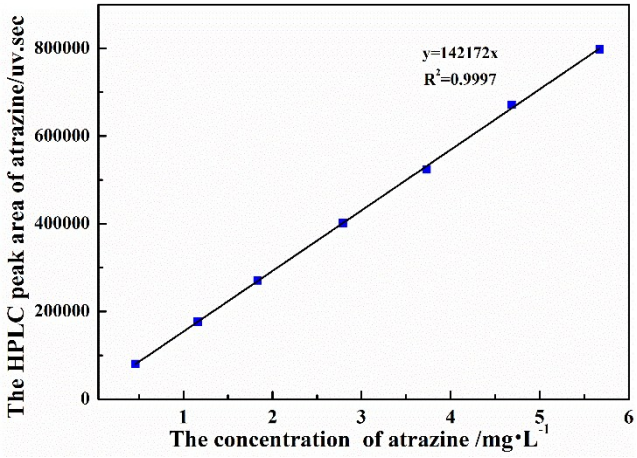
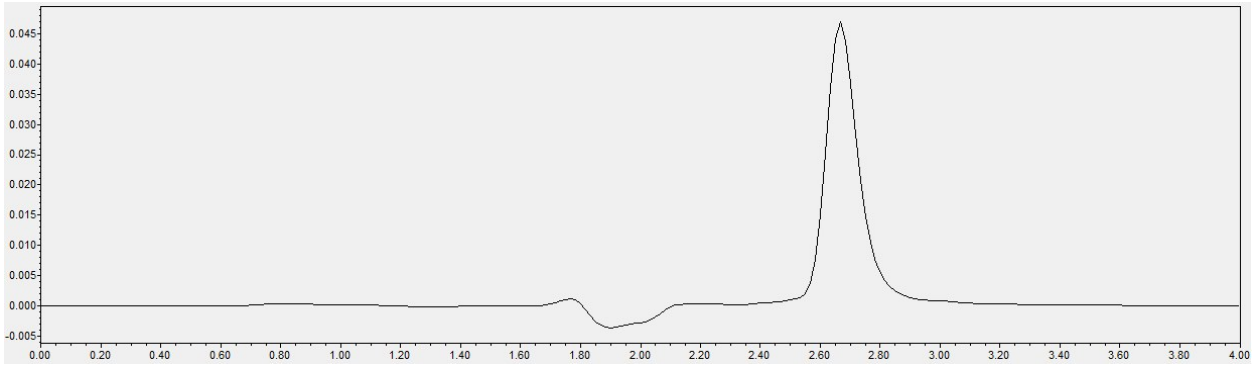
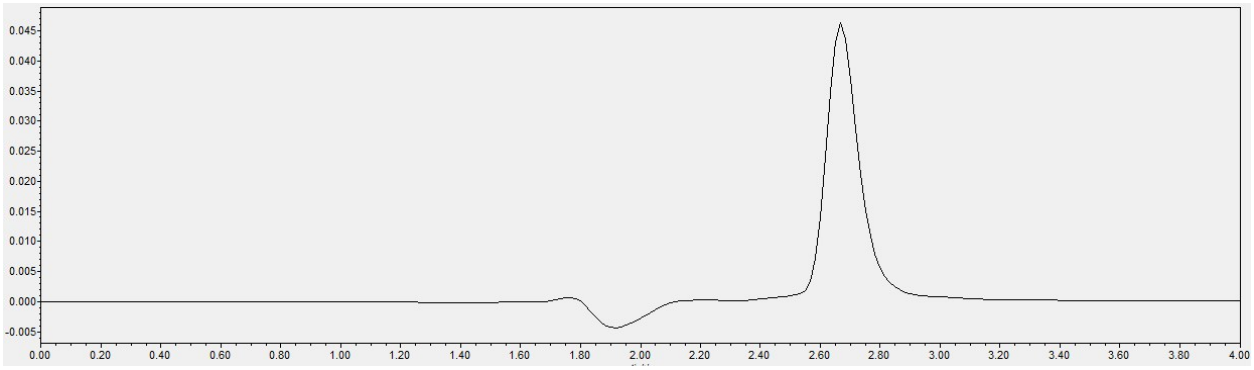


Fig.S1 The standard curve of atrazine in aqueous solution.



(a)



(b)

Fig.S2 (a) the High Performance Liquid Chromatography spectra of atrazine aqueous solution at 0 hour and (b) the High Performance Liquid Chromatography spectra of atrazine aqueous solution at 72 hours. The procedure of preparing atrazine aqueous solution was same as that in sorption experiment except that WS750 was not added.

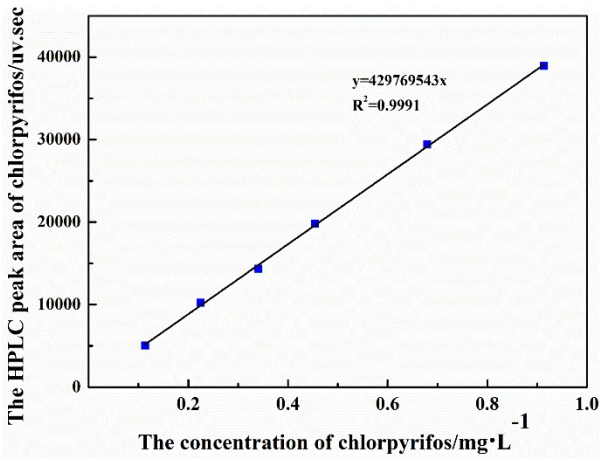
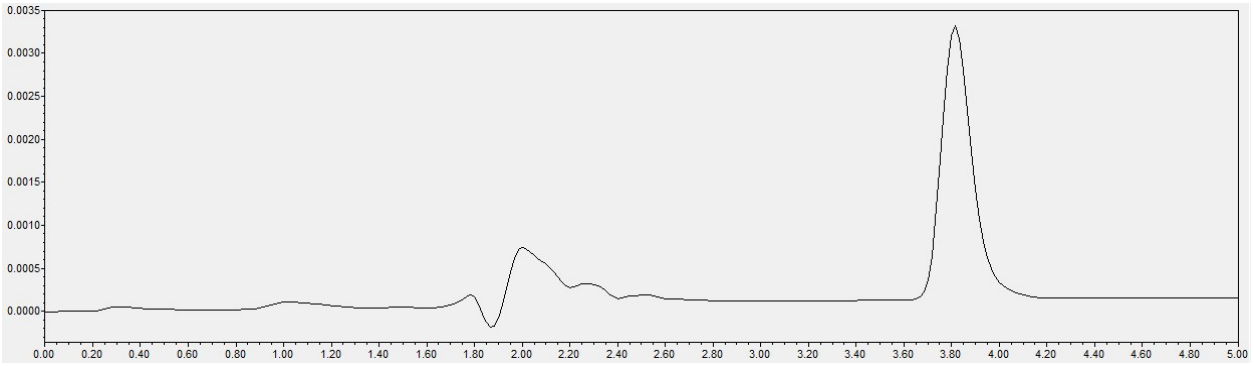
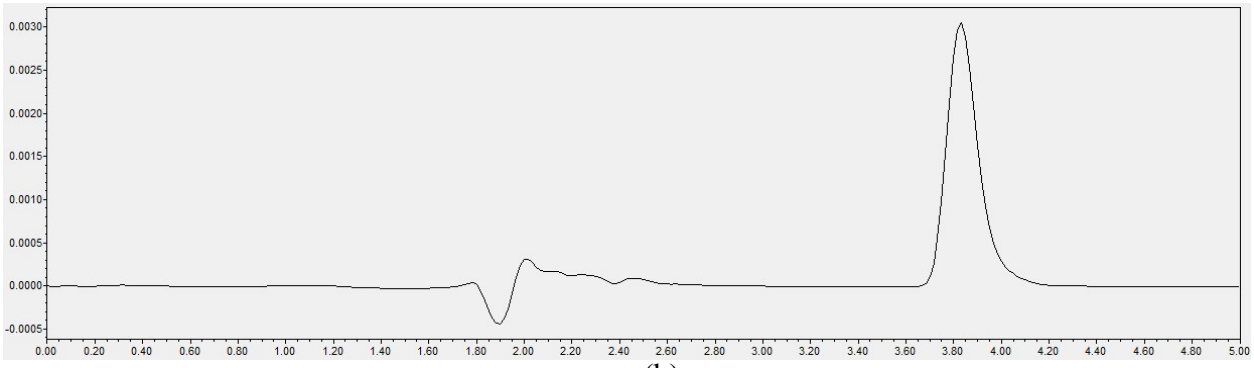


Fig.S3 The standard curve of chlorpyrifos in aqueous solution.



(a)



(b)

Fig.S4 (a) the High Performance Liquid Chromatography spectra of chlorpyrifos aqueous solution at 0 hour; (b) the High Performance Liquid Chromatography spectra of chlorpyrifos aqueous solution at 72 hours. The procedure of preparing chlorpyrifos aqueous solution was same as that in sorption experiment except that WS750 was not added.

Table S1 Summary of sorption experiments in 2.5 section. **Yes** implied that this kind of experiment had been done by the sample in the left column, while **No** implied this kind of experiment had not been done by the sample in the left column.

Experiments / **Samples**	sorption of atrazine (5.80 mg L^{-1}) by WS samples	pH effect on sorption of atrazine (5.80 mg L^{-1}) by WS750	effect of $CaCl_2$ concentration on sorption of atrazine (5.80 mg L^{-1}) by WS750	sorption of atrazine (5.80 mg L^{-1}) by the inorganic component in WS750	kinetics sorption of atrazine (5.80 mg L^{-1}) by WS750	isotherm sorption of atrazine by WS750	recycle experiment for sorption of atrazine (5.80 mg L^{-1}) by WS750	sorption of chlorpyrifos by WS750	sorption of atrazine by WS750	kinetics sorption of co-existing chlorpyrifos and atrazine by WS750	isotherm sorption of co-existing chlorpyrifos and atrazine by WS750	Recycle experiment for sorption of the coexisting atrazine and chlorpyrifos by WS750
		pH values were 4.9, 6.1, 7.1, 8.3, and 9.1 before sorption.	$CaCl_2$ concentrations ranged from 0.005 mol L^{-1}, 0.010 mol L^{-1}, 0.050 mol L^{-1} to 0.100 mol L^{-1}	inorganic component in WS750: SiO_2		atrazine concentrations ranged from 2.80 mg L^{-1} to 8.70 mg L^{-1}	three parallel experiments were performed. WS750 was washed with methanol to regenerate it sorption ability.	chlorpyrifos: 1.12 mg L^{-1} (0.0032 mmol L^{-1})	atrazine: 0.69 mg L^{-1} (0.0032 mmol L^{-1})	atrazine: 0.69 mg L^{-1} (0.0032 mmol L^{-1}) chlorpyrifos: 1.12 mg L^{-1} (0.0032 mmol L^{-1})	atrazine: 0.35 mg L^{-1} (0.0016 mmol L^{-1}) to 0.73 mg L^{-1} (0.0034 mmol L^{-1}) chlorpyrifos: 0.56 mg L^{-1} (0.0016 mmol L^{-1}) to 1.19 mg L^{-1} (0.0034 mmol L^{-1}).	three parallel experiments were performed. WS750 was washed with methanol to regenerate it sorption ability. atrazine: 0.69 mg L^{-1} (0.0032 mmol L^{-1}) chlorpyrifos: 1.12 mg L^{-1} (0.0032 mmol L^{-1})
	WS sample: 5 mg	WS750: 5 mg	WS750: 5 mg	sample: 5 mg	WS750: 5 mg	WS750: 5 mg	WS750: 5mg	WS750: 2.5 mg	WS750: 2.5 mg	WS750: 2.5 mg	WS750: 2.5 mg	WS750: 2.5 mg
WS250-WS650	**Yes**	**No**	**No**	**No**	**No**	**No**	**No**	**No**	**No**	**No**	**No**	**No**
WS750	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**	**Yes**

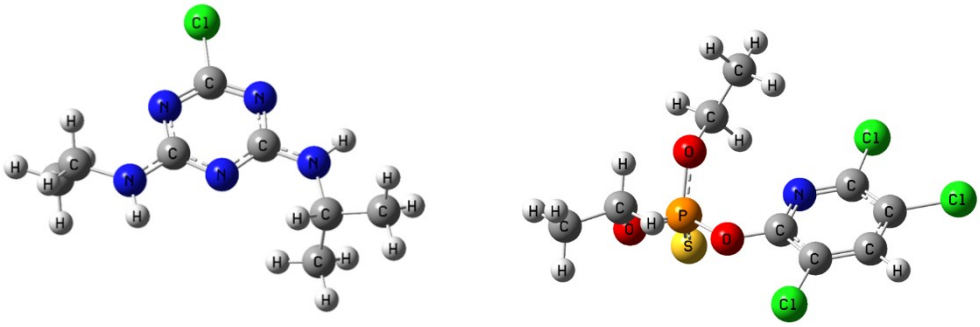


Fig.S5 The optimized structures of atrazine (left) and chlorpyrifos (right).

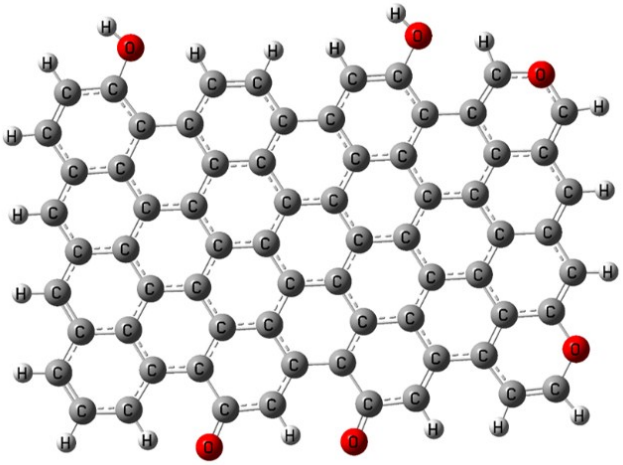


Fig. S6 The optimized structure of WSmodel.

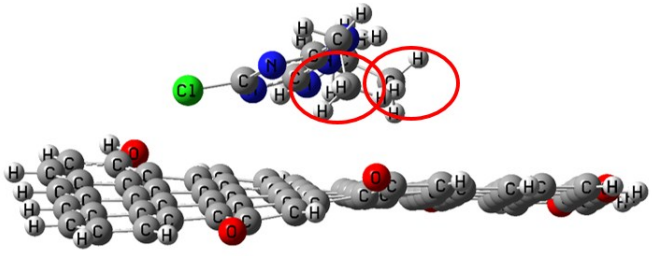


Fig. S7 The optimized structure of another atrazine···Wsmodel complex, in which the two methyl groups were pointed to the aromatic surface of WSmodel.

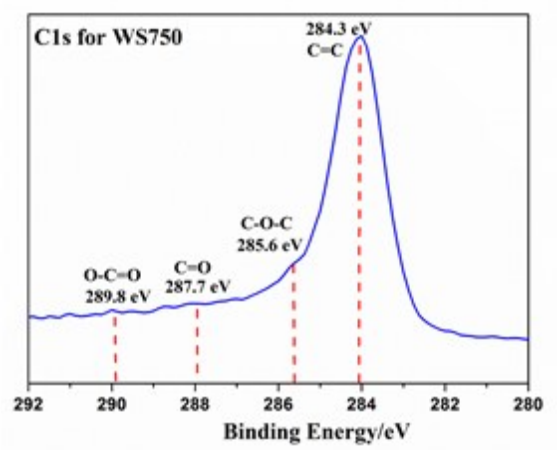


Fig. S8 XPS spectra of WS750.

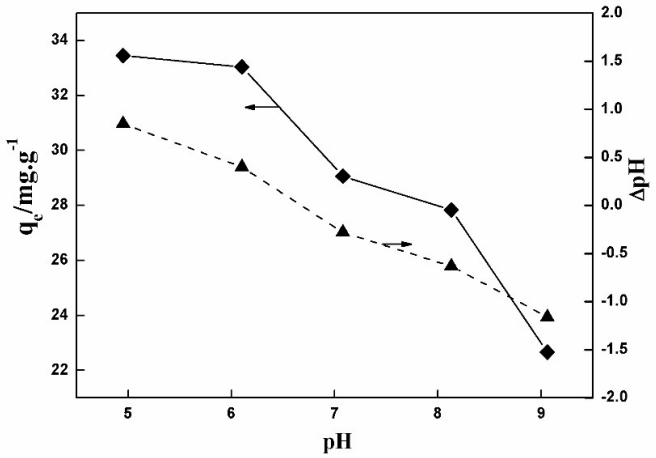


Fig.S9 The influence of pH on the sorption quantity of atrazine by WS750 (the full line with these diamond points and left Y-coordinate) as well as the change of each pH value before and after atrazine sorption by WS750 (the dotted line with these triangle points and right Y-coordinate). The concentration of atrazine is 5.80 mg L^{-1}.

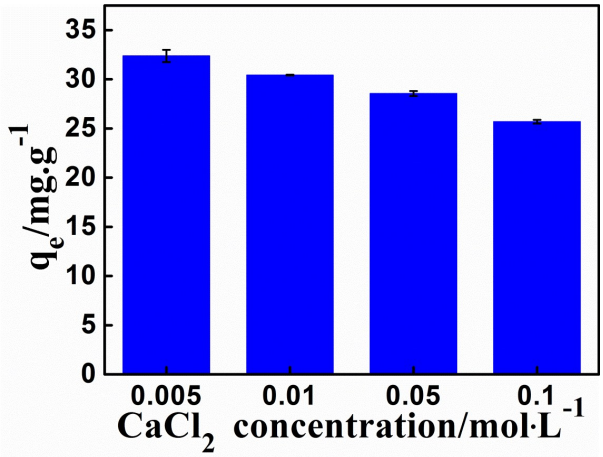
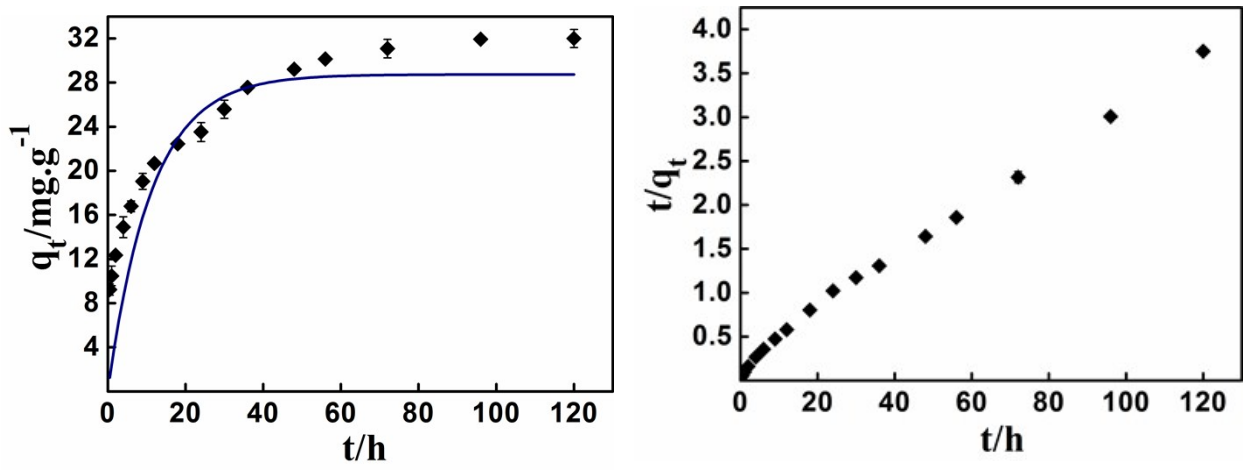


Fig.S10 The influence of $CaCl_2$ concentrations on atrazine sorption by WS750. The concentration of atrazine is 5.80 mg L^{-1}.

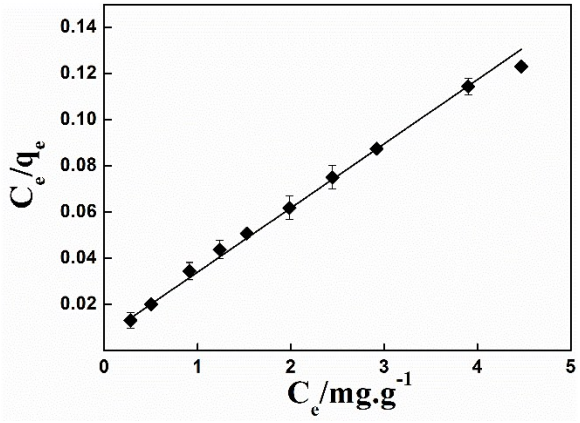


(a) (b)

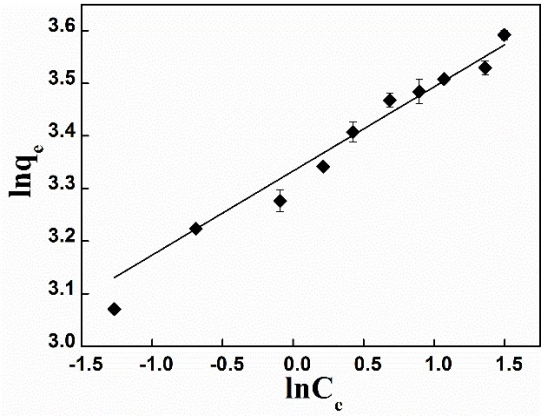
Fig. S11 (a) the kinetic sorption of atrazine by WS750 that was fitted by pseudo-first-order model; (b) the kinetic sorption of atrazine by WS750 that was fitted by pseudo-second-order model.

Table S2 Kinetic parameters for atrazine sorption by WS750.

model	parameters	values
pseudo-first-order	k_1, h^{-1}	0.089
	q_e, $mg \cdot g^{-1}$	28.734
	R^2	0.901
pseudo-second-order	k_2, $kg \cdot (mg \cdot h)^{-1}$	0.00517
	q_e, $mg \cdot g^{-1}$	33.333
	R^2	0.995



(a)



(b)

Fig. S12 (a) the isotherm sorption of atrazine by WS750 that was fitted by Langmuir model; (b) the isotherm sorption of atrazine by WS750 that was fitted by Freundlich model.

Table S3 Isotherm sorption parameters for atrazine by to WS750.

Model	parameters	values
Langmuir	Q_m	20.161
	b	15.5
	R^2	0.996
Freundlich	k	27.550
	1/n	0.179
	R2	0.982

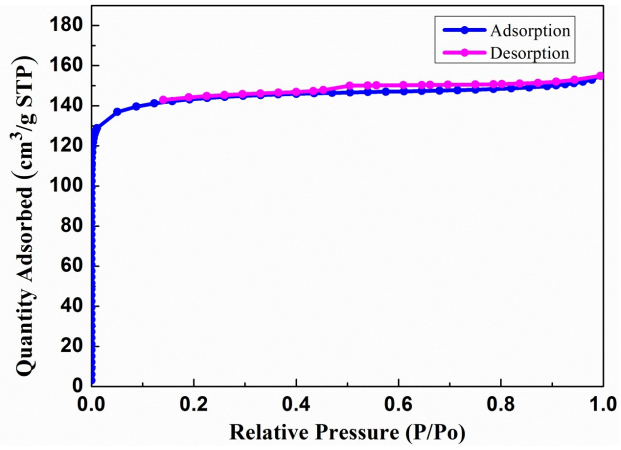


Fig.S13 N_2 adsorption-desorption isotherm of WS750.

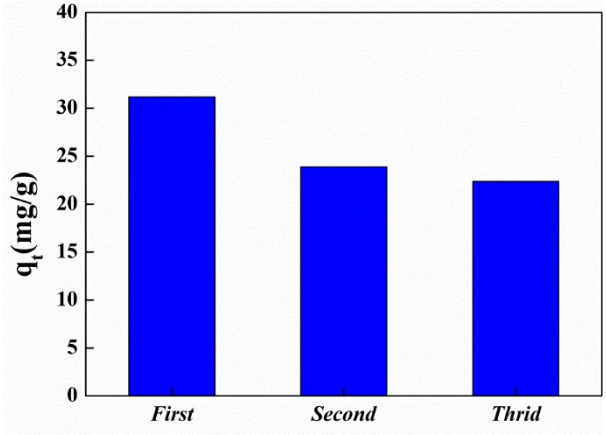
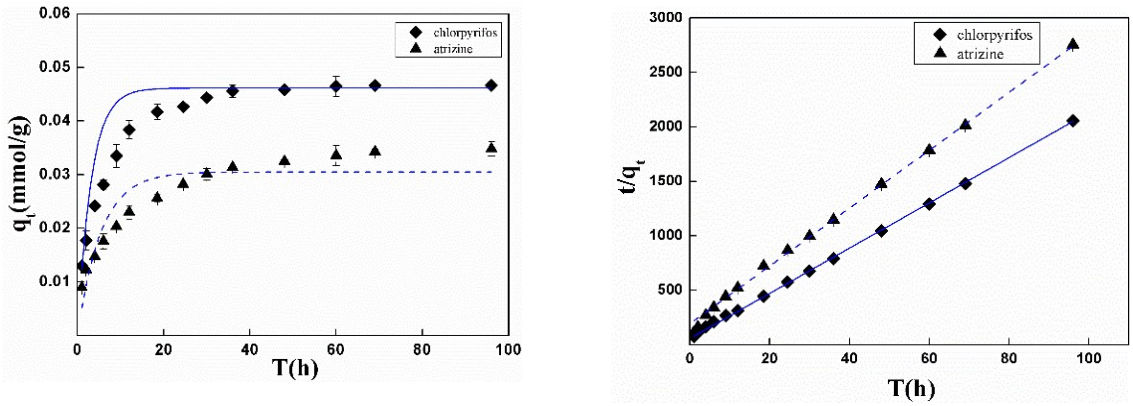


Fig. S14 Recycle experiments of WS750 for the sorption of atrazine. The concentration of atrazine is 5.8 mg L^{-1}.



(a) (b)

Fig S15. (a) the kinetic sorption of atrazine in the presence of chlorpyrifos (the dotted line with triangle points) and the kinetic sorption of chlorpyrifos in the presence of atrazine (the full line with rhombus points) that were fitted by pseudo-first-order model; (b) the kinetic sorption of atrazine in the presence of chlorpyrifos (the dotted line with triangle points) and the kinetic sorption of chlorpyrifos in the presence of atrazine (the full line with rhombus points) that were fitted by pseudo-second-order model.

Table S4 Kinetic parameters of chlorpyrifos in the presence of atrazine and kinetic parameters of atrazine in the presence of chlorpyrifos.

model	parameters	chlorpyrifos	atrazine
pseudo-first-order	k_1,(h^{-1})	0.3142	0.1846
	q_e,(mmol/g)	0.0461	0.0305
	R^2	0.992	0.907
pseudo-second-order	k_2, g/(mmol·h)	5.9597	4.3760
	q_e,(mmol/g)	0.0488	0.0369
	R^2	0.999	0.998

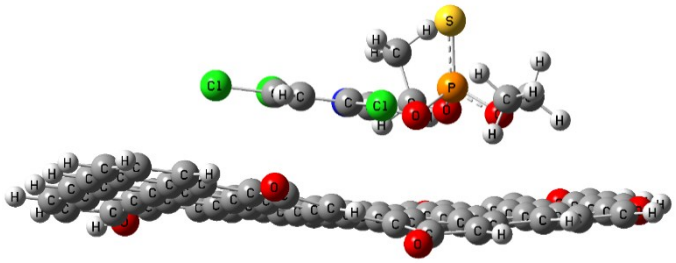


Fig.S16 The optimized structure of chlorpyrifos-WSmodel complex formed through pi-pi interaction.

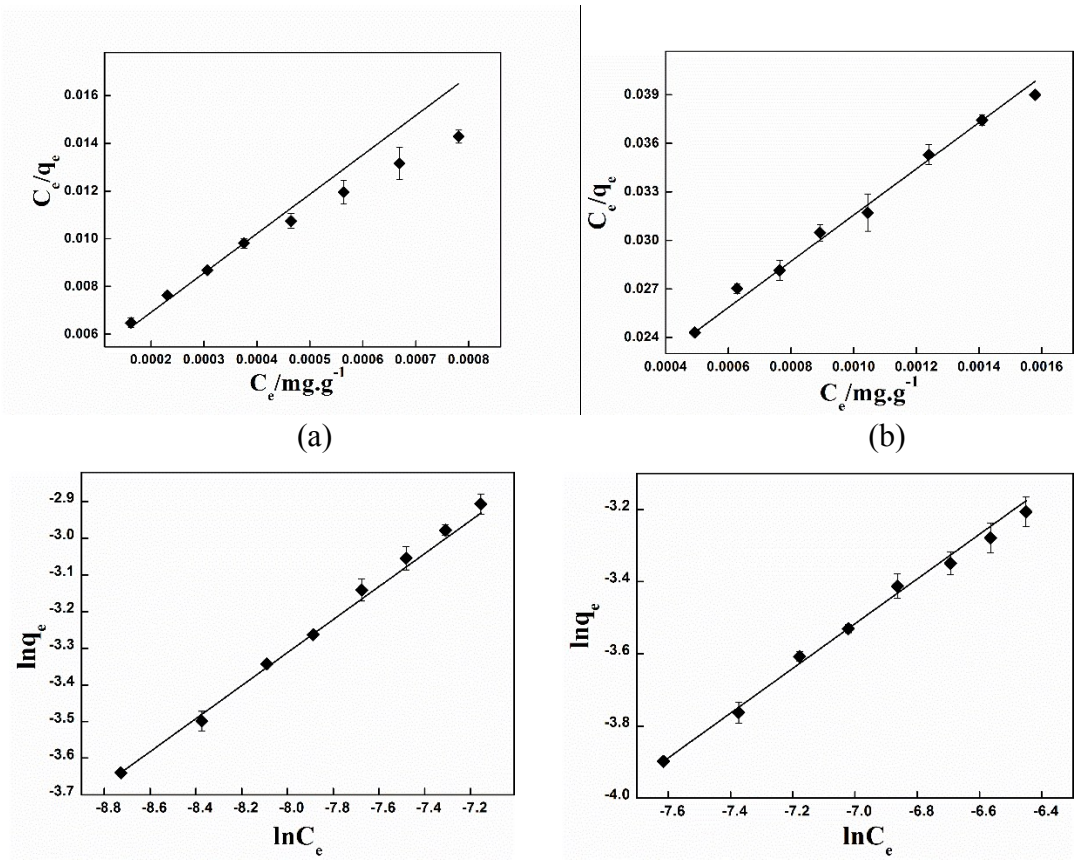
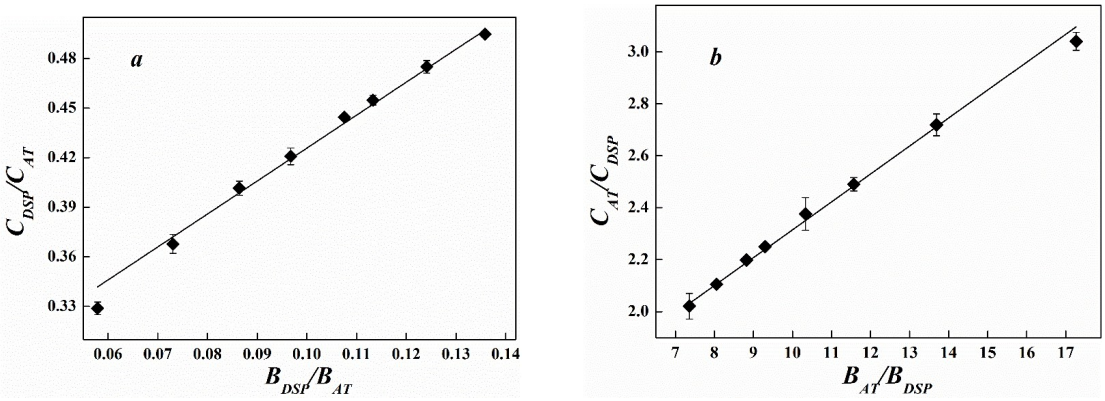


Fig S17 (a) the isotherm sorption of chlorpyrifos in the presence of atrazine that was fitted by Langmuir model; (b) the isotherm sorption of atrazine in the presence of chlorpyrifos that was fitted by Langmuir model; (c) the isotherm sorption of chlorpyrifos in the presence of atrazine that was fitted by Freundlich model; (b) the isotherm sorption of atrazine in the presence of chlorpyrifos that was fitted by Freundlich model.

Table S5. Isotherm sorption parameters of chlorpyrifos in the presence of atrazine and isotherm soprtion parameters of atrazine in the presence of chlorpyrifos.

model	parameters	chlorpyrifos	atrazine
Langmuir	Q_m (mmol/g)	0.0784	0.0737
	b （L/mmol）	2773.8	753.81
	R^2	0.989	0.993
Freundlich	K	1.635	1.865
	$1/n$	0.475	0.592
	R^2	0.998	0.994



(a) (b)

Fig. S18 (a) the competitive isotherm sorption fitted with Sheindorf–Rebuhn–Sheintuch equation for chlorpyrifos in the presence of atrazine; (b) the competitive isotherm sorption fitted with Sheindorf–Rebuhn–Sheintuch equation for atrazine in the presence of chlorpyrifos.

Table S6 . Competitive coefficients $a_{chlorpyrifos/atrazine}$ and $a_{atrazine/chlorpyrifos}$ derived from Sheindrof-Rebhun-Sheintuch equation.

model	parameters	chlorpyrifos/atrazine	atrazine/chlorpyrifos
Sheindrof-Rebhun-Sheintuch (SRS)	$a_{chlorpyrifos/atrazine}$	0.213	/
	$a_{atrazine/chlorpyrifos}$	/	1.287
	R^2	0.994	0.997